Spectral Evidence and Kinetics for Formation of the Sitting-Atop Complex of Copper(II) Ion with 5,10,15,20-Tetraphenylporphyrin in Acetonitrile

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The kinetic parameters for the formation of the sitting-atop (SAT) complex of the copper(II) ion with 5,10,15,20-tetraphenylporphyrin (H_2tpp) were directly determined in acetonitrile. The large $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values imply that deformation of the porphyrin ring is required during the activation process. In the SAT complex, the protons bound to the pyrrole nitrogens remain on the nitrogens and by the addition of a base such as pyridine, they are abstracted to form the Cu(tpp) complex, in which the copper(II) ion is incorporated into the porphyrin core.

The kinetics of metalloporphyrin formation between many metal ions and porphyrins have been widely investigated.[1] In previous studies, the sitting-atop (SAT) complex, in which the metal ion sits on the porphyrin plane, *i.e.*, the two pyrrole nitrogens coordinate to the metal ion and two N−H protons in the porphyrin are still present, has been proposed as an intermediate for the metalation process and the kinetic evidence for its existence has been reported.[2] However, the fast reaction corresponding to the SAT complex formation has not been directly detected, whereas the stability constant of the SAT complex has been reported as being on the order of 10^4 mol^{-1} dm^3 for the copper(II) ion.[2c] In this work, we have performed the kinetic investigation between the copper(II) ion and 5,10,15,20-tetraphenylporphyrin (H_2tpp) in acetonitrile and succeeded in the detection of the SAT complex and the evaluation of its formation kinetics.

The solutions for kinetic measurements were prepared by dissolving known amounts of $Cu(CF_3SO_3)_2$ and H_2tpp in acetonitrile under a dry nitrogen atmosphere. $Cu(CF_3SO_3)_2$ was prepared by dropping an aqueous solution of triflic acid (CF_3SO_3H, Wako) into an aqueous solution of suspended copper(II) oxide. The solution was stirred, filtered to remove the residue, and concentrated. The salt obtained by cooling was recrystallized from water and dried by heating at 300 °C. The composite of anhydrous $Cu(CF_3SO_3)_2$ was confirmed by EDTA titration. Acetonitrile (Wako) was distilled after dehydration using activated molecular sieves 4A (Wako). The stopped-flow rapid-detection system (Unisoku) was used for the kinetic measurements. Although all the measurements were carried out under the nitrogen atmosphere to prevent contamination by water, we confirmed that water present below 10^{-2} mol dm^{-3} did not affect all results.

Figure 1a shows the visible spectral change for the reaction between the copper(II) ion and H_2tpp. This process was completed within *ca.* 100 ms under the present experimental conditions and a spectrum of the reaction product (λ_{max} = 406 nm) was clearly different from that of the 5,10,15,20-tetraphenylporphyrinatocopper(II) species Cu(tpp) (λ_{max} = 414 nm). The product, the SAT complex, was stable for at least a few hours. The conditional first-order rate constants for this reaction, which was followed at 416 nm, were decided under the pseudo first-order conditions with excess copper(II) ion and evaluated to be proportional to [Cu^{2+}]. The second-order rate constants, k, were determined at several temperatures and the kinetic parameters were obtained as follows: k(298K) = 3.6×10^5 mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger} = 56 \pm 5$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 46 \pm 19$ J mol^{-1} K^{-1}.

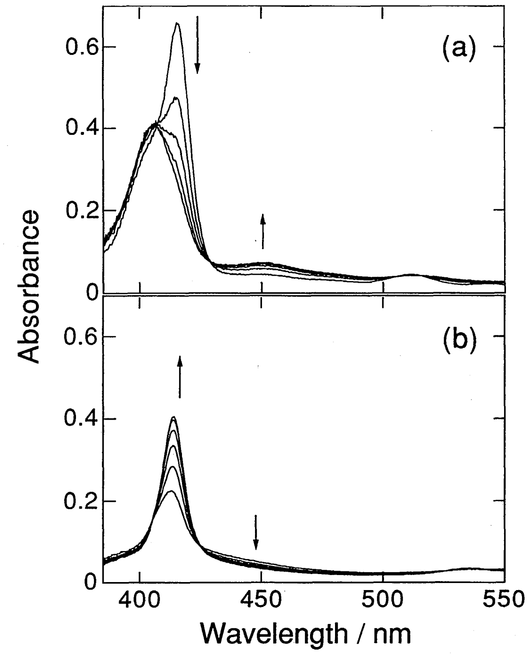

Figure 1. Spectral change for the formation of the SAT complex (a) and the reaction of proton abstraction from the SAT complex by pyridine (b) in acetonitrile. (a): the spectra at 10.4, 20.4, 30.4, 40.4, and 60.4 ms after start of the reaction, $[H_2tpp]_0 = 1.5 \times 10^{-6}$ mol dm^{-3}, [Cu^{2+}] = 5.47×10^{-4} mol dm^{-3}, and 25.0 ± 0.1 °C. (b): the spectra at 0.4, 30.4, 60.4, 90.4, 120.4, and 150.4 ms after the mixing of a py solution (3.64×10^{-2} mol dm^{-3}) and a solution of the SAT complex ([H_2tpp] = 1.6×10^{-6} mol dm^{-3} and [Cu^{2+}] = 5.48×10^{-4} mol dm^{-3}) at 25.0 ± 0.1 °C.

The ^{1}H-NMR measurements were performed using AMX400 spectrometer (Bruker) at 400.13 MHz and 21 °C.[3] For the spectrum of free H_2tpp in CD_3CN, the signals of the N−H and β-pyrrole protons were observed at a ratio of 1:4, and their chemical shifts were consistent with those previously reported.[4,5] On the other hand, for the SAT complex, the N−H protons and two kinds of β-pyrrole protons were observed at a ratio of 1:2:2 in signal intensity. The latter was attributed to those of the pyrrole groups coordinated and non-coordinated, respectively, to the copper(II) ion. A similar splitting is observed for the free H_2tpp at low temperature, because the N−H tautomerism is frozen out to observe them separately,[4] where the signal of the β-pyrrole protons of the pyrrole groups with N−H protons is observed at a lower field relative to those of the pyrrole groups without N−H protons. However, for the SAT complex, an opposite trend in chemical shift was observed, *i.e.*, the doublet peak assigned to the β-pyrrole protons with an N−H proton appears at a higher field. This strongly indicates that the two pyrrole nitrogens without an N−H proton bind to the paramagnetic copper(II) ion, because the dipole-dipole interaction with the paramagnetic center produces their downfield shift. Furthermore, the finding that the peak for the N−H protons is downfield shifted relative to that of the free H_2tpp indicates that the porphyrin ring in the SAT complex is distorted from a plane, because the pyrrole N−H protons in free H_2tpp are highly shifted to upper field due to the ring current of a planar porphyrin ring.

For the overall metalation process of H_2tpp, the release of the N−H protons is required for its completion. Figure 1b shows the spectral change after mixing of the solutions of the SAT complex and pyridine. The final spectrum is perfectly consistent with that of the independently prepared Cu(tpp) complex. This is evidence supporting the fact that the SAT complex contains the N−H protons. Such proton abstraction[6] followed the formation of the Cu(tpp) complex can also be observed in the presence of other strong bases, such as pyridine derivatives and *iso*-quinoline, but can not in the case of a weak base such as pyrazine. It should be noted that, because water can act as a base in this system, the proton abstraction was also observed in the presence of water over 0.1 mol dm^{-3}.

According to the electrochemical approach for the acidity of some acids in several solvents, the proton affinities are in the order of acetonitrile $<$ water $<$ *N,N*-dimethylformamide $<$ dimethyl sulfoxide $<$ pyridine.[7] This means that the proton in acetonitrile is not stabilized. The reaction of the copper(II) ion with H_2tpp in acetonitrile in the absence of strong bases is really stopped at the formation of the SAT complex because of the low proton affinity of acetonitrile. This observation clearly indicates that the SAT complex is formed prior to the metal ion incorporation process into the porphyrin core accompanying the release of N−H protons from the SAT complex.

It should be noted that the Soret band of the SAT complex is highly broadened relative to those of free H_2tpp and Cu(tpp) (see Figure 1). Because the broad Soret band is commonly observed for porphyrins with a deformed porphyrin ring, the porphyrin ring in the SAT complex should be deformed. The activation parameters for formation of the SAT complex with a deformed porphyrin ring provide important information about its kinetics. The rates of the solvent exchange and the complexation reactions of copper(II) ion are very fast due to lability at elongated axial sites of the copper(II) ion and the values of $\Delta H^{\ddagger}$ for the solvent exchange reactions are *ca.* $10 \sim 20$ kJ mol^{-1}.[8] The larger values of $\Delta H^{\ddagger}$ observed for the SAT complex formation is explained in terms of deformation of the porphyrin ring. To deform a highly conjugated π-system of the porphyrin must require positive enthalpy. Thus, it can be concluded that in the formation process of the SAT complex there exists an equilibrium for deformation of the porphyrin ring prior to the rate-determining release of a coordinating acetonitrile at the axial site of the copper(II) ion. The deformation pre-equilibrium should then lead to the large positive value of $\Delta S^{\ddagger}$ due to the increase in intermolecular freedom of the stretching and bending mode of the porphyrin ring.

This is the first report indicating direct evidence for the existence of the SAT complex in solution. The kinetics for the formation of the SAT complex and the proton abstraction process from the SAT complex are very important in order to understand the general metalation mechanism of porphyrins. An extensive study of these reactions with other metal ions and bases is now in progress.

References and Notes

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3 ^{1}H NMR (400 MHz, CD_3CN) for H_2tpp: δ −2.87 (s, pyrrole N−H), 7.80−7.87 (m, *m*- and *p*-phenyl H), 8.22−8.25 (m, *o*-phenyl H), 8.85 (s, β-pyrrole H); for the SAT complex ($Cu(H_2tpp)^{2+}$): −2.05 (s, pyrrole N−H), 7.50−7.31 (m, *m*- and *p*-phenyl H), 8.10−8.12 (m, *o*-phenyl H), 8.66 (d, uncoordinating β-pyrrole H), 8.77 (s, coordinating β-pyrrole H).

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6 According to our preliminary results, the proton abstraction proceeded *via* two paths; the one was first order in [py] and the other was second order. In the latter path, a py-coordinated SAT complex ($Cu(H_2tpp)(py)^{2+}$), which was formed in a pre-equilibrium, reacted with py.

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