

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

RAHMATOLLAH RAHIMI\* and FARIBA MOHARRAMI

*Department of Chemistry, University of Science and Technology, Tehran, Iran*

*Fax: (98)(21)77491204; Tel: (98)(21)77240290; Email: rahmatollah.rahimi@gmail.com*

The kinetics formation of labile complex Ag(I) tetra(*p*-carboxyphenyl)porphyrin (TCPP) was investigated at 25 °C and I = 0.1 M (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,  $k_1 = 4.67 \times 10^2$ . 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<sup>1-3</sup>. Porphyrins, being macrocyclic chelating ligands offer a convenient tool for studying the chemistry of unusual oxidation states of transition metals<sup>4</sup>. 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<sup>5</sup>. 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<sup>6</sup>. In the previous work, [N-methyltetraakis(4-sulfonatophenyl)porphinato] cobalt(II), -nickel(II) and -copper(II) [M<sup>2+</sup>(N-Me)TSPP] have been prepared, The Ni derivative, moreover, produced MeNi<sup>3+</sup>TSPP which was unstable and gave Ni<sup>2+</sup>TSPP and methyl radical<sup>7</sup>. 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>2+</sup> and Cu<sup>2+</sup> derivatives had a second term proportional to [H<sup>+</sup>][OAc<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<sup>8</sup>. 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<sup>9</sup>. 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