

# Study of Kinetics Incorporation of Ag with TCPP

Rahmatollah Rahimi, Fariba Moharrami

**Abstract**—The Kinetics formation of labile Complex Ag (I) tetra (p-carboxyphenyl) porphyrin, was investigated at 25°C and I=0.1M (NaNO<sub>3</sub>). By spectrophotometric titration, the composition ratio of the complex was established to be 2:1 (Ag : H<sub>2</sub>TCPP). The equilibrium constant, K, was found to be log 10<sup>-6.53</sup>. Binding of the first Ag (I) was found to be rate determining step with rate constant, k<sub>1</sub>= 4.67×10<sup>2</sup>. A plausible mechanism is discussed. We discuss theoretically why Ag(I)<sub>2</sub>TCPP is unstable.

**Keywords**—Kinetics, Silver, TCPP, Sitting-atop, Theoretical study

## I. INTRODUCTION

THIS porphyrins lie at the focus of several different fields of research [1-3]. Porphyrins, being macrocyclic chelating ligands offer a convenient tool for studying the chemistry of unusual oxidation states of transition metals [4]. Porphyrins, work as anti poison drugs in the biological systems in our previous work Co(III) in TPPS porphyrin, scavenges cyanide by forming an extremely stable monocyano adduct. [5]. Metalloporphyrins control the decisive steps in various natural and technological processes, which often involve the reversible attachment of a molecular ligand to the central metal ion [6]. In the previous work, [N-Methyltetrakis (4-sulfonatophenyl)porphinato] cobalt(II), -nickel(II), and -copper(II) [M<sup>II</sup>(N-Me)TSPP] have been prepared, The Ni derivative, moreover, produced MeNi<sup>III</sup>TSPP which was unstable and gave Ni<sup>II</sup>TSPP and methyl radical[7]. A kinetic study of the acid solvolysis reactions of divalent nickel, cobalt, zinc and copper complexes of N-methyl-tetra(4-sulfonatophenyl) porphyrin was done at 25°C in aqueous solution.

All reactions were first order in metalloporphyrin and first order in [H<sup>+</sup>]. Only the Zn<sup>II</sup> and Cu<sup>II</sup> derivatives had a second term proportional to [H<sup>+</sup>][Ac<sup>-</sup>]. Calculated formation constants of the uncatalyzed reactions were in the order Ni > Cu ~ Zn > Co > Cd. The results showed that kinetically N-alkylated metalloporphyrins require one less proton for acid solvolysis than do the corresponding metalloporphyrins[8]. Metalloporphyrins are kinetically inert complex. If, however,

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the ionic radius of the metal ions is too large to fit into cavity, they are located out of the ligand plane, distorting it and form sitting-atop complexes [9].

The SAT (sitting-atop) phenomena previously observed with TPYP, can be explained by 1. an unusual anion term in the rate law, 2. the strong increase in pK<sub>3</sub>, and pK<sub>4</sub> upon increase in ionic strength, and 3. the lack of reactivity of mono- and dication forms toward metal ions [10]. A series of sulfonated water-soluble, phenyl-substituted porphyrins has been reported, containing halogen or alkyl groups in the ortho, di-ortho or para positions. While the para-substituted compounds exhibited monomer-dimer behaviour, all the ortho and di-ortho substituted porphyrins were monomeric in aqueous solution at 0.1 M ionic strength [11]. From the absorption spectra of porphyrins the Soret bands assigned to the S<sub>0</sub>→S<sub>2</sub> transitions in the 380-440 nm range and the Q bands assigned S<sub>0</sub>→S<sub>1</sub> are shown in the 500-700 nm range.

Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state (H<sub>2</sub>P), in a regular (AIP) and in a SAT (HgP) metalloporphyrin are shown in Fig 1[9].

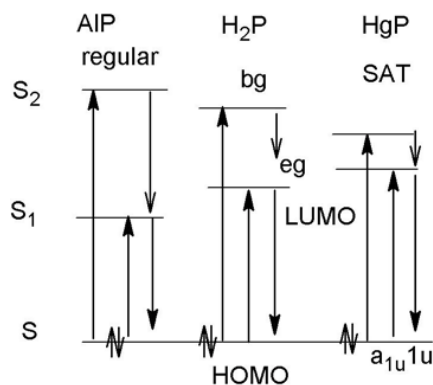


Fig. 1 Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state H<sub>2</sub>P, in a regular AIP and in a SAT HgP metalloporphyrin.

Kinetics studies of formation of metalloporphyrin are discussed by other researchers [12-16]. Incorporation of Ag into other porphyrins are studied by Krishnamurthy and et al [17], but we studied on tetra (p-carboxyphenyl) porphyrin, (H<sub>2</sub>TCPP) with Ag kinetically and discussed why Ag<sub>2</sub>TCPP is unstable and stable form of the product is AgTCPP.

## II. RELATED WORK

## A. Experimental Section

Shimadzu UV/visible spectrophotometer and Durrum stopped flow apparatus thermostatted at  $25 \pm 0.2$  °C were used for kinetic studies. All kinetic studies were carried out in presence of buffer, pH=9 and  $I=0.1$  M ( $\text{NaNO}_3$ ). Plots of  $\log(A_t - A_\infty)$  vs. time were linear for over three half lives. The  $\text{H}_2\text{TCPP}$  was synthesized by the method of Adler, pyrrole with 4-carboxy benzaldehyde and propionic acid with 2 hour reflux. Stable Ag (II) porphyrins are synthesized by mixing a porphyrin solution with a Ag (I) salt such as nitrate. On mixing the two, the red porphyrin solution becomes green momentarily then slowly changes to red, often accompanied by a silver mirror. The green colour is result of acidate during the dissociation of  $\text{H}^+$  from pyrrole and the final red colour is due to Ag(II)porphyrin, formed as a result of disproportionation of Ag(I) ions in macrocycle.

Theoretical study of silver porphyrin is measured by Gaussian and Hyper programs. Spectrophotometric titration were carried out by placing  $500 \text{ cm}^3$  of porphyrin solution, containing  $5.0 \text{ cm}^3$  of stock porphyrin,  $50.0 \text{ cm}^3$  of  $0.1$  M buffer solution and  $25 \text{ cm}^3$  of  $2.0$  M  $\text{NaNO}_3$  in a jacketed vessel. The solution was thermal equilibrated for 30 min. Different aliquots of  $0.1$  M  $\text{AgNO}_3$  solution were added, employing a microburette. Before each addition, the spectrum of porphyrin sample was recorded. By retaining this sample, the total volume was maintained close to  $500 \pm 50 \text{ cm}^3$  allowing for silver nitrate.

## III. RESULTS AND DISCUSSION

## A. Mechanism

The mechanism of TCPP synthesis is show in Fig 2. 4-carboxy benzaldehyde and pyrrole react in presence of propionic acid. After Porphyrinogen formation from dipyrrole oxids,  $\text{H}_2\text{TCPP}$  will synthesized and recognized with TLC.

## B. UV-Visible spectrometer

The Solution of  $10^{-5}$  M TCPP at pH 9 is pink and exhibits five absorption maxima; one in Soret band at  $414 \text{ nm}$  ( $3.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and four maxima in the "Q" range  $500-650 \text{ nm}$  at  $517, 554, 579$  and  $634 \text{ nm}$  with the molar absorption coefficients of  $1.2 \times 10^4, 6.5 \times 10^3, 5.2 \times 10^3$  and  $3.3 \times 10^3$ , respectively.

Spectra of porphyrin solutions during spectrophotometric titration are presented in Fig.4-a,b. On addition of Ag(I) ion, the absorption of free-base at  $420 \text{ nm}$  and  $517 \text{ nm}$  decreases whereas the absorption at  $460 \text{ nm}$  increased.

A plot of absorbance at  $460 \text{ nm}$ , the Soret of Ag(I)porphyrin, and at  $517 \text{ nm}$ , the major visible band of the free-base, as a function of the added silver ion concentrations is shown in Fig.5 a,b.

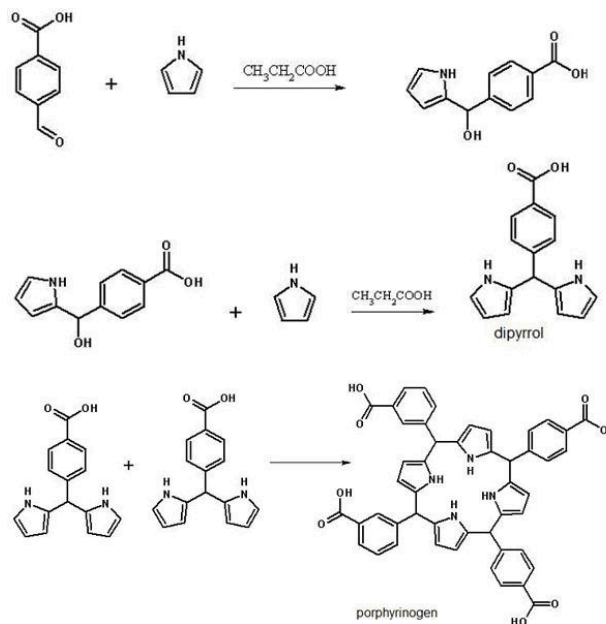


Fig. 2 Mechanism of synthesis TCPP

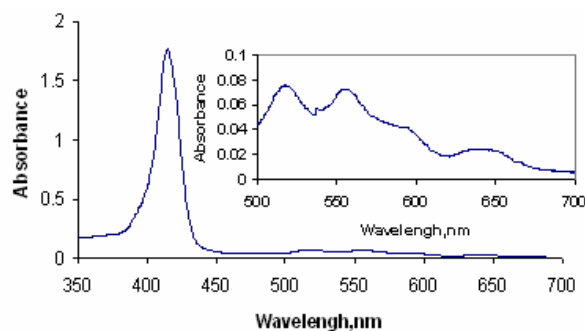
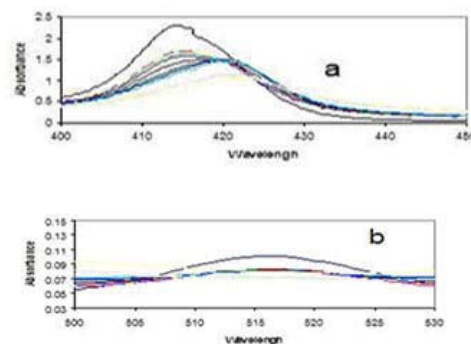


Fig. 3 Absorption of TCPP at pH=9

Fig. 4 (a) Variety of spectrum in the range of 400-450(nm) and(b) 500-530 (nm) during the titration of  $\text{H}_2\text{TCPP}$  with  $\text{Ag}^+$

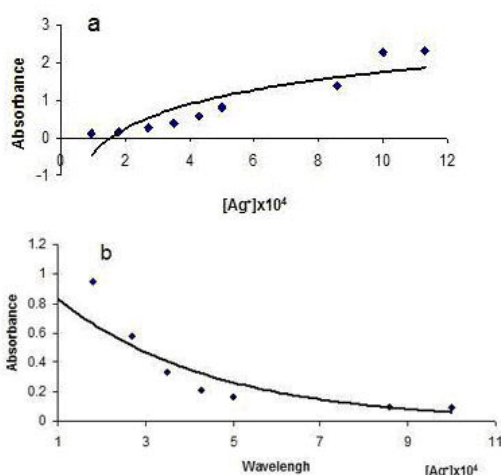


Fig. 5 (a) Plot of absorbance vs.  $[Ag^+]$  at 460(nm) and (b) at 570 (nm) during spectrophotometric titration of  $H_2TCPP$  with  $Ag^+$

### C. Reaction mechanism

Assuming a reaction of the type:



$$K = \frac{[H^+]^n [AgP]}{[H_2P][Ag^+]^n} \quad (2)$$

$$\log K = n \log [H^+] + \log [AgP] - \log [H_2P] - n \log [Ag^+] \quad (3)$$

$$\log [AgP] - \log [H_2P] = \log K - n \log [H^+] + n \log [Ag^+] \quad (4)$$

where n can be 1, 2, etc. one can derive the following:

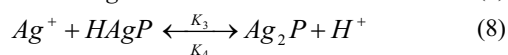
$$\log \left[ \frac{A_i - A}{A - A_f} \right] = n \log [Ag^+] + \log K - n \log [H^+] \quad (5)$$

In "(5)"  $A_i$ ,  $A$ ,  $A_f$  and  $K$  represent absorbance at the beginning of the titration, absorbance during the titration corresponding to  $[Ag^+]$ , and absorbance at the end of the titration and the equilibrium constant respectively. Plots of  $\log \left[ \frac{A_i - A}{A - A_f} \right]$  as a function of  $\log [Ag^+]$ , gives straight line with a slope of "n" and intercept of "K". Such a plot for the titration with  $H_2TCPP$  at 460 nm did indeed yield straight line with slopes of 2.05. From the intercept, log K values were extracted to be -6.53 and for the  $H_2TMPyP$   $n=1.8$ ,  $\log K=-5.8$  was reported.

Thus the following stoichiometry is formulated for the equilibrium "6":



This reaction was found to be first order in porphyrin and second order in  $Ag^+$ , so the probable mechanism for silver porphyrin formation is "7,8":



$$V = \frac{d[Ag_2P]}{dt} = k_3[HAG][Ag^+] - k_4[Ag_2P][H^+] \quad (9)$$

$$V = \left( \frac{k_1 k_3 [Ag^+]^2 + k_2 k_4 [H^+]^2}{k_3 [Ag^+] + k_2 [H^+]} \right) [H_2P]_t \quad (10)$$

$$V = K_{obs} ([Ag_2P]_{eq} - [Ag_2P]_t) \quad (11)$$

$$\frac{d[Ag_2P]}{dt} = (k_1 k_3 [Ag^+]^2 + k_2 k_4 [H^+]^2) / (k_2 [H^+] + k_3 [Ag^+]) ([Ag_2P]_{equ} - [Ag_2P]_t). \quad (12)$$

$$= k_{obs} ([Ag_2P]_{equ} - [Ag_2P]_t) \quad (13)$$

$$(k_1 k_3 [Ag^+]^2 + k_2 k_4 [H^+]^2) / (k_2 [H^+] + k_3 [Ag^+]) \quad (14)$$

If  $k_3 \gg K_2$

$$k_{obs} [Ag^+] = k_1 [Ag^+]^2 + k_2 k_4 / k_3 [H^+]^2 \quad (14)$$

A plot of  $k_{obs}[Ag^+]$  vs  $[Ag^+]^2$  should be linear with slope of  $k_1$  and intercept of  $\frac{k_2 k_4}{k_3 [H^+]^2}$ .

Values of  $k_1$  for TCPP in Fig. 6, and  $H_2TMPyP$  obtained from these plots are  $4.67 \times 10^2$  and  $2.28 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  respectively.

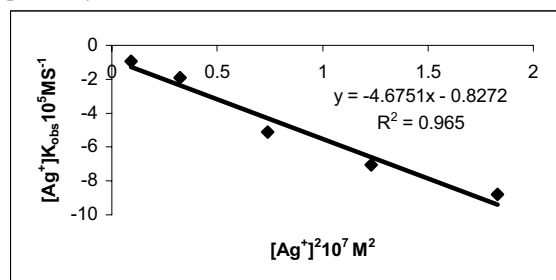


Fig. 6 Plot of  $K_{obs} \times [Ag^+]$  vs  $[Ag^+]^2$  for the reaction of  $Ag(I)$  with  $H_2TCPP$

Absorption spectra of the porphyrin solutions and silver porphyrin are compared in Fig.7.

The soret band of metalloporphyrins is shorter than porphyrins and four Q bands in porphyrins decrease to two bands in absorption spectra of metalloporphyrins.

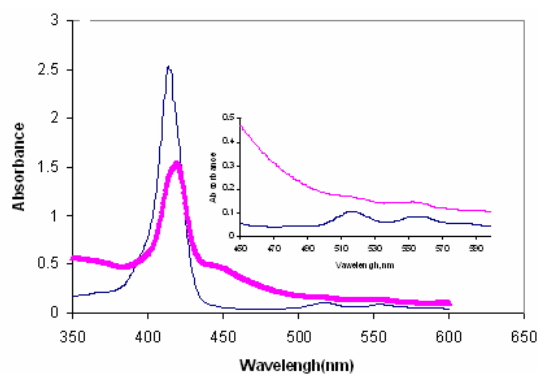
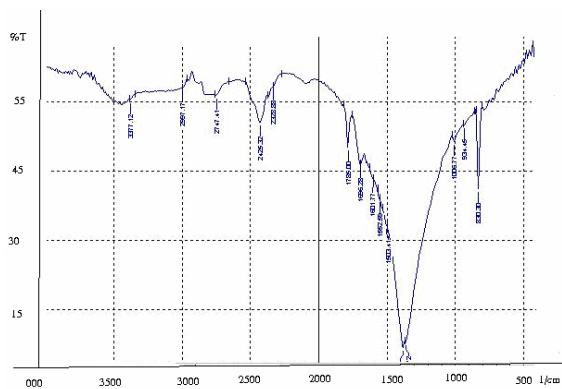


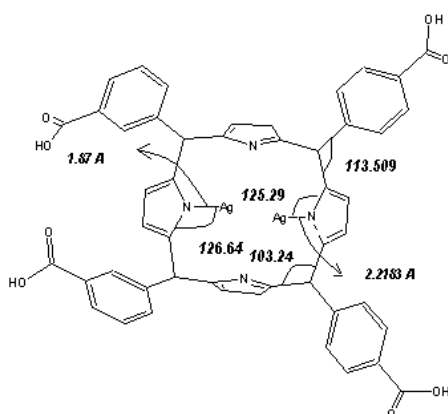
Fig. 7 Absorption spectra of TCPP, long soret band, and  $AgTCPP$ , short soret band

Fig. 8 IR spectra Ag<sub>2</sub>TCPP

The symmetry group of the free-base porphyrins is D<sub>2h</sub> due to the two hydrogen atoms on the diagonally located pyrrolic rings. In Ag<sub>2</sub>TCPP the metal centre is located out of the ligand plane, distorting it and causing lower symmetry C<sub>2</sub>. IR spectrum of metalloporphyrin is shown in Fig.8.

#### D.Theoretical investigation

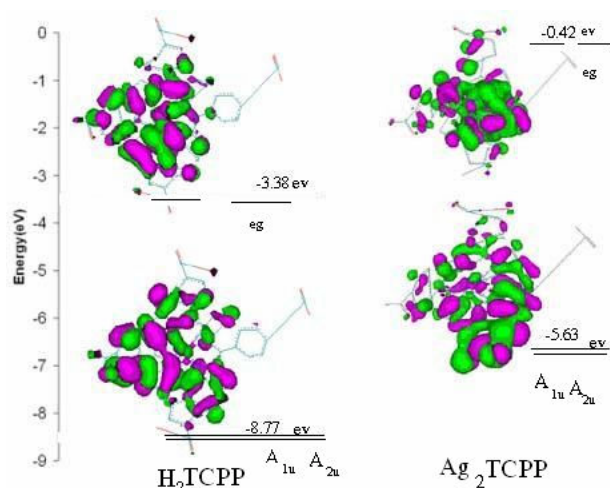
Fig. 9 shows the proposed geometry of the sitting-atop complex which the Angles and bonds of Ag<sub>2</sub>TCPP are determined by hyper program, One bond length of Ag-N is 1.87 Å and the other bond length is 2.3 Å. An activated complex of this type is also in conformity and this intermediate in solution termed AgTCPP.

Fig. 9 Geometry and bonds and angles of Ag<sub>2</sub>TCPP complex

HOMO and LUMO for H<sub>2</sub>TCPP and Ag<sub>2</sub>TCPP were calculated by Gaussian program and semi-empirical ZINDO/1 basis set. HOMO (A<sub>1u</sub>, A<sub>2u</sub>) is -8.377 eV and -5.63 eV for H<sub>2</sub>TCPP and Ag<sub>2</sub>TCPP respectively and LUMO (e<sub>g</sub>) is -3.38 eV and -0.42 eV for H<sub>2</sub>TCPP and Ag<sub>2</sub>TCPP respectively.

#### IV. CONCLUSION

In this study, the Kinetics incorporation of silver in H<sub>2</sub>TCPP was discussed and the metalloporphyrin was characterized by theoretical studies, UV-Vis and IR spectrum. Mechanism of reactions and theoretical study were investigated.

Fig. 10 Calculated of HOMO and LUMO of H<sub>2</sub>TCPP and Ag<sub>2</sub>TCPP (ZINDO/1) basis set.

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