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Oxidation of Tryptophan by Permanganate Ion in Acid, Neutral and Alkaline Media: A Comparative Kinetic and Mechanistic Study

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- Tryptophan;
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Abstract

Oxidation of tryptophan (Trp) by potassium permanganate in acid, neutral and alkaline media led to the formation of the corresponding aldehyde (indole-3-acetaldehyde), ammonia and carbon dioxide. The oxidation kinetics was studied by a spectrophotometric technique at fixed ionic strengths and at 25 °C. All the reactions showed a first order dependence on [MnO_4^-] and fractional-first order kinetics in [Trp]. Fractional-second order kinetics in [H^+] and fractional-first order dependence with respect to [OH^-] were revealed in acid and alkaline media, respectively. An increase in the ionic strength in alkaline medium increased the oxidation rate of tryptophan, whereas it had a negligible effect on the oxidation rate in acid medium. Plausible oxidation mechanisms in all media were suggested and the rate-laws expressions were derived. Furthermore, the reactions constants included in the various steps of the suggested mechanisms were evaluated.

1. Introduction

Various kinetic studies on the oxidations of amino acids using different oxidizing agents have been performed earlier [1-11] due to their biological importance and to understanding the mechanisms of such biological redox reactions. One of the essential amino acids is tryptophan (Trp) that employs as a biochemical precursor for the production of Serotonin (a neurotransmitter) [12], niacin (nicotinic acid) [13] and auxin (a phytohormone) [14]. Furthermore, it has various applications in pharmaceuticals and medicine.

Potassium permanganate is considered as the most powerful multi-electron oxidant employed in the kinetic studies in acid, neutral and alkaline media [21]. The mechanism of oxidation by this eco-friendly oxidant depends not only on the reductant but also on the reaction medium. Throughout permanganate oxidation, Mn(VII) species in permanganate is reduced to various oxidation states in different media. Although, the kinetics of permanganate oxidations of various amino acids were studied elsewhere [15-20, 22-30], no work has been reported on the oxidations of amino acids by this oxidant in all media or at a wide range of pH in the same investigation.

In view of the forgoing arguments, the title reactions have been investigated which represent a full kinetic study on the oxidations of tryptophan by permanganate ion in different media in order to establish the optimum conditions affecting such oxidations, to understand the different kinetically active species of the reactants in these media, and finally to elucidate plausible oxidations mechanisms on the basis of the obtained kinetic and spectral results.

2. Experimental details

2.1. *Materials*

A stock solution of tryptophan was prepared by dissolving the required amount of the sample (E. Merck) in double-distilled water. A fresh solution of potassium permanganate was prepared and standardized as reported earlier [31]. Perchloric acid and sodium hydroxide solutions were used to provide the required acidity and

alkalinity, respectively. Potassium phosphate buffer (Sigma-Aldrich) was also employed to keep the neutral medium (pH = 7.0).

2.2 *Kinetics Measurements*

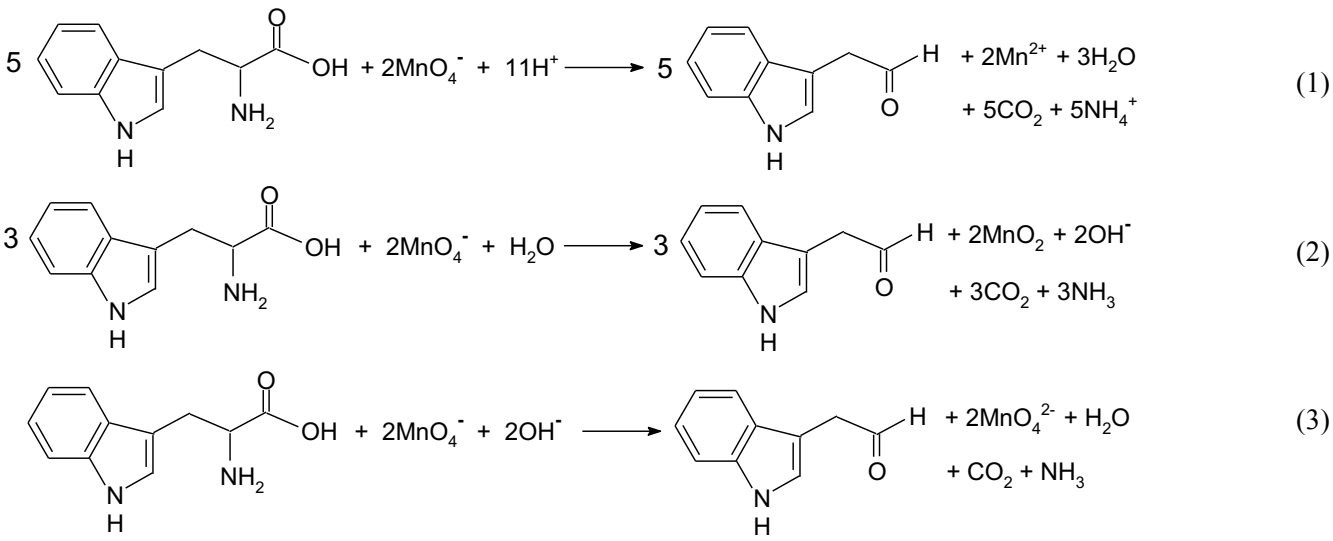
Kinetic runs were carried out under pseudo-first order conditions where [Trp] >> [MnO_4^-]. The ionic strength was maintained constant using sodium perchlorate as an inert electrolyte. The reactions temperature (25 ^oC) was controlled within ±0.1 ^oC. Kinetics of the oxidation reactions in all media were followed spectrophotometrically within the UV–Vis spectral range by recording the decay of the permanganate absorbance as a function of time at λ = 526 nm. These measurements were performed on a thermostatted Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer.

The observed-first order rate constants (k_{obs}) were calculated as the gradients of ln(absorbance) – time plots, which were straight for about 75-85% of the reactions completion. The rate constants were reproducible to within 3-4%. The orders of the oxidation reactions with respect to the reactants concentrations were determined from the plots of log k_{obs} versus log (conc.) by varying the concentrations of tryptophan, perchloric acid and sodium hydroxide, in turn, while keeping all others constant.

3. Results and Discussion

3.1. *Stoichiometry and Product Analysis*

In all three media, different sets of reactions mixtures containing varying ratios of permanganate to tryptophan were mixed at constant pH and ionic strength, then were kept for about 24 hours. Estimation of the remaining permanganate concentrations confirm that the stoichiometries were 5 : 2 in perchloric acid, 3 : 2 in neutral and 1 : 2 in alkaline medium which holds by the following equations (Scheme 1),



Scheme 1. Oxidation of tryptophan by permanganate ion in: (1) acid, (2) neutral and (3) alkaline media.

The above equations were consistent with the results of product analysis. The products were identified as the corresponding aldehyde (indole-3-acetaldehyde) by spot test [32], intermediate manganate(VI) by its visible spectrum, ammonia by Nessler's reagent [33] and carbon dioxide by lime water. The product, indole-3-acetaldehyde was also estimated quantitatively as its 2,4-dinitrophenylhydrazone derivative [33]. Similar oxidation products have been also reported earlier [18-20].

3.2.*Time-Resolved Spectra*

Time-resolved spectra throughout oxidations of tryptophan by permanganate ion in acid, neutral and alkaline media are shown in Fig 1 (a), (b) and (c), respectively. The Figure showed gradual disappearance of permanganate band at λ = 526 nm in all media. In neutral medium, there was two isosbestic points appeared at wavelengths of about 578 and 505 nm, Fig. 1b. In alkaline medium, there was a corresponding growth of new intermediate absorption maxima at wavelengths of 606 and 435 nm with appearance of two isosbestic points at wavelengths 575 and 473 nm, Fig. 1c.

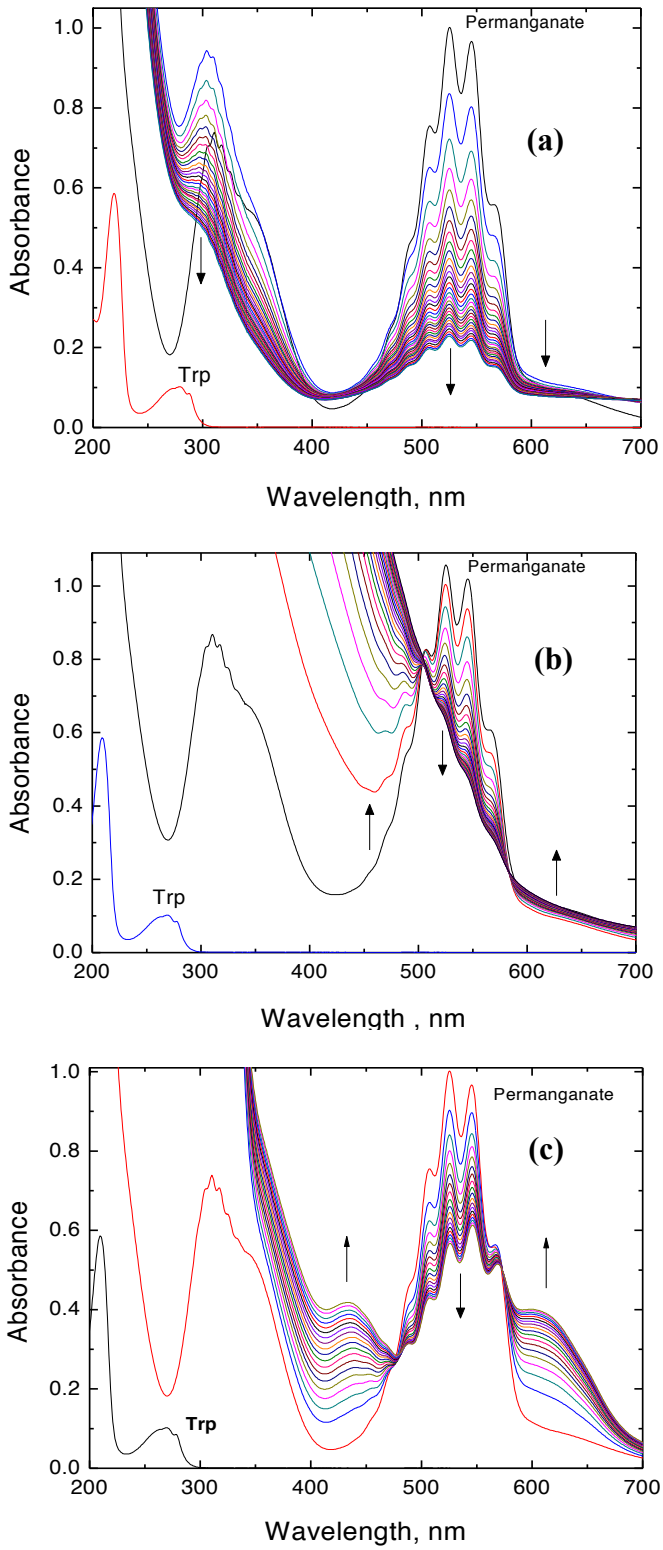


Figure 1. Time-resolved spectra during the oxidation of tryptophan by permanganate ion in: (a) perchloric acid medium, $[H^+]$ = 1.0 and I = 2.0 mol dm^{-3}, (b) neutral medium, and (c) sodium hydroxide medium, $[OH^-]$ = 0.02, I = 0.1 mol dm^{-3}. [Trp] = 6.0 x 10^{-3}, $[MnO_4^-]$ = 4.0 x 10^{-4} mol dm^{-3} at 25 ^{o}C. Scanning time intervals = 1.0 min.

3.3. *Effect of Permanganate Concentration on the Oxidation Rates*

Permanganate ion concentration was varied in all three media between (2.0 - 10.0) x 10^{-4} mol dm^{-3} at constant concentrations of other reactants. The order with respect to $[MnO_4^-]$ was found to be unity in all media, as plots of ln(absorbance) versus time were linear up to about 75-85% of the reactions completion. Furthermore, the non-variation of the values of k_{obs} at different initial $[MnO_4^-]$, as listed in Table 1 for the neutral medium as an example, confirmed the first order dependence of the reactions on $[MnO_4^-]$.

3.4. *Effect of Tryptophan Concentration on the Oxidation Rates*

The values of k_{obs} in all three media were measured at different initial concentrations of the reductant tryptophan keeping all other reactants concentrations constant. It was found that k_{obs} increased with increasing the concentration of tryptophan as listed in Table 1. Plots of k_{obs} versus [Trp] were found to be linear with positive intercepts on k_{obs} axes as shown in Fig. 2 suggesting that the orders with respect to [Trp] in all media were less than unity.

Table 1. Effects of variation of $[MnO_4^-]$, [Trp], $[H^+]$ (in acid medium), $[OH^-]$ (in alkaline medium), and ionic strength, *I,* on the observed first order rate constants (k_{obs}) in the oxidations of tryptophan by permanganate ion in acid, neutral and alkaline media at 25 ^oC

Neutral medium		**10^3 [Trp]**	**Acid medium**		**Alkaline medium**		**10^4 k_{obs}**
10^4 $[MnO_4^-]$ (mol dm^{-3})	**10^3 [Trp] (mol dm^{-3})**	**(mol dm^{-3})**	**$[H^+]$ (mol dm^{-3})**	***I*** **(mol dm^{-3})**	**$[OH^-]$ (mol dm^{-3})**	***I*** **(mol dm^{-3})**	**(s^{-1})**
2.0	6.0						133.6
4.0	6.0						134.2
6.0	6.0						135.4
8.0	6.0						132.9
10.0	6.0						135.8
4.0	**2.0**						51.0
4.0	**4.0**						93.2
4.0	**6.0**						134.2
4.0	**8.0**						169.8
4.0	**10.0**						198.9
4.0		**2.0**	1.0	2.0			65.3
4.0		**4.0**	1.0	2.0			114.9
4.0		**6.0**	1.0	2.0			159.6
4.0		**8.0**	1.0	2.0			205.0
4.0		**10.0**	1.0	2.0			239.2
4.0		6.0	**0.4**	2.0			34.9
4.0		6.0	**0.6**	2.0			75.2
4.0		6.0	**1.0**	2.0			159.6
4.0		6.0	**1.4**	2.0			284.9
4.0		6.0	**1.8**	2.0			436.1
4.0		6.0	1.0	**2.0**			159.6
4.0		6.0	1.0	**2.5**			157.2
4.0		6.0	1.0	**3.0**			161.2
4.0		6.0	1.0	**3.5**			155.1
4.0		6.0	1.0	**4.0**			163.4
4.0		**2.0**			0.05	0.10	44.5
4.0		**4.0**			0.05	0.10	85.2
4.0		**6.0**			0.05	0.10	122.0
4.0		**8.0**			0.05	0.10	155.3
4.0		**10.0**			0.05	0.10	179.8
4.0		6.0			**0.01**	0.10	49.0
4.0		6.0			**0.03**	0.10	89.7
4.0		6.0			**0.05**	0.10	122.0
4.0		6.0			**0.07**	0.10	145.3
4.0		6.0			**0.09**	0.10	174.6
4.0		6.0			0.05	**0.10**	122.0
4.0		6.0			0.05	**0.15**	131.3
4.0		6.0			0.05	**0.20**	141.2
4.0		6.0			0.05	**0.25**	149.6
4.0		6.0			0.05	**0.30**	157.1

Experimental error ± 3%

3.5. *Effect of pH of the Medium on the Oxidation Rates*

In order to study the effect of pH of the medium on the rates, kinetic runs were carried out by varying the hydrogen ion concentration (0.2– 1.8 mol dm^{-3}) using perchloric acid (in acid medium) and by varying the hydroxyl ion concentration (0.1– 0.9 mol dm^{-3}) using sodium hydroxide (in alkaline medium) while keeping the concentrations of all other reactants constant. It was observed that the rates of the reactions in both acid and alkaline media were found to increase with increasing $[H^+]$ and $[OH^-]$, respectively, as listed in Table 1. In acid medium, a plot of log k_{obs} versus log $[H^+]$ was linear with a slope of 1.82 (Fig. 3) suggesting that the order with respect to $[H^+]$ was fractional-second. In alkaline medium, a plot of log k_{obs} versus log $[OH^-]$ was also linear with a slope of 0.63 (Fig. 4) showing a less than unit order dependence for the reaction with respect to $[OH^-]$.

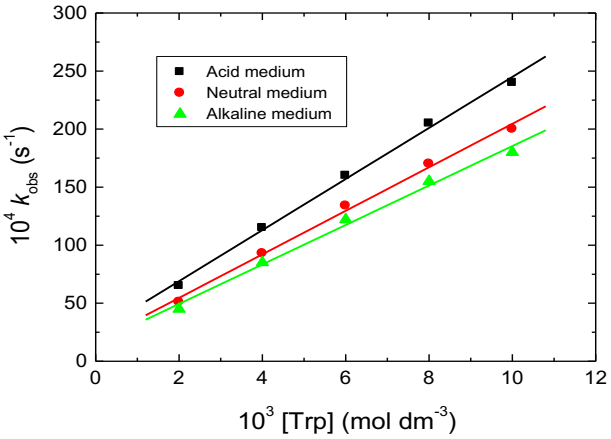


Figure 2. Plots of k_{obs} versus [Trp] in the oxidations of tryptophan by permanganate ion in acid ($[H^+]$ = 1.0 and I = 2.0 mol dm^{-3}), neutral and alkaline ($[OH^-]$ = 0.05 and I = 0.1 mol dn^{-3}), media. $[MnO_4^-]$ = 4.0 x 10^{-4} at 25 °C

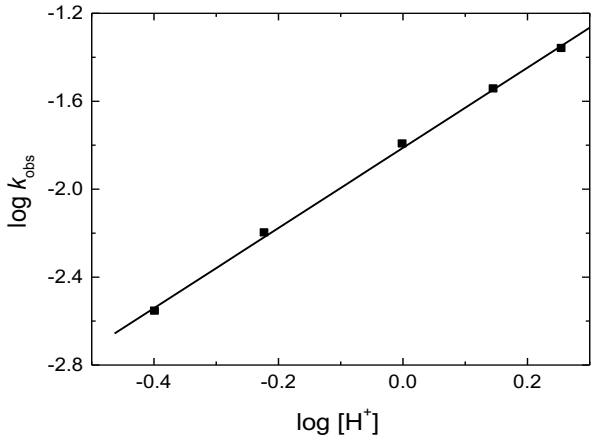


Figure 3. Plot of log k_{obs} versus log $[H^+]$ in the oxidation of tryptophan by permanganate ion in acid medium. [Trp] = 6.0 x 10^{-3}, $[MnO_4^-]$ = 4.0 x 10^{-4} and I = 2.0 mol dm^{-3} at 25 °C

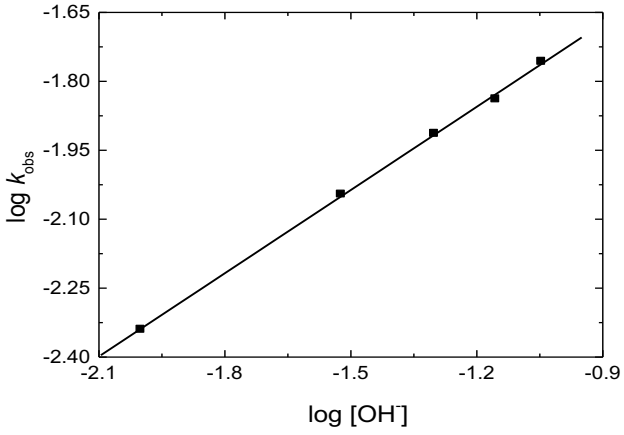


Figure 4. Plot of log k_{obs} versus log $[OH^-]$ in the oxidation of tryptophan by permanganate ion in alkaline medium. [Trp] = 6.0 x 10^{-3}, $[MnO_4^-]$ = 4.0 x 10^{-4} and I = 0.1 mol dm^{-3} at 25 °C

3.6. *Effect of Ionic Strength on the Oxidation Rates*

At constant concentrations of the reactants and with other conditions constant, the ionic strength was varied in the range of 2.0 - 4.0 mol dm^{-3} in acid medium and between 0.1 and 0.3 mol dm^{-3} in alkaline medium using sodium perchlorate. The results listed in Table 1 indicated that increasing ionic strength in alkaline medium increased the oxidation rate as shown in Fig. 5, whereas it had a negligible effect on the oxidation rate in acid medium.

3.7. *Test for Free Radical Intermediates*

Known quantities of acrylonitrile monomer were added to the reactions mixtures in all media and were kept in an inert atmosphere for about 6 hours. When the reactions mixtures were diluted with methanol, progressive white precipitates were formed suggesting intervention of free radicals during these reactions. This indicates that the reactions were routed through free radical paths.

3.8. *Mechanism of Oxidation*

Potassium permanganate provides excellent results when employed as an oxidant in the kinetic studies on the oxidation reactions in acidic, neutral and alkaline media. Permanganate ion is stable in both neutral and slightly alkaline media, whereas it disproportionates to form Mn(V) (hypomanganate) or Mn(VI) (manganate) in strongly alkaline media [21]. Permanganate, Mn(VII), is reduced to Mn(II) during oxidation processes via many manganese species such as Mn(VI), Mn(V), Mn(IV) and Mn(III) depending on the reaction conditions and the type of the reductant used.

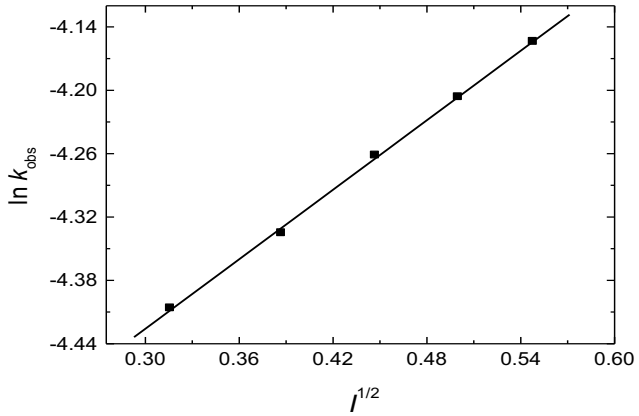


Figure 5. Debye-Huckel plot in the oxidation of tryptophan by permanganate ion in alkaline medium. [Trp] = 6.0 x 10^{-3}, [MnO_4^-] = 4.0 x 10^{-4} and [OH^-] = 0.05 mol dm^{-3} at 25 ^oC

In neutral or slightly alkaline solutions, permanganate used as a powerful oxidizing agent (E_o = +1.23 V) (Eq. 4):

$$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^- \quad (4)$$

In very strong alkaline medium, manganate ion, Mn(VI), is produced (E_o = +0.56 V) (Eq. 5):

$$MnO_4^- + e = MnO_4^{2-} \quad (5)$$

In acid medium, permanganate is reduced to Mn(II) (E_o = +1.51 V) (Eq. 6):

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \quad (6)$$

Since MnO_4^- oxidizes Mn(II) (E_o = +0.46 V), the product in the presence of an excess of permanganate is MnO_2 according to the following equation:

$$2\ MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+ \quad (7)$$

In all three media, the rate-determining step involves a one-electron change, but the stoichiometry is different, being 5 : 2 in acid, 3 : 2 in neutral and 1 : 2 in alkaline medium [21].

Many investigators [22-28] suggested that many oxidation reactions using permanganate ion as an oxidant proceed through intermediate complexes formation between oxidant and substrate. Appearance of new bands in the time-resolved spectra at about 606 nm as well as two isosbestic points especially in both neutral and alkaline media (Fig. 1 b and c) are considered as spectral evidences for complexes formation [34,35]. Also, formation of Mn(VI) and/or Mn(V) intermediate species was proved by the change in the solutions color as the reactions proceeded from purple-pink, Mn(VII), to blue, Mn(V), to green, Mn(VI) [36,37]. The kinetic evidences that

supports formation of such intermediate complexes were the linearity of the plots of $1/k_{obs}$ versus 1/[Trp] with positive intercepts [38] as illustrated in Fig. 6.

3.8.1. *Mechanism of Oxidation in Acid Medium*

In acid medium, increasing the oxidation rate with increasing acid concentration and the chemistry of permanganate ion [21,39] supports formation of permanganic acid which considered as a more powerful oxidant as illustrated by the first equilibrium in Scheme 2.

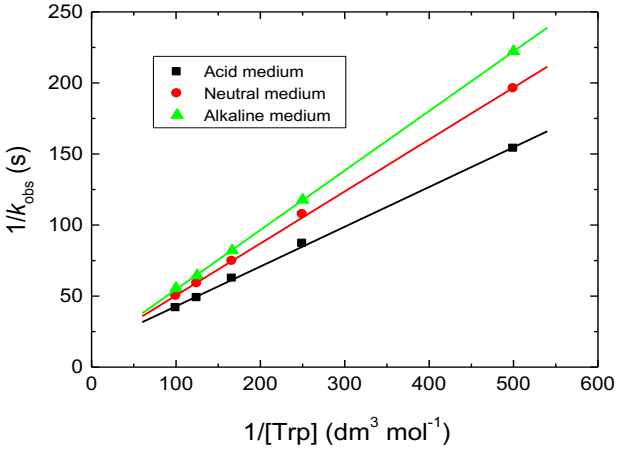
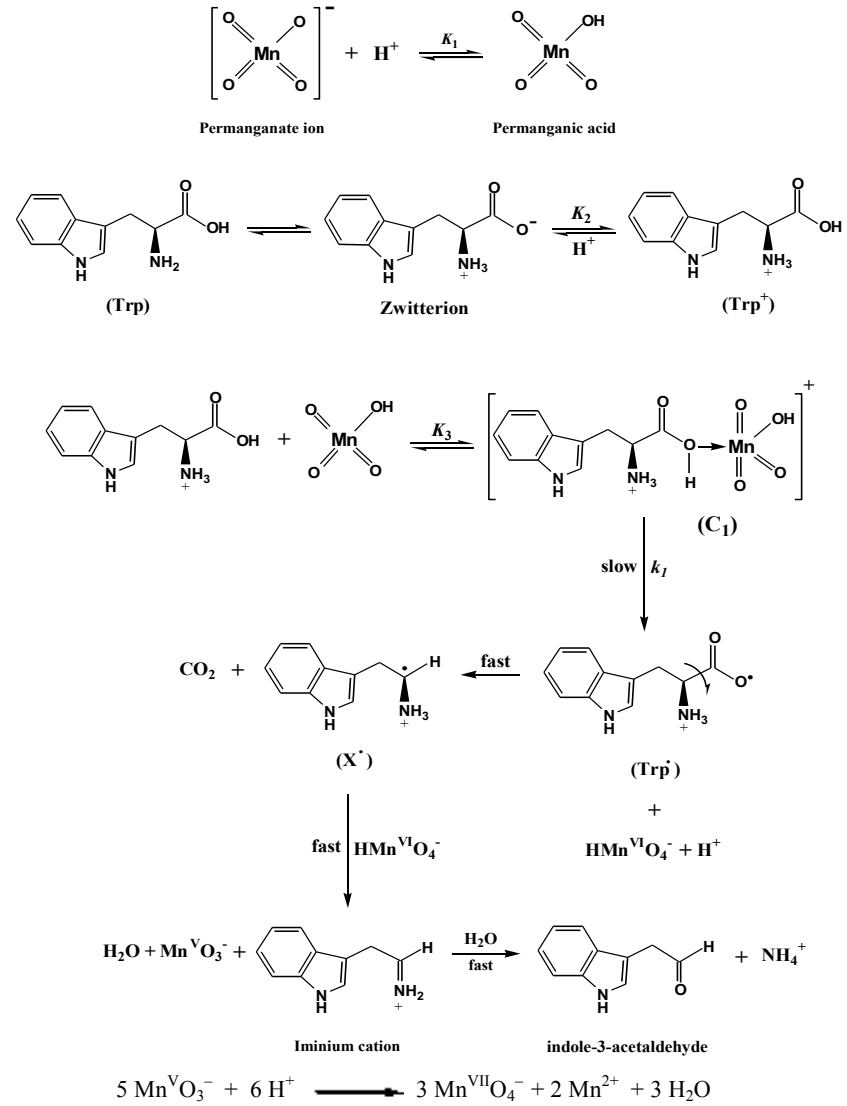


Figure 6. Plots of 1 / k_{obs} versus 1 / [Trp] in the oxidations of tryptophan by permanganate ion in acid ([H^+] = 1.0 and I = 2.0 mol dm^{-3}), neutral, and alkaline ([OH^-] =0.05 and I = 0.1 mol dn^{-3}), media. [MnO_4^-] = 4.0 x 10^{-4} at 25 ^{o}C



Scheme 2. Mechanism of oxidation of tryptophan by permanganate ion in acid medium

Also, it is reported [40] that amino acids tend to protonate in strong acid media as depicted by the second equilibrium in Scheme 2. The obtained fractional-second order dependence of the reaction with respect to $[H^+]$ supports protonation of both permanganate and tryptophan to be the kinetically reactive species in the rate-determining step. On the other hand, the obtained less than unit order dependence with respect to [Trp] supports complex formation between the kinetically active species of both permanganate and tryptophan prior to the rate-determining step. The negligible effect of ionic strength on the oxidation rate confirmed that the reaction occurred between two neutral molecules or between a neutral molecule and a charged ion [41,42], i.e. between $HMnO_4$ and Trp^+.

In view of the above aspects, the following reaction mechanism may be suggested (illustrated in Scheme 2) which involves attack of the powerful oxidant, acid permanganate, on the protonated tryptophan leading to the formation a complex (C_1) in a pre-equilibrium step. The cleavage of such complex leads to the formation of a free radical intermediate of tryptophan and Mn(VI) followed by decarboxylation of tryptophan free radical forming a new radical intermediate ($X^{\cdot}$). The later is rapidly attacked by Mn(VI) species of the oxidant to yield the final oxidation products. The instability in Mn(V) species in strong acid medium leads to conversion of Mn(V) into Mn(II) and Mn(VII) by means of a rapid disproportionation. Based on the above-mentioned mechanism, the relationship between the rate of oxidation and the oxidant, substrate and hydrogen ion concentrations can be deduced to give the following rate law expression:

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [MnO_4^-][Trp][H^+]^2}{1 + K_1[H^+] + K_1 K_2 K_3 [Trp][H^+]^2} \quad (8)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (9)

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \quad (9)$$

Comparing Eqs. (8) and (9) and rearrangement, the following relationship is obtained:

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 K_3 [H^+]^2} \right) \frac{1}{[Trp]} + \frac{1}{k_1} \quad (10)$$

According to Eq. (10), a plot of $1/k_{obs}$ versus 1/[Trp] at constant $[H^+]$ should be straight line with a positive intercept on $1/k_{obs}$ axis as observed experimentally (Fig. 6). From the intercept of such plot, the rate constant value of the slow step, k_1, was determined as 5.87×10^{-2} s^{-1}.

The small intercept manifested in Fig. 6 leads to simplification of Eq. (10) to the following equation:

$$\frac{[Trp][H^+]}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2 K_3} \right) \frac{1}{[H^+]} + \frac{1}{k_1 K_2 K_3} \quad (11)$$

Therefore, a plot of $[Trp][H^+] / k_{obs}$ against $1/[H^+]$ at constant [Trp] should give a straight line with a positive intercept as obtained experimentally (Fig. 7). From the slope and intercept of such plot, the value of K_1 was calculated as 0.53 dm^3 mol^{-1} which in an agreement with that reported earlier [43,44].

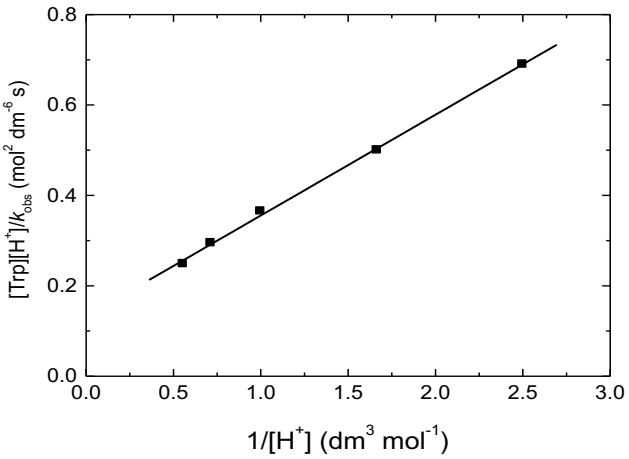
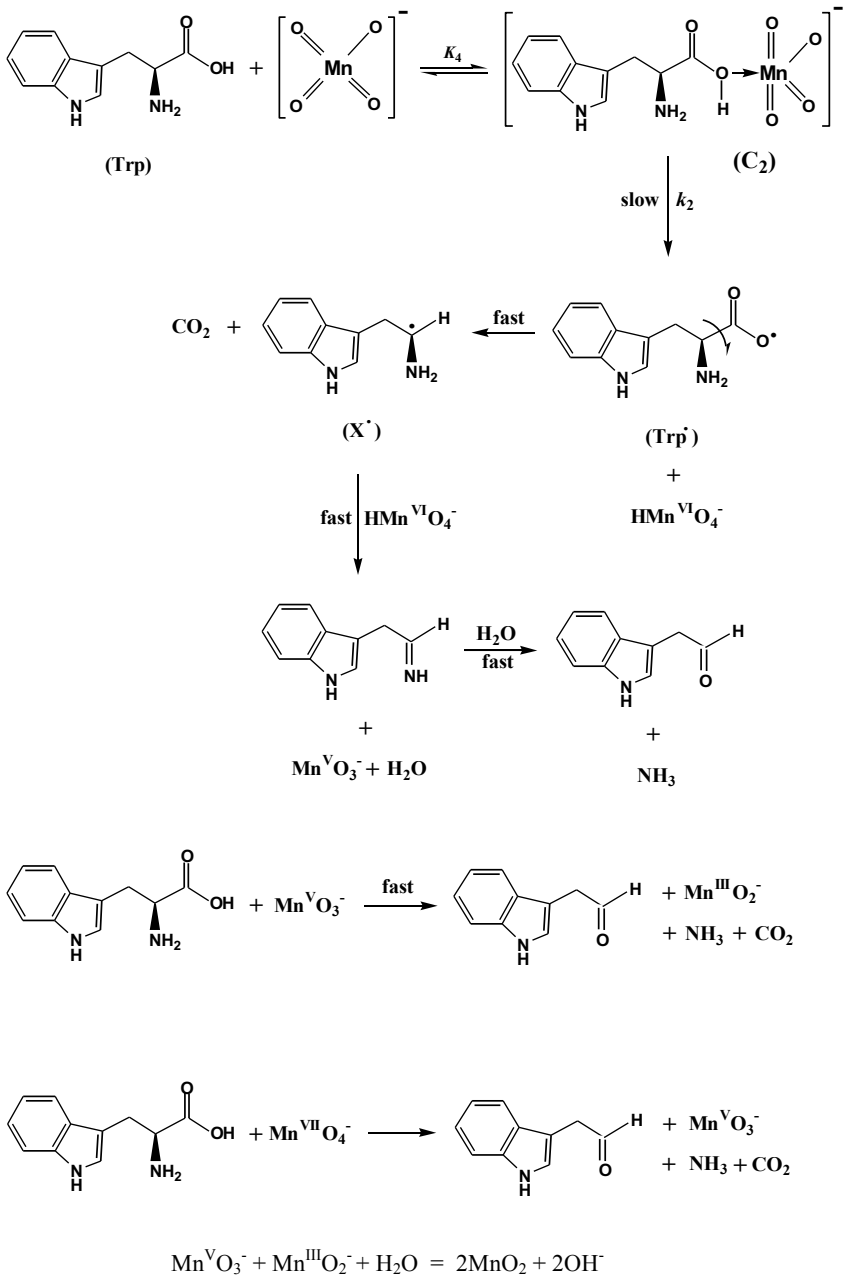


Figure 7. Verification of Eq. (14) in the oxidation of tryptophan by permanganate ion in acid medium. $[MnO_4^-] = 4.0 \times 10^{-4}$ and I = 2.0 mol dn^{-3} at 25 ^oC

3.8.2. *Mechanism of Oxidation in Neutral Medium*

The reaction between tryptophan and permanganate in neutral medium in the presence of phosphate buffer solution has a stoichiometry of 3:2 (Trp : MnO_4^-) with a first-order dependence on [MnO_4^-], apparent less than unit order in [Trp]. Based on the experimental results, permanganate ion is suggested to react with one mole of tryptophan in a pre-equilibrium step to give a complex (C_2). Such complex decomposes to form tryptophan free radical and Mn(VI) intermediate species followed by decarboxylation of free radical to yield a new radical intermediate ($X^{\cdot}$). Such intermediate is rapidly attacked by Mn(VI) ion to give rise to the final oxidation products of tryptophan and Mn(V) intermediate species. In further fast steps the intermediate Mn(V), being very active and unstable, reacts with another mole of tryptophan to give rise to the oxidation products of tryptophan and an intermediate Mn(III) species. This step is further followed by other fast steps to yield the final oxidation product. The proposed mechanism is illustrated in Scheme 3.



$$Mn^{V}O_3^- + Mn^{III}O_2^- + H_2O = 2MnO_2 + 2OH^-$$

Scheme 3. Mechanism of oxidation of tryptophan by permanganate ion in neutral medium

According to the mechanistic Scheme 3, the following rate law expression was deduced:

$$\text{Rate} = \frac{k_2 K_4 [\text{Trp}][\text{MnO}_4^-]}{1 + K_4[\text{Trp}]} \quad (12)$$

Under pseudo-first order conditions, the rate-law can be expressed as

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-] \quad (13)$$

Comparing Eqs (12) and (13), and with rearrangement the following relationship is obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_2 K_4}\right)\frac{1}{[\text{Trp}]} + \frac{1}{k_2} \quad (14)$$

According to Eq. (14), a plot of $1/k_{\text{obs}}$ versus 1/[Trp] should be straight line with a positive intercept on $1/k_{\text{obs}}$ axis as observed experimentally (Fig. 6). From the intercept and slope of such plot, the rate constant value of the slow step, k_2, and the formation constant of the intermediate complex, K_4, were determined as 6.16 x 10^{-2} s^{-1} and 0.33 dm^3 mol^{-1}, respectively.

3.8.3. *Mechanism of Oxidation in Alkaline Medium*

In aqueous alkaline medium [45,46] permanganate ion reacts with alkali in the first step to form an alkali-permanganate species, $[MnO_4 . OH]^{2-}$, as described by the first equilibrium in Scheme 4. The formation of $[MnO_4 . OH]^{2-}$ in the present study was further supported by the linear plot of $1/k_{\text{obs}}$ versus $1/[OH^-]$ shown in Fig. 8. Also, amino acid in alkaline medium is known [47] to exist as anion (deprotonate) as defined by the second equilibrium in Scheme 4. In view of the above arguments, the following reaction mechanism can be suggested which involve attack of the active species of permanganate, $[MnO_4 . OH]^{2-}$, on the deprotonated tryptophan leading to the formation of a complex (C_3) in a prior equilibrium step. This was confirmed, as discussed before, by both spectroscopic evidence (Fig. 1c) and kinetic evidence (Fig. 8). The complex decomposes leading to formation of a free radical intermediate derived from tryptophan and Mn(VI) intermediate followed by decarboxylation of tryptophan free radical to form a new radical intermediate ($X^{\cdot}$). This intermediate is rapidly attacked by another mole of the oxidant to yield the final oxidation products. The suggested mechanism is illustrated in (Scheme 4).

Owing to the above-mentioned mechanism, the rate of oxidation can be expressed by the following rate-law equation:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_3[\text{C}_3] \quad (15)$$

The rate law expressed the change of the oxidation rate with the substrate, hydroxyl ion and oxidant concentrations was deduced to give the following equation:

$$\text{Rate} = \frac{k_3 K_5 K_6 [\text{Trp}][\text{OH}^-][\text{MnO}_4^-]}{1 + K_5[\text{OH}^-] + K_5 K_6 [\text{Asn}][\text{OH}^-]} \quad (16)$$

Under pseudo-first order condition, the rate law can be expressed by Eq (17),

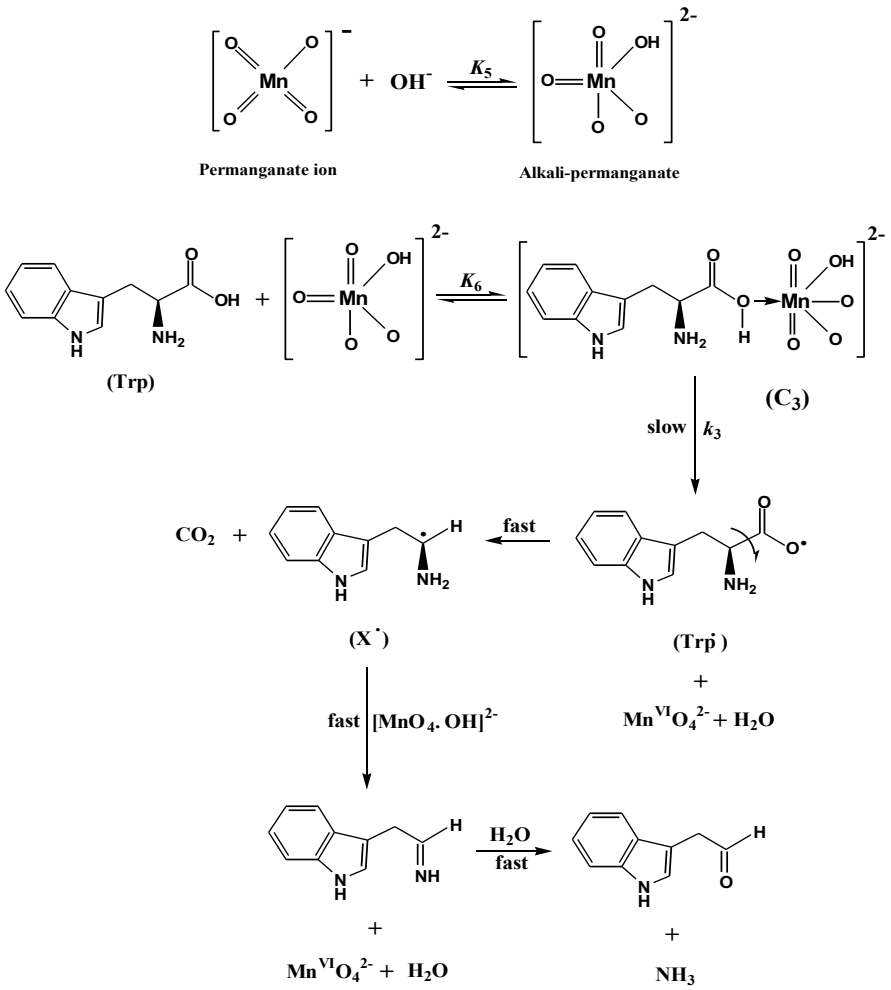
$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-] \quad (17)$$

Comparing Eqs (17) and (18) and rearrangement, the following two equations are obtained:

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_5[\text{OH}^-]}{k_3 K_5 K_6 [\text{OH}^-]}\right)\frac{1}{[\text{Trp}]} + \frac{1}{k_3} \quad (18)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_3 K_5 K_6 [\text{Trp}]}\right)\frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_3 K_6 [\text{Trp}]} + \frac{1}{k_3}\right) \quad (19)$$

Equation (19) requires that the relationship between $1/k_{\text{obs}}$ and 1/[Trp] at constant $[OH^-]$ to be linear with a non-zero intercept on the $1/k_{\text{obs}}$ axis as was experimentally satisfied (Fig. 6), from the intercept of such plot, the value of the rate constant of the slow step (k_3) was evaluated as 5.27 x 10^{-2} s^{-1}. Also, regarding to Eq. (24), the plot of $1/k_{\text{obs}}$ versus $1/[OH^-]$ at constant [Trp] also should give a straight line with a positive intercept on $1/k_{\text{obs}}$ axis as was experimentally observed, Fig 8. Values of the equilibrium constants; K_5 and K_6 were calculated from the slope and intercept of such plot (and the obtained k_3 value) as 13.09 and 131.78 dm^3 mol^{-1}. The value of K_5 was found to be in a good agreement with that reported in earlier works [24,26].



Scheme 4. Mechanism of oxidation of tryptophan by permanganate ion in alkaline medium

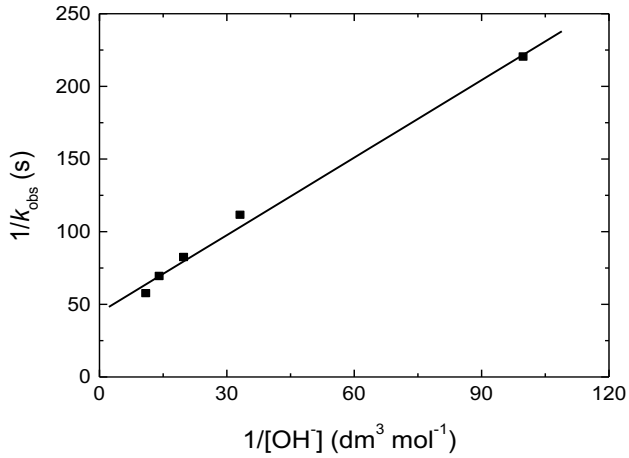


Figure 8. Plot of $1/k_{obs}$ versus $1/[OH^-]$ in the oxidation of tryptophan by permanganate ion in alkaline medium. [Trp] = 6.0 x 10^{-3}, $[MnO_4^-]$ = 4.0 x 10^{-4} and I = 0.1 mol dm^{-3} at 25 °C

Conclusions

A comparative kinetic and mechanistic study of oxidation of tryptophan by permanganate ion was performed in acid, neutral and alkaline media. Regardless of the pH values, the oxidation rate increases in the order: acid medium > neutral medium > alkaline medium. Under our experimental conditions, $HMnO_4$, MnO_4^- and $[MnO_4.OH]^{2-}$ are regarded as the kinetically active species of permanganate ion in acid, neutral and alkaline media, respectively. The final oxidation products of tryptophan in all three media were identified as indole-3-acetaldehyde, ammonia and carbon dioxide. The appropriate rate laws are deduced and the reaction constants involved in the different steps of the mechanisms are evaluated.

References

1. T.P. Sanjeevagowda, A.A. Mahantesh, L.H. Abdulazizkhan, *J. Solution. Chem*. 37 (2008) 1795.
2. A. Fawzy, *Transition Met. Chem*. 39 (2014) 567.
3. Fawzy A. *Int. J. Chem. Kinet*. 47 (2015) 1.
4. Fawzy A., Asghar B.H., *Transition Met. Chem*. 40 (2015) 287.
5. Asghar B.H., Altass H.M., Fawzy A. *Transition Met. Chem*. 40 (2015) 587.
6. Asghar B.H., Altass H.M., Fawzy A. *J. Env. Chem. Eng*. 4 (2016) 617.
7. Khalid M.A.A. *Arabian J. Sci. Eng*. 33 (2007) 199.
8. Goel A., Sharma S. *Transition Met. Chem*. 35 (2010) 549.
9. Yathirajan H.S., Raju C.R., Mohana K.N., Sheena S., Padmarajaiah N. *Turk. J. Chem*. 27 (2003) 571.
10. Zahedi M., Bahrami H. *Kinet. Cat*. 45 (2004) 351.
11. Ionita G.A., Sahini V.E., Semenescu G., Ionita P. *Acta Chim. Slov*. 47 (2000) 111.
12. Schaecheter J.D., Wurtman R.J. *Brain Res*. 532 (1990) 203.
13. Ikeda M., Tsuji H., Nakamura S., Ichiyama A., Nishizuka Y., Hayaishi O. *Biol. Chem*. 240 (1965) 1395.
14. Palme K., Nagy F. *Cell*. 133 (2008) 31.
15. Sharma V.K., Sharma K., Tiwari P.S., Khare D. *Int. J. Pharm. Life Sci*. 2 (2001) 1223.
16. Shetti N.P., Hosamani R.R., Nandibewoor S.T. *Open Catal. J*. 2 (2009) 130.
17. Anweting I.B., Iyun J.F., Idris S.O. *Adv. Appl. Sci. Res*. 3 (2012) 3401.
18. Asghar B.H., Altass H.M., Fawzy A. *J. Saudi. Chem. Soc*. (2016) in press.
19. Fawzy A. *J. Chem. Sci.* 128 (2016) 247.
20. Fawzy A., Ashour S.S., Musleh M.A., Hassan R.M., Asghar B.H. *J. Saudi Chem. Soc*. 20 (2016) 450.
21. Cotton F.A., Wilkinson G. *Advanced Inorganic Chemistry*, p. 747, John Wiley and Sons, New York, (1980).
22. Fawzy A., Ashour S.S., Musleh M.A. *Int. J. Chem. Kinet.* 46 (2014) 370; Asghar B.H., Fawzy A. *J. Saudi Chem. Soc.* 20 (2016) 561.
23. Perez Benito J.F., Mata Perez F., Brillas E. *Can. J. Chem*. 65 (1987) 2329.
24. Fawzy A., Ashour S.S., Musleh M.A. *React. Kinet. Mech. Catal*. 111 (2014) 443.
25. Mahesh R.T., Bellakki M.B., Nandibewoor S.T. *J. Chem. Res*. 1 (2005) 13.
26. Jose T.P., Nandibewoor S.T., Tuwar S.M. *E-J. Chem*. 2 (2005) 75.
27. Kini A.K., Farokhi S.A., Nandibewoor S.T. *Transition Met. Chem*. 27 (2002) 532.
28. Halligudi L.L., Desai S.M., Mavalangi A.K., Nandibewoor S.T. *Monatsh. Chem*. 131 (2000) 321; Halligudi L.L., Desai S.M., Mavalangi A.K., Nandibewoor S.T. *Transition Met. Chem*. 26 (2001) 28.
29. Verma R.S., Reddy J.M., Shastry V.R. *J. Chem. Soc. Perkin Trans*. 124 (1974) 469.
30. Mohanty B., Behera J., Acharya S., Mohanty P., Pantaik A.K. *Chem. Sci. Trans*. 2 (2013) 51.
31. Vogel I.A. *A Text Book of Quantitative Inorganic Analysis*. 4th edn, p. 352. ELBS, Longman, (1978).
32. Feigl F. *Spot Tests in Organic Analysis*, p. 195. Elsevier, New York, (1975).
33. Vogel A.I. *Text Book of Practical Organic Chemistry Including Quantitative Organic Analysis*, 3rd edn, p. 332. ELBS, Longman, (1973).
34. Laider K.J. *Chemical Kinetics*. p. 51. McGraw-Hill, New York, (1965).
35. Entelis S.G., Tiger R.P. *Reaction Kinetics in the Liquid Phase*. Wiley, New York, (1976).
36. Ahmed G.A., Fawzy A., Hassan R.M. *Carbohydr. Res*. 342 (2007) 1382.
37. Zimmerman C.L. Ph. D. Thesis University of Chicago, (1949).
38. Michaelis L., Menten M.L. *Biochem. Z.* 49 (1913) 333.
39. Zahedi M., Bahrami H. *Kinet. Catal.* 45 (2004) 351.
40. Martell A.E., Smith R.M. *In Critical Stability Constants*, Vol. I, p. 321. Plenum Press, New York, (1974).
41. Amis E.S. *Solvent Effect on Reaction Rates and Mechanism*, p. 28. Academic Press, New York, (1966).
42. Frost A.A., Person R.G., *Kinetics and mechanism*, p. 147. Wiley Eastern, New Delhi, (1970).
43. Hosahalli R.V., Savanur A.P., Nandibewoor S.T., Chimatadar S.A., *J. Solution Chem*. 41 (2012) 567.
44. Farokhi S.A., Nandibewoor S.T. *Can. J. Chem*. 82 (2004) 137.
45. Panari R.G., Chougale R.B., Nandibewoor S.T., *J. Phys. Org. Chem*. 11 (1998) 448.
46. De Oliveira L.A., Toma H.E., Giesbrecht E., *Inorg. Nucl. Chem. Lett*. 2 (1976) 195.
47. Chang R., *Physical Chemistry with Applications to Biological Systems*. MacMillan, New York, (1981).

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