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Study of Kinetics of Silver with Tetra(*p*-carboxyphenyl)porphyrin

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The kinetics formation of labile complex Ag(I) *tetra*(*p*-carboxyphenyl)porphyrin (TCPP) was investigated at 25 ºC and I = 0.1 M ($NaNO_3$). By spectrophotometric titration, the composition ratio of the complex was established to be 2:1 (Ag:H_2TCPP). 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, $k_1 = 4.67 \times 10^2$. A plausible mechanism is discussed.

Key Words: Kinetics, Silver, Tetra(*p*-carboxyphenyl)porphyrin, Sitting-atop, Theoretical study.

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-methyl*tetrakis*(4-sulfonatophenyl)-porphinato] cobalt(II), -nickel(II) and -copper(II) [M^{2+}(N-Me)TSPP] have been prepared, The Ni derivative, moreover, produced $MeNi^{3+}$TSPP which was unstable and gave Ni^{2+}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 ºC in aqueous solution. All reactions were first order in metalloporphyrin and first order in $[H^+]$. Only the Zn^{2+} and Cu^{2+} derivatives had a second term proportional to $[H^+][OAc^-]$. 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 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_3 and pK_4 upon increase in ionic strength and (3) the lack of reactivity of mono- and di-cation 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 $S_0 \rightarrow S_2$ transitions in the 380-440 nm range and the Q bands assigned $S_0 \rightarrow S_1$ are shown in the 500-700 nm range.

Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state (H_2P), in a regular (AlP) and in a SAT (HgP) metalloporphyrin[9] are shown in Fig. 1.

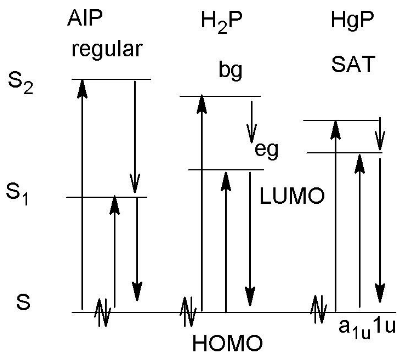

Fig. 1. Simplified energy-level diagram of the frontier orbital of a porphyrin in free-base state H_2P, in a regular AlP and in a SAT HgP metalloporphyrin

Kinetics studies of formation of metalloporphyrin are discussed by previous workers[12-16]. Incorporation of Ag into other porphyrins are studied by Krishnamurthy *et al.*[17], but we studied on tetra(*p*-carboxyphenyl)porphyrin, (H_2TCPP) with Ag kinetically and discussed why Ag_2TCPP is unstable and stable form of the product is AgTCPP.

EXPERIMENTAL

Shimadzu UV/visible spectrophotometer and Durrum stopped flow apparatus thermostatted at 25 ± 0.2 ºC 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_∞) *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 h reflux. Stable Ag(II) porphyrins are synthesized by mixing a porphyrin solution with a silver 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 formation of Ag(II) porphyrin 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 mL of porphyrin solution, containing 5.0 mL of stock porphyrin, 50.0 mL of 0.1 M buffer solution and 25 mL of 2.0 M $NaNO_3$ in a jacketed vessel. The solution was thermal equilibrated for 0.5 h. 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 ± 50 mL allowing for silver nitrate.

RESULTS AND DISCUSSION

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 recognized with TLC.

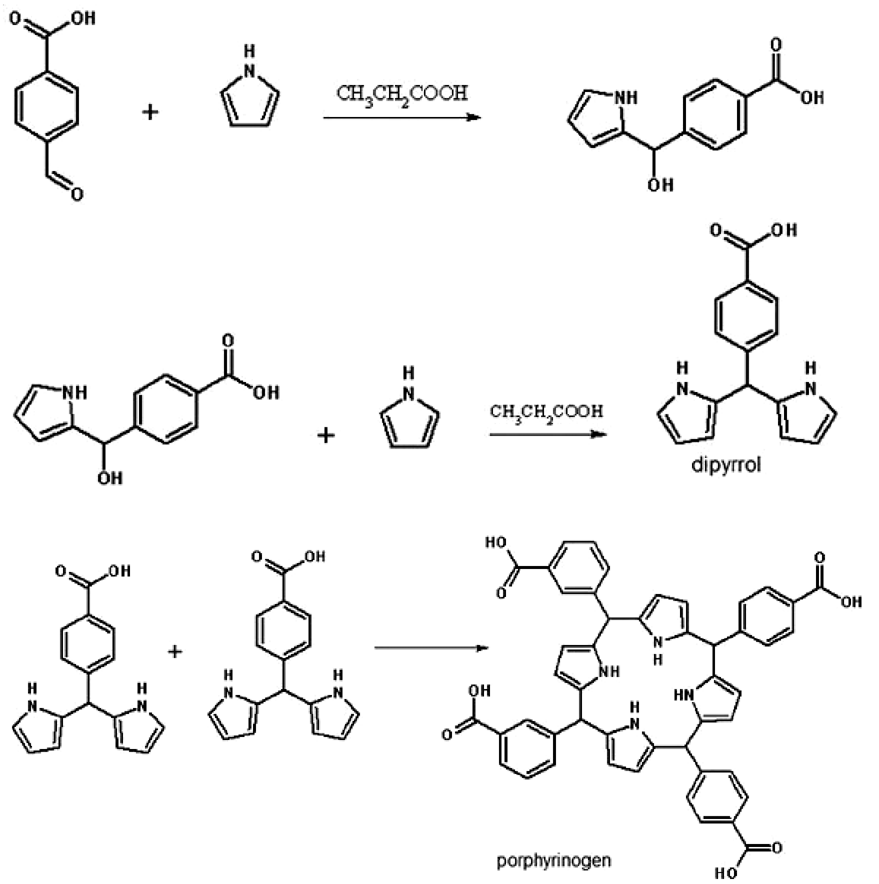

Fig. 2. Mechanism of synthesis of TCPP

The solution of 10^{-5} M TCPP at pH 9 is pink and exhibits five absorption maxima; one in Soret band at 414 nm (3.5×10^5 M^{-1} 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 (Fig. 3).

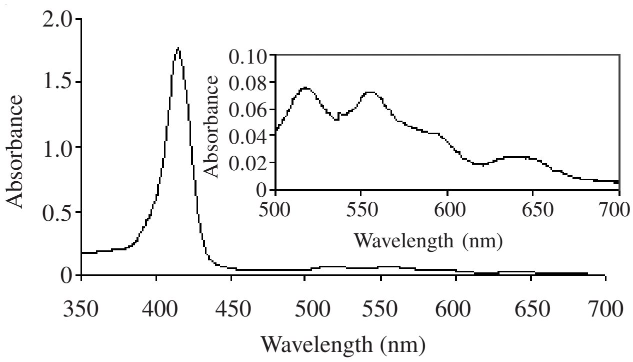

Fig. 3. Absorption of TCPP at pH = 9

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

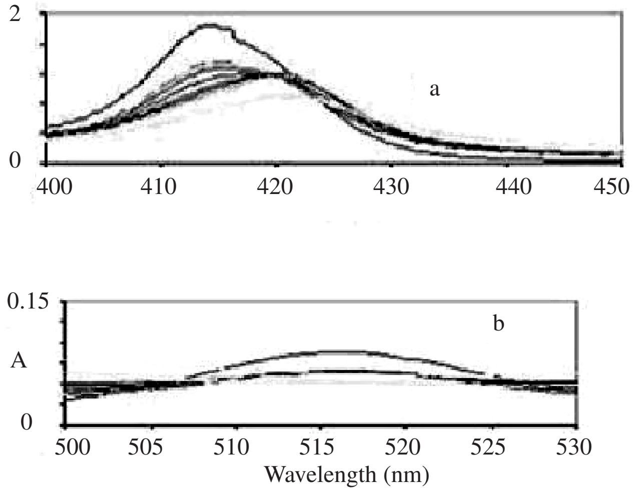

Fig. 4. (a) Variety of spectrum in the range of 400-450 nm
(b) 500-530 nm during the titration of H_2TCPP with Ag^+

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. 5a,b.

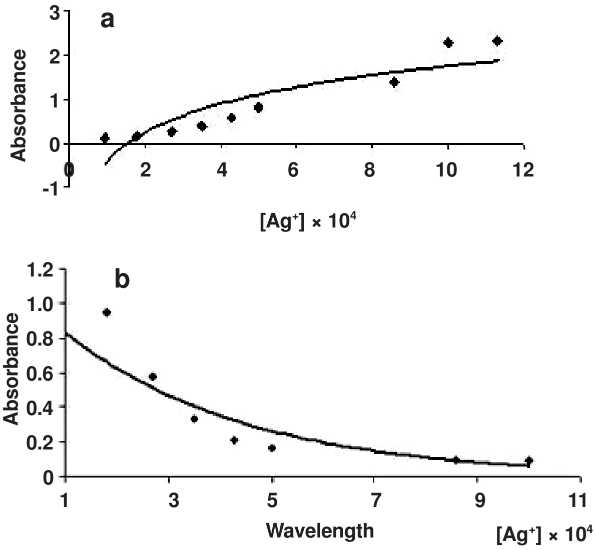

Fig. 5. (a) Plot of absorbance *vs.* [Ag^+] at 460 nm and (b) at 570 nm during spectrophotometric titration of H_2TCPP with Ag^+

Assuming a reaction of the type:

$$nAg^+ + H_2TCPP \leftrightarrow H_{2-n}Ag_nTCPP + nH^+ \quad (1)$$

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

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

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

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

$$\log[(A_i - A)/(A - A_f)] = n\log[Ag^+] + \log K - n\log[H^+] \quad (5)$$

In 'eqn. 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 (eqn. 6):

$$2Ag^+ + H_2TCPP \leftrightarrow Ag_2TCPP + 2H^+ \quad (6)$$

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

$$Ag^+ + H_2P \xleftrightarrow{K_1} HAgP + H^+ \tag{7}$$

$$Ag^+ + HAgP \xleftrightarrow[K_4]{K_3} Ag_2P + H^+ \tag{8}$$

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

$$V = \left(\frac{k_1k_3[Ag^+]^2 + k_2k_4[H^+]^2}{k_3[Ag^+] + k_2[H^+]}\right)[H_2P]_t \tag{10}$$

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

$$\begin{aligned} &d[Ag_2P]/dt = (k_1k_3[Ag^+]^2 + k_2k_4[H^+]^2) \\ &/(k_2[H^+] + k_3[Ag^+])([Ag_2P]_{equ} - [Ag_2P]_t). \\ &= k_{obs}([Ag_2P]_{equ} - [Ag_2P]_t) \end{aligned} \tag{12}$$

$$(k_1k_3[Ag^+]^2 + k_2k_4[H^+]^2)/(k_2[H^+] + k_3[Ag^+]) \tag{13}$$

If $k_3 >> K_2$

$$k_{obs}[Ag^+] = k_1[Ag^+]^2 + k_2k_4/k_3[H^+]^2 \tag{14}$$

A plot of $k_{obs}[Ag^+]$ *vs.* $[Ag^+]^2$ should be liner with slope of k_1 and intercept of $k_2k_4 / k_3[H^+]^2$.

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

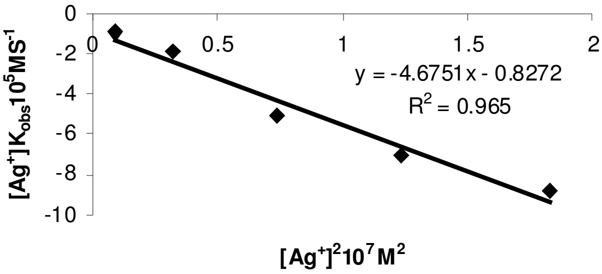

Fig. 6. Plot of $K_{obs} \times [Ag^+]$ *vs.* $[Ag^+]^2$ for the reaction of Ag(I) with H_2TCPP

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.

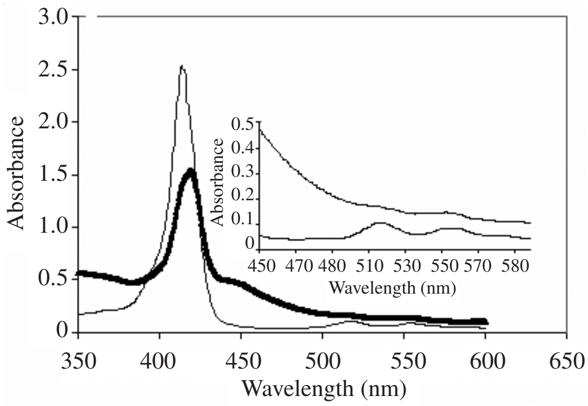

Fig. 7. Absorption spectra of TCPP, long soret band and AgTCPP, short soret band

The symmetry group of the free-base porphyrins is D_{2h} due to the two hydrogen atoms on the diagonally located pyrrolic rings. In Ag_2TCPP the metal centre is located out of the ligand plane, distorting it and causing lower symmetry C_2. IR spectrum of metalloporphyrin is shown in Fig. 8.

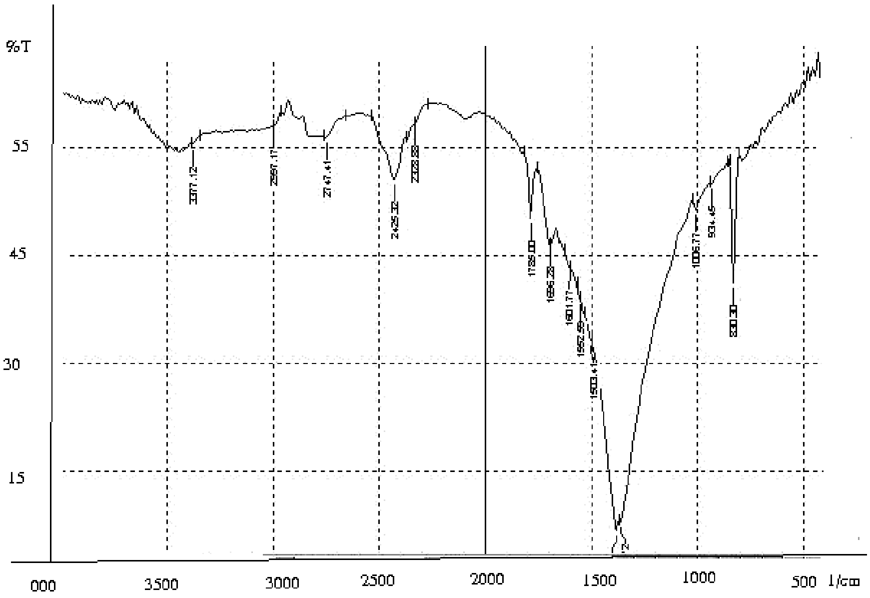

Fig. 8. IR spectra Ag_2TCPP

Theoretical investigation: Fig. 9 shows the proposed geometry of the sitting-atop complex which the Angels and bonds of Ag_2TCPP 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.

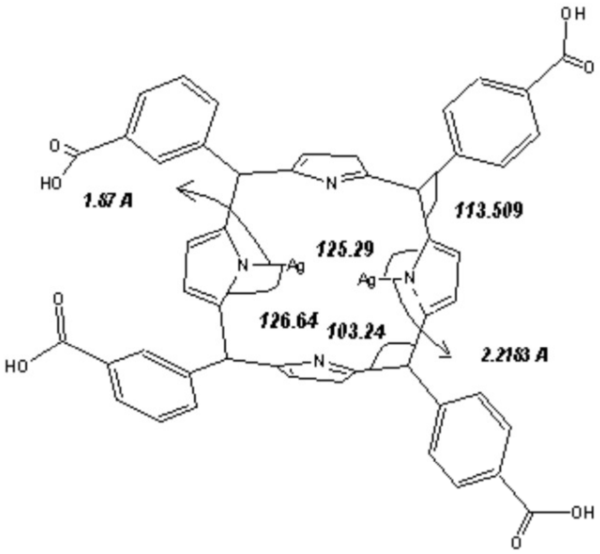

Fig. 9. Geometry and bonds and angels of Ag_2TCPP complex

HOMO and LUMO for H_2TCPP and Ag_2TCPP were calculated by Gussian program and semi-emprical ZINDO/1 basis set. HOMO (A_{1u}, A_{2u})is -8.377 and -5.63 ev for H_2TCPP and Ag_2TCPP, respectively and LUMO (e_g) is -3.38 and -0.42 ev for H_2TCPP and Ag_2TCPP, respectively (Fig. 10).

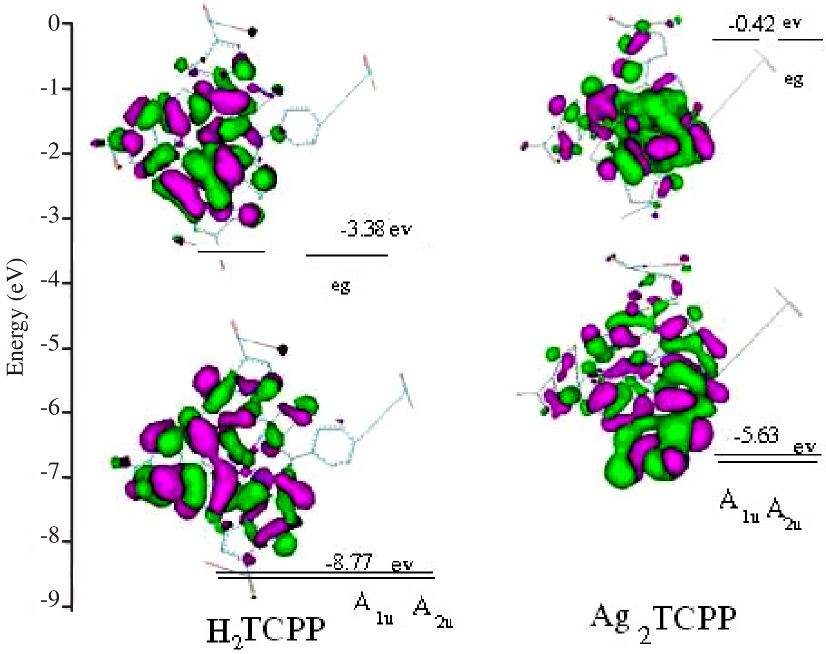

Fig. 10. Calculation of HOMO and LUMO of H_2TCPP and Ag_2TCPP (ZINDO/1) basis set

Conclusion

The composition ratio of the complex was established to be 2:1 (Ag: H_2TCPP) and the equilibrium constant (K), was found to be log $10^{-6.53}$.

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