Palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium: a kinetic and mechanistic approach

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Abstract. The catalytic effect of palladium(II) on the oxidation of L-tryptophan by potassium hexacyanoferrate(III) has been investigated spectrophotometrically in aqueous perchloric acid medium. A first order dependence in [hexacyanoferrate(III)] and fractional-first order dependences in both [L-tryptophan] and [palladium(II)] were obtained. The reaction exhibits fractional-second order kinetics with respect to $[H^+]$. Reaction rate increased with increase in ionic strength and dielectric constant of the medium. The effect of temperature on the reaction rate has also been studied and activation parameters have been evaluated and discussed. Initial addition of the reaction product, hexacyanoferrate(II), does not affect the rate significantly. A plausible mechanistic scheme explaining all the observed kinetic results has been proposed. The final oxidation products are identified as indole-3-acetaldehyde, ammonium ion and carbon dioxide. The rate law associated with the reaction mechanism is derived.

Keywords. Kinetics; oxidation; L-tryptophan; hexacyanoferrate(III); palladium(II).

1. Introduction

A large number of kinetic investigations on the oxidation of amino acids are being carried out using various oxidants under different experimental conditions[1–16] because of their biological significance, selectivity towards the oxidants and to understand the mechanism of such biological redox reactions. In many cases,[5–14] it was reported that amino acids undergo oxidative decarboxylation and deamination. L-Tryptophan (Trp) is one of the essential amino acids that is required in human diet. It is a reducing agent in chemical and biochemical systems. The rate of reduction depends on the oxidant and pH of the medium. Our literature survey reveals that the kinetic studies on the oxidation of L-tryptophan by different oxidants have received limited attention.[10–16]

The most important iron(III) cyanide complex is the hexacyanoferrate(III) anion (HCF), $[Fe(CN)_6]^{3-}$, in which the Fe^{3+} center is bound in octahedral geometry to six cyanide ligands. Hexacyanoferrate(III) is an efficient one-electron oxidant and has been observed to be a "substitution inert-transition metal complex".[17] Oxidation by HCF in alkaline medium is well understood, for organic[17–23] and inorganic[24–30] compounds. Its usefulness may be due to its unequivocal stability, water

solubility, single equivalent change and its moderate reduction potential of 0.45 V, leading to its reduction to hexacyanoferrate(II), a stable product. In addition, it adds less error to the experimental results, and the data can be analyzed meticulously to establish the reaction path. On the other hand, studies involving HCF as an oxidant in acid media are limited.[28–33] Furthermore, hexacyanoferrate(III) is very sensitive to the solvent and acidity and forms different intermediate species in acid media.[28]

It was shown by the previous workers that the oxidation of amino acids by hexacyanoferrate(III) proceeds very slowly in the absence of a catalyst while it follows a complex kinetics in the presence of it.[34] Transition metals are known to catalyze many oxidation–reduction reactions because they involve multiple oxidation states. In recent years, the use of transition metal ions such as ruthenium, osmium, palladium, manganese, chromium, and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest.[35] Although the mechanism of the catalysis depends on the nature of the substrates, oxidant and experimental conditions, it has been shown[36] that metal ions acts as catalysts by one of several different paths such as formation of complexes with reactants, oxidation of substrates themselves or through formation of free radicals.

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No work, however, has been reported on the oxidation of L-tryptophan by hexacyanoferrate(III) in acid medium in either absence or presence of a catalyst. The present report deals with the title reaction in order to understand the active species of oxidant and catalyst, to check the reactivity of L-tryptophan towards hexacyanoferrate(III) in perchloric acid medium, to examine the catalytic activity of the catalyst and to propose an appropriate reaction mechanism.

2. Experimental

2.1 *Materials*

All the chemicals employed in the present work were of reagent grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. A stock solution of L-tryptophan (E. Merck, US) was prepared afresh by dissolving the amino acid sample in bidistilled water. A fresh solution of hexacyanoferrate(III) was prepared by dissolving potassium hexacyanoferrate(III) (BDH, USA) in water and its concentration was ascertained by iodometric titration.[37a] Hexacyanoferrate(II) solution was prepared by dissolving potassium hexacyanoferrate(II) (SD Fine Chemicals, India; Aldrich, USA) in water and standardizing it with cerium(IV) solution.[37b] The Palladium(II) chloride solution was prepared by dissolving a known weight of the sample (SD Fine Chemicals) in hydrochloric acid and stored in a black coated bottle to prevent any photochemical deterioration. Perchloric acid and sodium perchlorate were used to vary the acid concentration and ionic strength in the reaction medium, respectively.

2.2 *Kinetic measurements*

The kinetic runs were carried out under pseudo-first order conditions keeping L-tryptophan always in excess over hexacyanoferrate(III) concentration at a constant ionic strength of 3.0 mol dm^{-3} and at a constant temperature of $(25 \pm 0.1)°$C unless otherwise stated. The progress of the reaction was followed spectrophotometrically by monitoring the decrease in the absorbance of HCF at its absorption maximum, $\lambda_{max} = 420$ nm, as a function of time using Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer keeping the cell compartment at constant temperature. Solutions of the oxidant and the mixture containing L-tryptophan substrate, perchloric acid and palladium(II) chloride catalyst were separately thermostated for nearly 30 min. The oxidant was then added to the mixture, the overall reaction mixture was transferred to the cell of path

length 1 cm, and 3-4 experimental readings were taken in each run. It was observed that the oxidation reaction did not proceed in the absence of palladium(II) catalyst. Good straight lines for ln(absorbance) versus time plots were obtained for about 85% of the reaction completion and the pseudo-first order rate constant values (k_C) were calculated as the gradients of such plots. The rate constants were reproducible to within 4%.

3. Results and Discussion

3.1 *Stoichiometry and product analysis*

Reaction mixtures containing varying ratios of hexacyanoferrate(III) to L-tryptophan in 2.0 mol dm^{-3} perchloric acid at a constant ionic strength of 3.0 mol dm^{-3} were kept for over 24 h at 25°C in a closed vessel for completion of the reaction. The unreacted [HCF] was analyzed spectrophotometrically by measuring its absorption at 420 nm. The results indicated that two moles of HCF are consumed by one mole of L-tryptophan to yield the oxidation products as shown in the following stoichiometric equation (1),

Tryptophan   Indole-3-acetaldehyde

$$\tag{1}$$
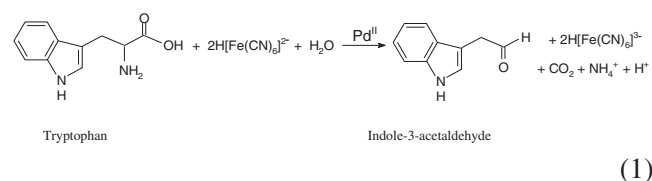
The product obtained was tested for the aldehyde, indole-3-acetaldehyde by TLC. One spot was obtained when the chromatogram was assayed with 2,4-dinitrophenylhydrazine. An aliquot (5 mL) was pipetted into 50 mL of 2.0 N HCl saturated with 2,4-dinitrophenylhydrazine which was filtered, washed, dried and weighed. The yield was calculated from the amount of 2,4-dinitrophenylhydrazone formed and was found to about 84%. Further proof of the formation of the corresponding aldehyde was obtained by isolating the aldehyde using the standard method.[38] The byproducts were identified as ammonia by Nessler's reagent[39] and carbon dioxide by limewater. Similar oxidation products with different experimental conditions have been also reported earlier.[10–16]

3.2 *Spectroscopic changes*

The spectroscopic changes associated with the palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium are shown in figure 1. The scanned spectra shown in figure 1a indicate gradual disappearance of HCF(III) band located at $\lambda = 420$ nm with time as a result
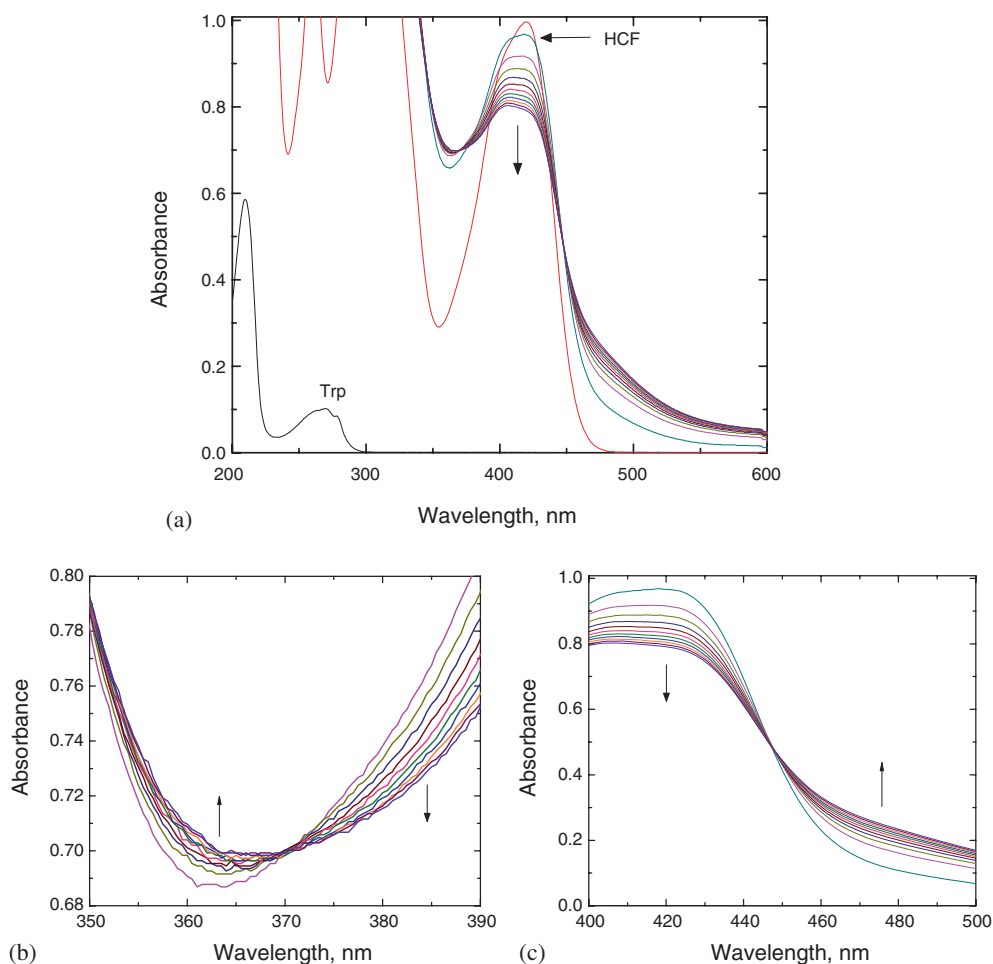
Figure 1. (a) Spectroscopic changes associated with palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. (b, c) Careful examination of the spectroscopic changes around the two isosbestic points. $[Trp] = 0.01$, $[HCF] = 7.0 \times 10^{-4}$, $[H^+] = 2.0$, $[Pd^{II}] = 5.0 \times 10^{-5}$ and $I = 3.0$ mol dm^{-3} at 25°C. Scan time intervals $= 2$ min.

of its reduction to HCF(II). A careful examination of the spectroscopic changes, figure 1b and c, manifests a simultaneous growing of an absorption band located above 445 nm and exhibit two isosbestic points centered at wavelengths 370 and 444 nm. These spectroscopic features are consistent with the formation of an adduct between palladium(II) catalyst and L-tryptophan substrate.

3.3 *Reaction orders*

The reaction orders with respect to the reactants were determined from plots of log k_C versus log (conc.) by varying the concentrations of L-tryptophan substrate, perchloric acid and palladium(II) chloride catalyst, in turn, while keeping the others constant.

The effect of [HCF] on the rate of reaction was studied by varying its concentration in the range 3.0×10^{-4} to 11.0×10^{-4} mol dm^{-3} at fixed [Trp], [H$^+$], [Pd^{II}]

and ionic strength and temperature. The order with respect to [HCF] was found to be unity, as plots of ln [absorbance] against time were linear with no variation in the slope for different [HCF] as shown in table 1.
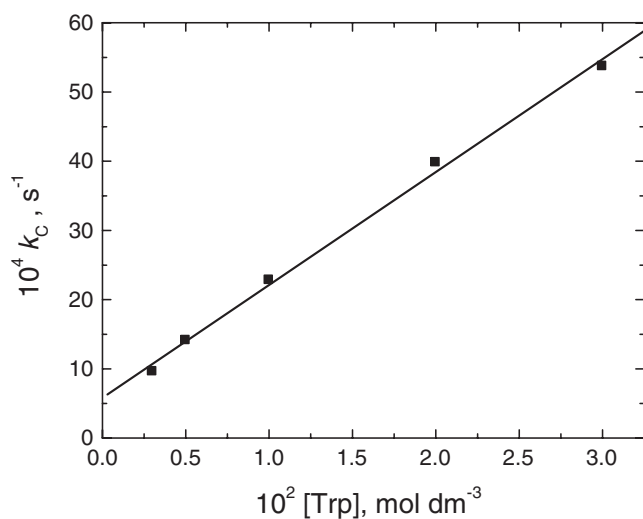
The rate constant was determined at different initial concentrations of the reductant L-tryptophan keeping all other reactant concentrations constant including palladium(II) catalyst. It was found that the rate of reaction increased with increasing the concentration of L-tryptophan as listed in table 1. The plot of k_C versus [Trp], figure 2, gave a good straight line with a positive intercept on k_C axis suggesting that the order of reaction with respect to [Trp] is less than unity.

At constant ionic strength of 3.0 mol dm^{-3} and other conditions remaining constant, perchloric acid was varied from 1.0 to 3.0 mol dm^{-3}. It was noticed that as [H$^+$] increased the rate of reaction increased (table 1) with a fractional-second order as indicated by the plot of k_C versus [H$^+$]^2 (figure 3).

Table 1. Effect of variation of [HCF], [Trp], [H$^+$], [Pd^{II}] and ionic strength, I, on the pseudo-first order rate constant (k_C) in the paladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium at 25°C.

10^4[HCF] (mol dm^{-3})	10^2[Trp] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	10^5[Pd^{II}] (mol dm^{-3})	I (mol dm^{-3})	$10^4\,k_C$ (s^{-1})
3.0	1.0	2.0	5.0	3.0	22.1
5.0	1.0	2.0	5.0	3.0	23.2
7.0	1.0	2.0	5.0	3.0	22.8
9.0	1.0	2.0	5.0	3.0	23.5
11.0	1.0	2.0	5.0	3.0	22.7
7.0	0.3	2.0	5.0	3.0	9.6
7.0	0.5	2.0	5.0	3.0	14.1
7.0	1.0	2.0	5.0	3.0	22.8
7.0	2.0	2.0	5.0	3.0	39.8
7.0	3.0	2.0	5.0	3.0	53.7
7.0	1.0	1.0	5.0	3.0	6.6
7.0	1.0	1.5	5.0	3.0	13.8
7.0	1.0	2.0	5.0	3.0	22.8
7.0	1.0	2.5	5.0	3.0	34.5
7.0	1.0	3.0	5.0	3.0	47.7
7.0	1.0	2.0	1.0	3.0	7.7
7.0	1.0	2.0	3.0	3.0	15.5
7.0	1.0	2.0	5.0	3.0	22.8
7.0	1.0	2.0	7.0	3.0	30.8
7.0	1.0	2.0	9.0	3.0	40.0
7.0	1.0	2.0	5.0	3.0	22.8
7.0	1.0	2.0	5.0	3.3	23.3
7.0	1.0	2.0	5.0	3.6	24.1
7.0	1.0	2.0	5.0	4.0	25.0
7.0	1.0	2.0	5.0	4.5	25.9

Experimental error ± 4%.

Figure 2. Plot of k_C vs [Trp] in the paladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [HCF] = 7.0×10^{-4}, [H$^+$] = 2.0, [Pd^{II}] = 5.0×10^{-5} and I = 3.0 mol dm^{-3} at 25°C.
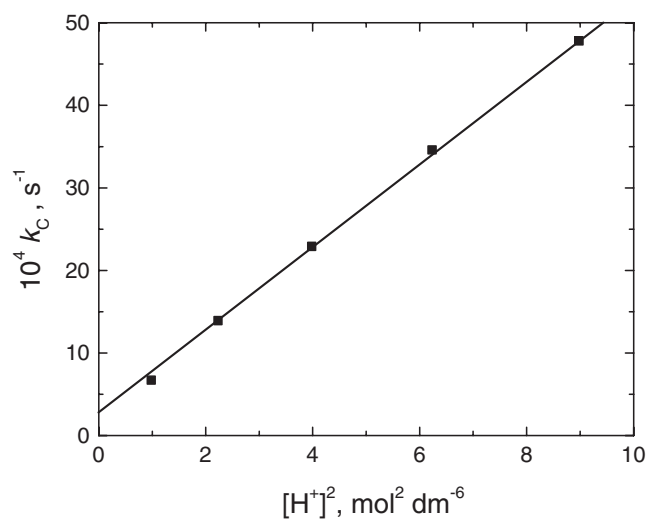
Figure 3. Plot of k_C versus [H$^+$]^2 in the paladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [Trp] = 0.01, [HCF] = 7.0×10^{-4}, [Pd^{II}] = 5.0×10^{-5} and I = 3.0 mol dm^{-3} at 25°C.

The palladium(II) catalyst concentration was varied from 1.0×10^{-5} to 9.0×10^{-5} mol dm^{-3} at constant concentrations of Trp, HCF, H$^+$ and at constant ionic strength and temperature. Reaction rate was found to increase with increasing [Pd^{II}] (table 1). The order was found to be less than unity as shown in figure 4.

3.4 *Effect of ionic strength and dielectric constant*

The effect of ionic strength was studied in the concentration range 3.0-4.5 mol dm^{-3} at constant [HCF], [Trp], [Pd^{II}], [H$^+$] and temperature by varying the concentration of NaClO$_4$. The results are presented in table 1. These results show that the pseudo-first order rate constant k_C increased with increasing ionic strength of the medium and the Debye-Hückel plot was found to be linear with a positive slope, figure 5a.

In order to determine the effect of dielectric constant (*D*) of the medium on the rate, the oxidation of L-tryptophan by HCF was studied at different solvent compositions (v/v) of acetic acid and water. The dielectric constant of the medium at different compositions was calculated using dielectric constants of water and

Figure 4. Plot of k_C versus [Pd^{II}] in the paladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [Trp] = 0.01, [HCF] = 7.0 × 10^{-4}, [H$^+$] = 2.0 and I = 3.0 mol dm^{-3} at 25°C.

acetic acid (78.5 and 6.15 at 25°C, respectively). The data clearly reveals that the rate constant k_C decreased with the increase in acetic acid content, i.e., decrease in dielectric constant of the solvent mixture. The plot of log k_C versus 1/*D* was linear with a negative slope as shown in figure 5b.

3.5 *Effect of initially added product [HCF(II)]*

The effect of added hexacyanoferrate(II) product was studied also in the concentration range 3.0 × 10^{-4} to 11.0 × 10^{-4} mol dm^{-3} at fixed concentrations of the oxidant, reductant, perchloric acid and catalyst. It was found that HCF(II) did not have any significant effect on the rate of reaction.

3.6 *Test for free radicals*

It is well known that hexacyanoferrate(III) is a generator of free radicals due to its single equivalent change in redox reactions. Hence, the involvement of free radical species in the organic substrate, L-tryptophan, was assayed by a polymerization test. A known quantity of acrylonitrile monomer was added initially to a reaction mixture in an inert atmosphere, with the result of progressive formation of a white precipitate in the whole reaction mixture, indicating presence of free radicals during the reaction. When the experiment was repeated in the absence of L-tryptophan under similar condition, the test was negative. This indicates that the reaction was routed through a free radical path.

3.7 *Effect of temperature*

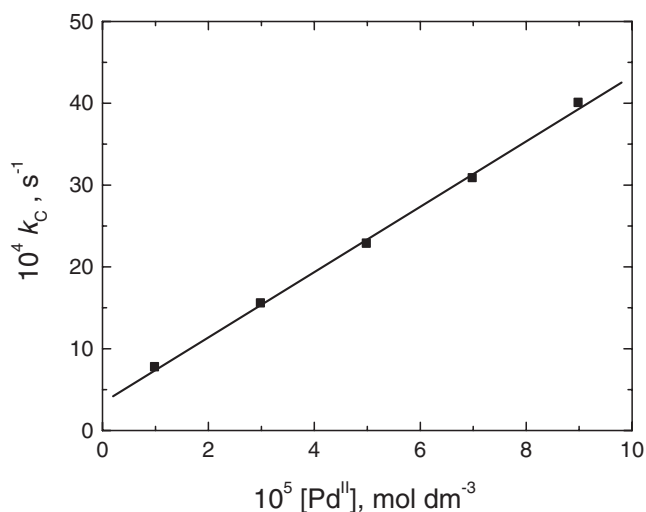The kinetics was studied at different temperatures, 288, 293, 298, 303 and 308 K, at constant concentrations of
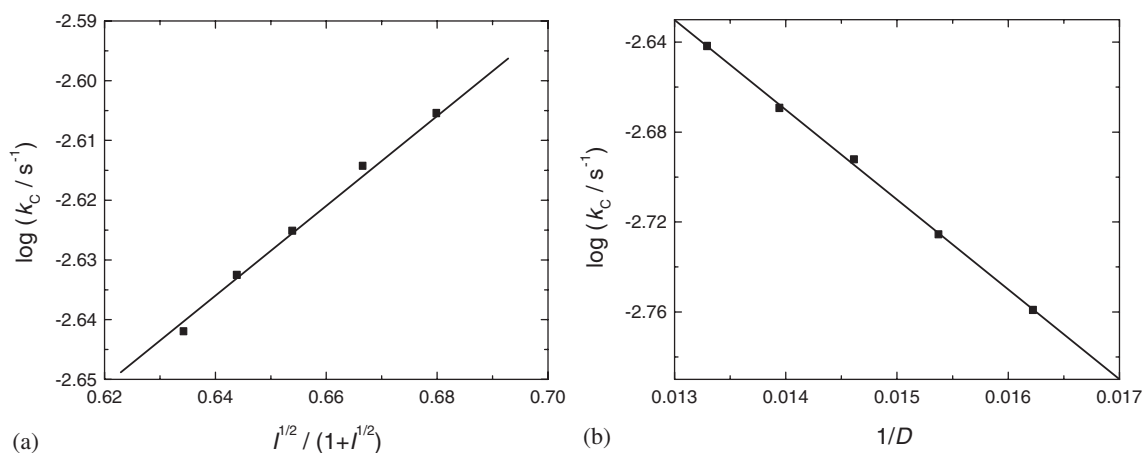

(a)   (b)

Figure 5. Effect of, a) ionic strength (*I*) and, b) dielectric constant (*D*) of the medium on the rate of paladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [Trp] = 0.01, [HCF] = 7.0 × 10^{-4}, [H$^+$] = 2.0 and [Pd^{II}] = 5.0 × 10^{-5} mol dm^{-3} at 25°C.
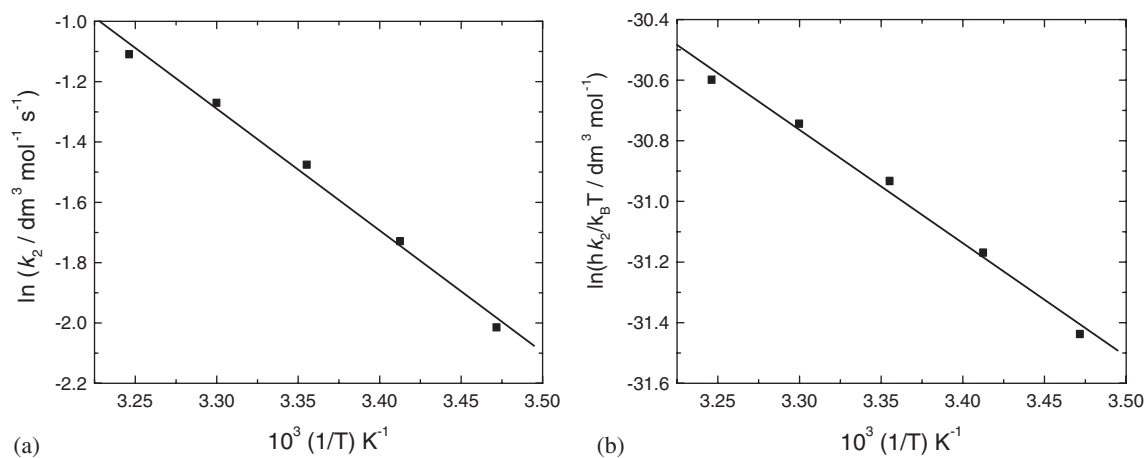
Figure 6. (a) Arrhenius and, (b) Eyring plots in the palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [Trp] = 0.01, [HCF] = 7.0×10^{-4}, [H$^+$] = 2.0, [Pd^{II}] = 5.0×10^{-5} and $I = 3.0$ mol dm^{-3}.

Table 2. Activation parameters of the second order rate constant k_2 in the palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. [Trp] = 0.01, [HCF] = 7.0×10^{-4}, [H$^+$] = 2.0, [Pd^{II}] = 5.0×10^{-5} and $I = 3.0$ mol dm^{-3}.

$\Delta S^{\neq}$, J mol^{-1}K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}	$E^{\neq}_a$, kJ mol^{-1}
-152.98	31.04	76.63	33.54

Experimental error $\pm$ 4%

the reactants and ionic strength. The obtained results indicate that the pseudo-first order rate constant k_C was increased with raising temperature. The activation parameters of the second order rate constant, k_2 ($k_2 = k_C$/ [Trp]), are calculated using Arrhenius, (figure 6a) and Eyring (figure 6b) plots and are listed in table 2.
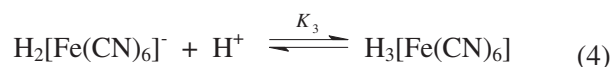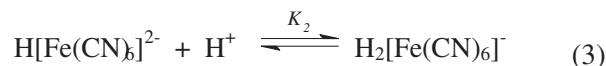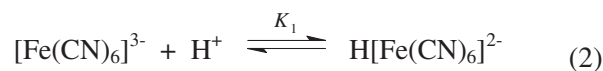
3.8 *Behavior of L-tryptophan in acid media*

Martell and Smith[40] reported that amino acids exist as zwitterions in neutral media and predominantly tend to protonate in acid media (Eq. (5) in scheme 1). The high concentration of hydrogen ion employed in the present reaction as well as the observed enhancement of the reaction rate upon increasing acid concentration suggesting protonation of L-tryptophan in a pre-equilibrium step and its protonated form (Trp$^+$) appears to be the reactive species in the rate-determining step.

3.9 *Behavior of hexacyanoferrate(III) in acid media*

In perchloric acid media, hexacyanoferrate(III) forms different protonated species as shown in the equilibria (2)–(4) with the stability constants: $\beta_1 = K_1$, $\beta_2 =$

$K_1 K_2$ and $\beta_3 = K_1 K_2 K_3$ belonging to the species with one, two and three protons, respectively.[41]

$$[Fe(CN)_6]^{3-} + H^+ \xrightleftharpoons{K_1} H[Fe(CN)_6]^{2-} \quad (2)$$

$$H[Fe(CN)_6]^{2-} + H^+ \xrightleftharpoons{K_2} H_2[Fe(CN)_6]^{-} \quad (3)$$

$$H_2[Fe(CN)_6]^{-} + H^+ \xrightleftharpoons{K_3} H_3[Fe(CN)_6] \quad (4)$$

where $K_3 < K_2 < K_1 < 10$.

The existence of higher protonated complexes is ruled out as they exist at relatively higher [H$^+$].[42] Thus, a single protonated ferricyanide, H[Fe(CN)$_6$]$^{2-}$, may be the reactive species in the present investigation.

3.10 *Behavior of palladium(II) species in acid media*

In most of the studies using palladium(II) as a homogenous catalyst, it has been employed in the form of palladium(II) chloride. It is important to know the probable species of palladium(II) chloride in acid media. The different possible mononuclear complexes of palladium(II) such as [PdCl$_3$L]$^-$, [PdCl$_2$L$_2$], [PdClL$_3$]$^+$and [PdL$_4$]$^{2+}$ (where L represents a ligand like amine,

phosphine, sulphide) are reported.[43] It is dissolved in the presence of Cl⁻. Elding[44] reported that in the presence of chloride ion, palladium(II) chloride exists as $[PdCl_4]^{2-}$ and in the aqueous solution, it may be further hydrolyzed to $[PdCl_3(H_2O)]^-$.

3.11 *Reaction mechanism*

The hexacyanoferrate(III) oxidation of L-tryptophan occurs in measurable quantities in the presence of small amounts of palladium(II) catalyst in perchloric acid medium. The reaction has a stoichiometry of 2:1, i.e., two moles of hexacyanoferrate(III) requires one mole of L-tryptophan. The order with respect to [HCF] was found to be unity and less than unity each with respect to both [Trp] and [Pd^{II}]. As [H$^+$] increases, the reaction rate also increases with fractional-second order dependence suggesting protonation of both L-tryptophan and hexacyanoferrate(III). The rate is not considerably affected by HCF(II) suggesting that the probability of any fast equilibrium with the product preceding the rate-determining step was ruled out. The rate-determining step should be irreversible as is generally the case for one electron oxidants[45] and the oxidation takes place through generation of a free radical
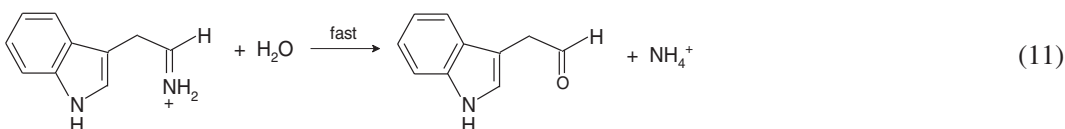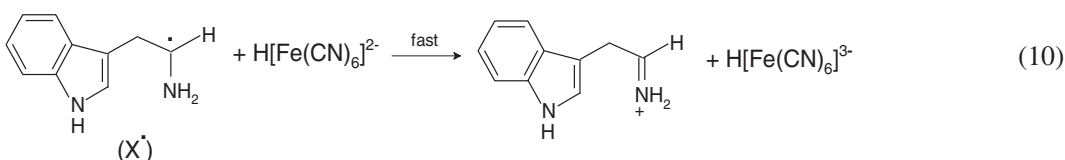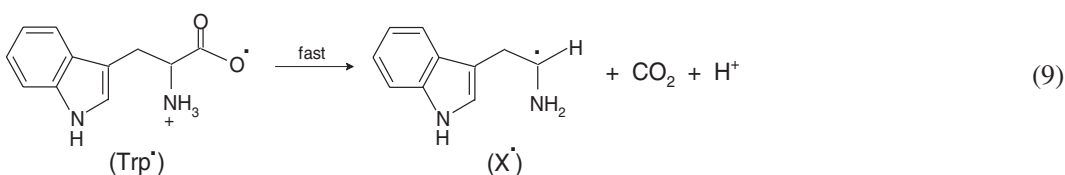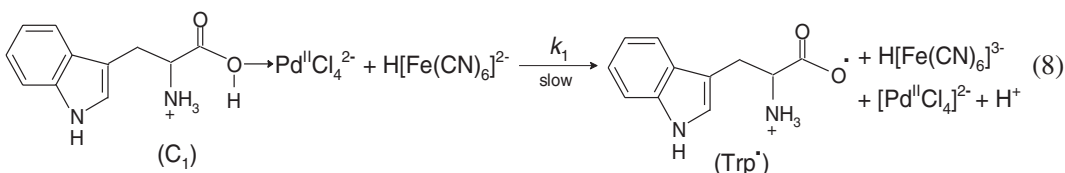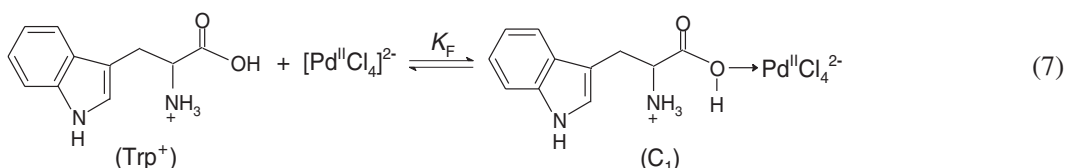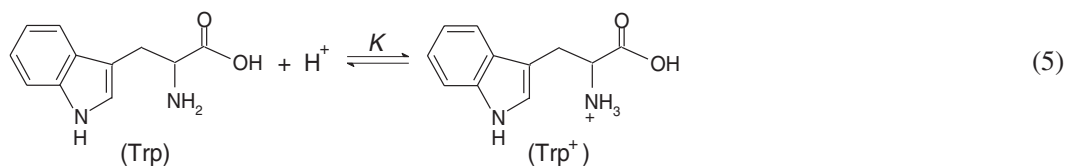
Scheme 1. Mechanism of palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium.

as confirmed experimentally. The effect of ionic strength and dielectric constant on the reaction rate suggests that similarly charged species are interacting in the rate-determining step.[46]

Based on the experimental results, the proposed mechanism (scheme 1) involves protonation of both L-tryptophan and hexacyanoferrate(III) followed by complexation of the protonated L-tryptophan with Pd^{II} species, $[PdCl_4]^{2-}$, to form an adduct C_1 prior to the rate-determining step. It is reported[5–7] that amino acids form adducts with some transition metal ions owing to the availability of electron pair on oxygen atom of the carboxylate group. Within protolytic amino acid system, there are carboxylate and amine groups which may act as nucleophiles, depending on the pH of the medium. The protolytic group with the highest basicity interacts with the transition metal ion. Thus, at low pH, where the amine group is protonated, the carboxylate group should be able to attack the metal ion. Complex formation was proved spectrophotometrically as shown in figure 1a–c as well as kinetically by the non-zero intercept of the plot $[Pd^{II}]/k_C$ versus $1/[Trp]$ (figure 7). Such a complex between amino acid and palladium(II) catalyst has been reported in earlier studies.[47] Then, the active species of the oxidant, $H[Fe(CN)_6]^{2-}$, attacks the formed intermediate complex in a slow (rate-determining) step to yield L-tryptophan free radical and HCF(II) with regeneration of the catalyst Pd^{II}. This is followed by decarboxylation of L-tryptophan free
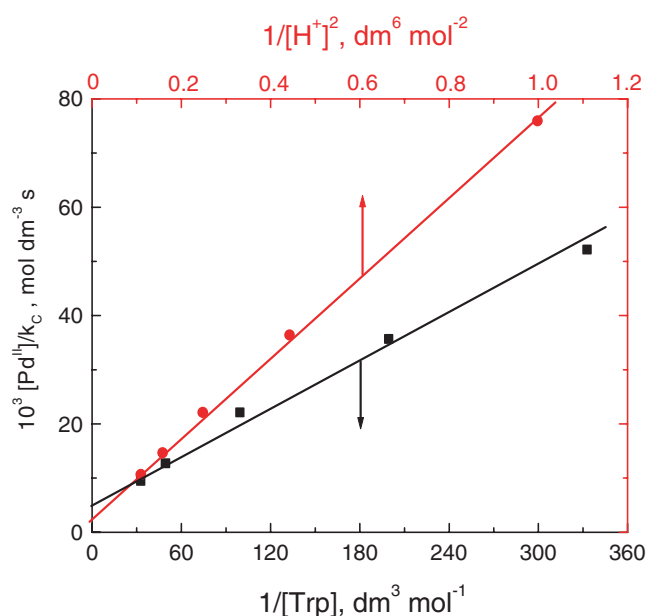

Figure 7. Verification of the rate law (17) in the form of Eq. (19) in the palladium(II)-catalyzed oxidation of L-tryptophan by hexacyanoferrate(III) in perchloric acid medium. $[HCF] = 7.0 \times 10^{-4}$ and $I = 3.0\ mol\ dm^{-3}$ at 25°C.

radical forming a new radical intermediate $(X^{\cdot})$. The latter reacts with another $H[Fe(CN)_6]^{2-}$ species in a subsequent fast step to give rise to the final oxidation products.

The suggested mechanism leads to the following rate law (see Appendix),

$$\text{Rate} = \frac{k_1 K K_1 K_F[\text{Trp}][\text{Fe(CN)}_6^{3-}][\text{H}^+]^2[\text{Pd}^{II}]}{1 + K[\text{H}^+] + K_1[\text{H}^+] + K K_1[\text{H}^+]^2 + K K_F[\text{Trp}][\text{H}^+] + K K_1 K_F[\text{Trp}][\text{H}^+]^2} \quad (12)$$

$$k_C = \frac{\text{Rate}}{[\text{Fe(CN)}_6^{3-}]} = \frac{k_1 K K_1 K_F[\text{Trp}][\text{H}^+]^2[\text{Pd}^{II}]}{1 + K[\text{H}^+] + K_1[\text{H}^+] + K K_1[\text{H}^+]^2 + K K_F[\text{Trp}][\text{H}^+] + K K_1 K_F[\text{Trp}][\text{H}^+]^2} \quad (13)$$

Equation (13) can be rearranged to the following form, which is suitable for verification:

$$\frac{[\text{Pd}^{II}]}{k_C} = \left(\frac{1+m}{k_1 K K_1 K_F[\text{H}^+]^2}\right)\frac{1}{[\text{Trp}]} + \frac{1}{k_1 K_1[\text{H}^+]} + \frac{1}{k_1} \quad (14)$$

where, $m = [\text{H}^+](K + K_1 + K K_1[\text{H}^+])$.

According to Eq. (14), other conditions being constant, plots of $[Pd^{II}]/k_C$ versus $1/[Trp]$ and $[Pd^{II}]/k_C$ versus $1/[H^+]^2$ should be linear which were found to be so (figure 7).

Activation parameters listed in table 2 may be discussed as follows. The observed large negative values of $\Delta S^{\neq}$ confirms the compactness of the formed L-tryptophan-palladium(II) adduct and such activated adduct is more ordered than the reactants due to loss of degree of freedom.[48] The experimental values of $\Delta H^{\neq}$

and $\Delta S^{\neq}$ were both favorable for electron transfer process. Again, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate the endothermic formation of adduct and its non-spontaneity, respectively.

4. Conclusions

The reaction between L-tryptophan and hexacyanoferrate(III) in perchloric acid medium does not proceed in the absence of a catalyst and occurs in a significant rate in the presence of small amount of palladium(II) catalyst. The mode of electron transfer has been indicated through an adduct between L-tryptophan and palladium(II) catalyst *via* the carboxyl group rather than the amine group. The overall mechanistic sequence described here is consistent with the experimental results and product analysis.

Appendix

Derivation of rate law:

According to the suggested mechanism and regarding to reaction (8),

$$\text{Rate} = \frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k_1[\text{C}][\text{HFe(CN)}_6^{2-}] \quad (15)$$

from reactions (6)–(8)

$$K = \frac{[\text{Trp}^+]}{[\text{Trp}][\text{H}^+]} , \, [\text{Trp}^+] = K[\text{Trp}][\text{H}^+] \quad (16)$$

and

$$K_1 = \frac{[\text{HFe(CN)}_6^{2-}]}{[\text{Fe(CN)}_6^{3-}][\text{H}^+]} , \, [\text{HFe(CN)}_6^{2-}]$$

$$= K_1[\text{Fe(CN)}_6^{3-}][\text{H}^+] \quad (17)$$

$$K_F = \frac{[\text{C}]}{[\text{Trp}^+][\text{Pd}^{II}]} , \, [\text{C}] = K_F[\text{Trp}^+][\text{Pd}^{II}]$$

$$= K K_F[\text{Trp}][\text{H}^+][\text{Pd}^{II}] \quad (18)$$

Substituting Eqs. (17) and (18) into Eq. (15) leads to,

$$\text{Rate} = k_1 K K_1 K_F[\text{Trp}][\text{Fe(CN)}_6^{3-}][\text{H}^+]^2[\text{Pd}^{II}] \quad (19)$$

The total concentration of Trp is given by:

$$[\text{Trp}]_T = [\text{Trp}]_F + [\text{Trp}^+] + [\text{C}] \quad (20)$$

where 'T' and 'F' stand for total and free concentrations.

Substituting Eqs. (16) and (18) into Eq. (20) and rearrangement gives,

$$[\text{Trp}]_T = [\text{Trp}]_F + K[\text{Trp}][\text{H}^+]$$

$$+ K K_F[\text{Trp}][\text{H}^+][\text{Pd}^{II}] \quad (21)$$

$$[\text{Trp}]_T = [\text{Trp}]_F(1 + K[\text{H}^+] + K K_F[\text{H}^+][\text{Pd}^{II}]) \quad (22)$$

Therefore,

$$[\text{Trp}]_F = \frac{[\text{Trp}]_T}{1 + K[\text{H}^+] + K K_F[\text{H}^+][\text{Pd}^{II}]} \quad (23)$$

In view of the low concentration of Pd^{II}, the third denominator term $KK_F[\text{H}^+][\text{Pd}^{II}]$ in the above equation is neglected. Therefore,

$$[\text{Trp}]_F = \frac{[\text{Trp}]_T}{1 + K[\text{H}^+]} \quad (24)$$

Also,

$$[\text{Fe(CN)}_6^{3-}]_T = [\text{Fe(CN)}_6^{3-}]_F + [\text{HFe(CN)}_6^{2-}] \quad (25)$$

Substituting Eq. (17) into Eq. (25),

$$[\text{Fe(CN)}_6^{3-}]_T = [\text{Fe(CN)}_6^{3-}]_F(1 + K_1)[\text{H}^+]) \quad (26)$$

Therefore,

$$[\text{Fe(CN)}_6^{3-}]_F = \frac{[\text{Fe(CN)}_6^{3-}]_T}{1 + K_1[\text{H}^+]} \quad (27)$$

Similarly,

$$[\text{Pd}^{II}]_T = [\text{Pd}^{II}]_F + [\text{C}] \quad (28)$$

Substituting Eq. (18) into Eq. (28) and rearrangement gives,

$$[\text{Pd}^{II}]_T = [\text{Pd}^{II}]_F(1 + K K_F[\text{Trp}][\text{H}^+]) \quad (29)$$

$$[\text{Pd}^{II}]_F = \frac{[\text{Pd}^{II}]_T}{1 + K K_F[\text{Trp}][\text{H}^+]} \quad (30)$$

In view of the high concentrations of $[\text{H}^+]$,

$$[\text{H}^+]_T = [\text{H}^+]_F \quad (31)$$

Substituting Eqs. (24), (27), (30) and (31) into Eq. (19) (and omitting 'T' and 'F' subscripts) leads to,

$$\text{Rate} = \frac{k_1 K K_1 K_F[\text{Trp}][\text{Fe(CN)}_6^{3-}][\text{H}^+]^2[\text{Pd}^{II}]}{(1 + K[\text{H}^+])(1 + K_1[\text{H}^+])(1 + K K_F[\text{Trp}][\text{H}^+])} \quad (32)$$

$$\text{Rate} = \frac{k_1 K K_1 K_F[\text{Trp}][\text{Fe(CN)}_6^{3-}][\text{H}^+]^2[\text{Pd}^{II}]}{1 + K[\text{H}^+] + K_1[\text{H}^+] + K K_1[\text{H}^+]^2 + K K_F[\text{Trp}][\text{H}^+] + K K_1 K_F[\text{Trp}][\text{H}^+]^2 + K^2 K_F[\text{Trp}][\text{H}^+]^2 + K^2 K_1 K_F[\text{Trp}][\text{H}^+]^3} \quad (33)$$

The terms $K^2 K_F[\text{Trp}][\text{H}^+]^2$ and $K^2 K_1 K_F[\text{Trp}][\text{H}^+]^3$ in the denominator of Eq. (33) are negligibly small compared to unity in view of the low concentration of Trp used. Therefore, Eq. (33) can be written as:

$$\text{Rate} = \frac{k_1 K K_1 K_F[\text{Trp}][\text{Fe(CN)}_6^{3-}][\text{H}^+]^2[\text{Pd}^{II}]}{1 + K[\text{H}^+] + K_1[\text{H}^+] + K K_1[\text{H}^+]^2 + K K_F[\text{Trp}][\text{H}^+] + K K_1 K_F[\text{Trp}][\text{H}^+]^2} \quad (34)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (35),

$$\text{Rate} = \frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k_C[\text{Fe(CN)}_6^{3-}] \quad (35)$$

Comparing Eqs. (34) and (35), the following relationship is obtained,

$$k_C = \frac{k_1 K K_1 K_F[\text{Trp}][\text{H}^+]^2[\text{Pd}^{\text{II}}]}{1 + K[\text{H}^+] + K_1[\text{H}^+] + K K_1[\text{H}^+]^2 + K K_F[\text{Trp}][\text{H}^+] + K K_1 K_F[\text{Trp}][\text{H}^+]^2} \quad (36)$$

and with rearrangement,

$$\frac{[\text{Pd}^{\text{II}}]}{k_C} = \left(\frac{1+m}{k_1 K K_1 K_F[\text{H}^+]^2}\right)\frac{1}{[\text{Trp}]} + \frac{1}{k_1 K_1[\text{H}^+]} + \frac{1}{k_1} \quad (37)$$

where,

$$m = [H^+](K + K_1 + K K_1[\text{H}^+]).$$

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