

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 (NaNO₃). By spectrophotometric titration, the composition ratio of the complex was established to be 2:1 (Ag : H₂TCPP). The equilibrium constant, K, was found to be log 10^{-6.53}. Binding of the first Ag (I) was found to be rate determining step with rate constant, k₁= 4.67×10². A plausible mechanism is discussed. We discuss theoretically why Ag(I)₂TCPP 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^{II}(N-Me)TSPP] have been prepared. The Ni derivative, moreover, produced MeNi^{III}TSPP which was unstable and gave Ni^{II}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⁺]. Only the Zn^{II} and Cu^{II} derivatives had a second term proportional to [H⁺][Ac⁻]. 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,

Rahmatollah.Rahimi, Department of chemistry, University of Science and Technology, Tehran, Iran, phone: 9821-77240290; fax: 9821-77491204; e-mail:.,Rahmatollah.Rahimi@just.ac.com

Fariba.Moharrami, Department of chemistry, University of Science and Technology, Tehran, Iran phone: 9821-77240290; fax: 9821-77491204; e-mail:.,Moharame@gmail.com

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 pK₃, and pK₄ 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 S₀→S₂ transitions in the 380-440 nm range and the Q bands assigned S₀→S₁ are shown in the 500-700 nm range.

Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state (H₂P), in a regular (AIP) and in a SAT (HgP) metalloporphyrin are shown in Fig 1[9].

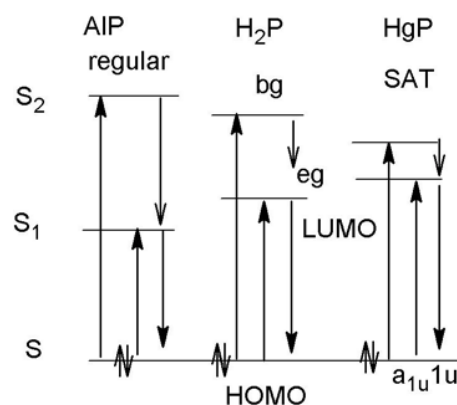


Fig. 1 Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state H₂P, in a regular AIP and in a SAT HgP metalloporphyrin.

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, (H₂TCPP) with Ag kinetically and discussed why Ag₂TCPP 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 ± 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 (NaNO_3). Plots of $\log(A_t - A_\infty)$ vs. time were linear for over three half lives. The H_2TCPP 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 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 cm^3 of porphyrin solution, containing 5.0 cm^3 of stock porphyrin, 50.0 cm^3 of 0.1 M buffer solution and 25 cm^3 of 2.0 M NaNO_3 in a jacketed vessel. The solution was thermal equilibrated for 30 min. Different aliquots of 0.1 M 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 pyrrol react in presence of propionic acid. After Porphyrinogen formation from dipyrrole oxids, H_2TCPP will synthesized and recognaized 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 nm ($3.5 \times 10^5 \text{ M}^{-1} \text{cm}^{-1}$) and four maxima in the "Q" range 500-650 nm at 517, 554, 579 and 634 nm with the molar absorption coefficients of 1.2×10^4 , 6.5×10^3 , 5.2×10^3 and 3.3×10^3 , 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 nm and 517 nm decreases whereas the absorption at 460 nm increased.

A plot of absorbance at 460 nm, the Soret of Ag(I)porphyrin, and at 517 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.

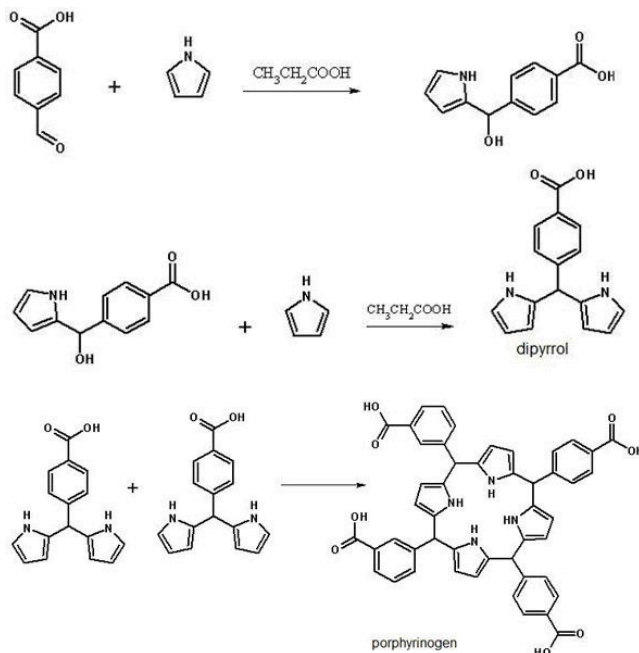


Fig. 2 Mechanism of synthesis TCPP

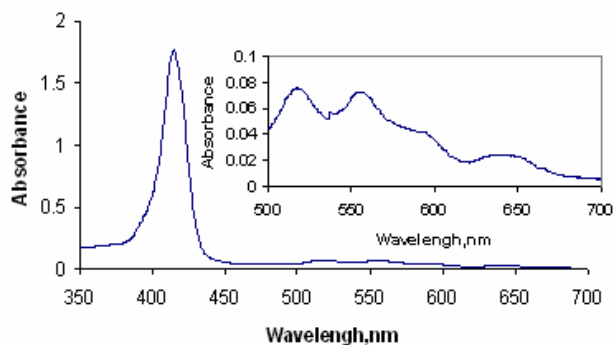


Fig. 3 Absorption of TCPP at pH=9

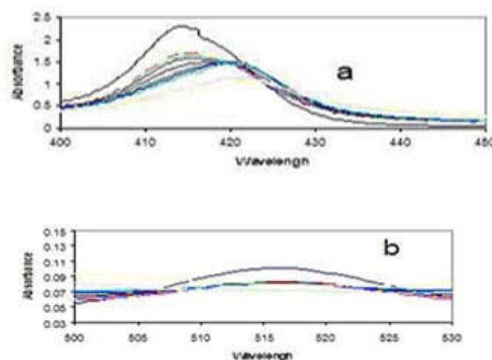


Fig. 4 (a) Variety of spectrum in the range of 400-450(nm) and(b) 500-530 (nm) during the titration of H_2TCPP with Ag^+

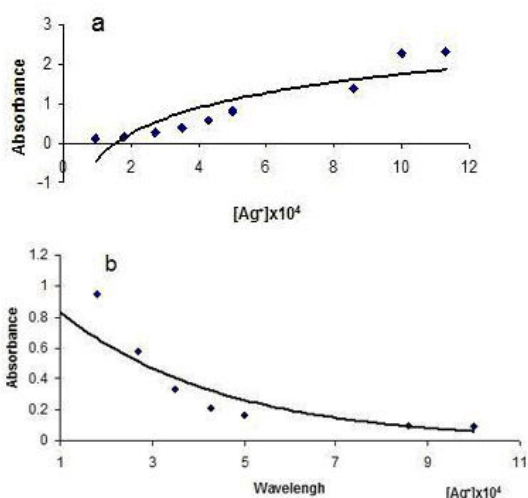


Fig. 5 (a) Plot of absorbance vs. $[Ag^+]$ at 460(nm) and (b) at 570 (nm) during spectrophotometric titration of H_2TCPP with Ag^+

C. Reaction mechanism

Assuming a reaction of the type:



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

$$\log K = n \log[H^+] + \log[AgP] - \log[H_2 - P] - n \log[Ag^+] \quad (3)$$

$$\log[AgP] - \log[H_2 - P] = \log K - n \log[H^+] + n \log[Ag^+] \quad (4)$$

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

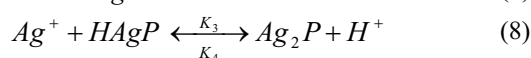
$$\log\left(\frac{A_i - A}{A - A_f}\right) = n \log[Ag^+] + \log K - n \log[H^+] \quad (5)$$

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 $\log[(A_i - A)/(A - A_f)]$ 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":



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

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

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

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

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

$$(k_1 k_3 [Ag^+]^2 + k_2 k_4 [H^+]^2) / (k_2 [H^+] + k_3 [Ag^+]) \quad (13)$$

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 4.67×10^2 and $2.28 \times 10^3 M^{-1}s^{-1}$ respectively.

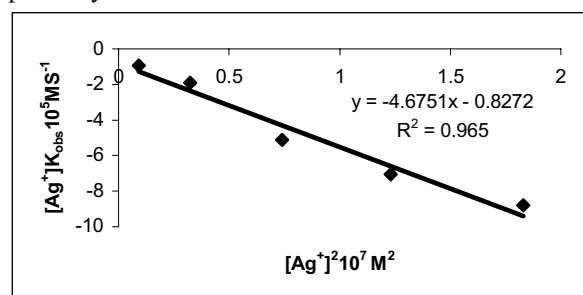


Fig. 6 Plot of $K_{obs} \times [Ag^+]$ vs $[Ag^+]^2$ for the reaction of $Ag(I)$ with H_2TCPP

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.

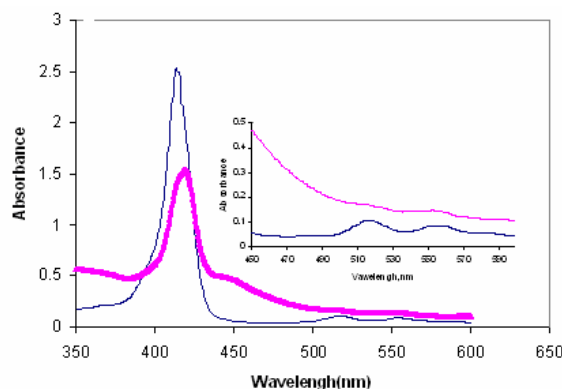


Fig. 7 Absorption spectra of TCPP, long Soret band, and $AgTCPP$, short Soret band

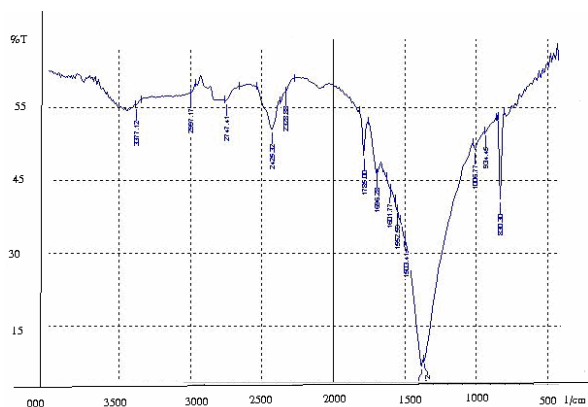


Fig. 8 IR spectra Ag₂TCPP

The symmetry group of the free-base porphyrins is D_{2h} due to the two hydrogen atoms on the diagonally located pyrrolic rings. In Ag₂TCPP the metal centre is located out of the ligand plane, distorting it and causing lower symmetry C₂. 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 Ag₂TCPP 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.

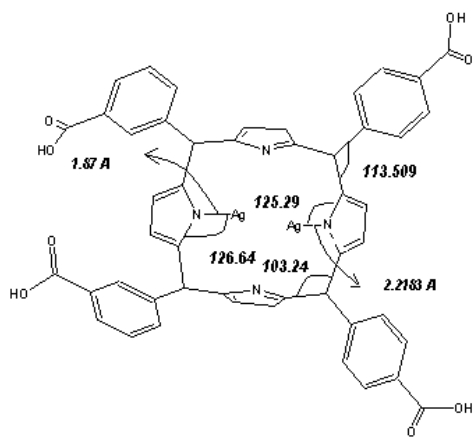


Fig. 9 Geometry and bonds and angles of Ag₂TCPP complex

HOMO and LUMO for H₂TCPP and Ag₂TCPP were calculated by Gaussian program and semi-empirical ZINDO/1 basis set. HOMO (A_{1u}, A_{2u}) is -8.377 eV and -5.63 eV for H₂TCPP and Ag₂TCPP respectively and LUMO (e_g) is -3.38 eV and -0.42 eV for H₂TCPP and Ag₂TCPP respectively.

IV. CONCLUSION

In this study, the Kinetics incorporation of silver in H₂TCPP was discussed and the metalloporphyrin was characterized by theoretical studies, UV_Vis and IR spectrum. Mechanism of reactions and theoretical study were investigated.

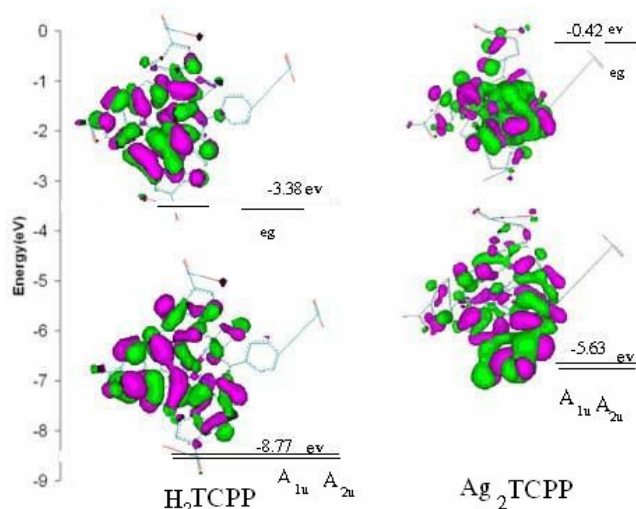


Fig. 10 Calculated of HOMO and LUMO of H₂TCPP and Ag₂TCPP (ZINDO/1) basis set.

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Dr. Rahmatollah Rahimi



Place of Birth: Saveh, Iran; Date of Birth: 2-3-1955
Education Background: B.Sc. Chemistry 1983, Howard University Washington DC USA. M.Sc. Physical Chemistry 1987, Howard University Washington DC USA
Ph.D. Inorganic Chemistry 1992, Howard University Washington DC USA
Employment Background: Chemistry Department, Howard University, Washington DC. USA from 1985 to 1991 Laboratory Assistant Instructor.

Chemistry Department, Iran University of science and Technology from 1991 to now Instructor of Chemistry under graduate and graduate courses.