

Kinetics and Mechanism for the Metalation Reaction of 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin with Diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)nickel(II) in Supercritical Carbon Dioxide

Shijun Liu,[#] Yasuhiro Inada, and Shigenobu Funahashi*

Laboratory of Analytical Chemistry, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602

(Received November 15, 2002)

The nickel(II) ion incorporation reaction into 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H_2tpfpp) to form the $[Ni(tpfpp)]$ complex has been kinetically investigated using diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)nickel(II), $[Ni(hfac)_2(H_2O)_2]$, in supercritical carbon dioxide ($scCO_2$) medium in a spectrophotometric cell at various temperatures and pressures. The metalation reaction is first order with respect to porphyrin under the conditions where $[Ni(hfac)_2(H_2O)_2]$ is in a large excess relative to H_2tpfpp . The saturation dependence was observed for the conditional first-order rate constants as a function of the mole fraction (x_{Ni}) of the excess $[Ni(hfac)_2(H_2O)_2]$. Such dependence suggests that the metalation reaction consists of a fast pre-equilibrium of the formation of the outer-sphere association between $[Ni(hfac)_2(H_2O)_2]$ and H_2tpfpp and a first-order rate-determining nickel(II) ion incorporation into the porphyrin core. The conditional first-order rate constants k_{obs} are well expressed by $k_{obs} = Kkx_{Ni}/(1 + Kx_{Ni})$, where K is the equilibrium constant for the formation of the outer-sphere association and k is the first-order rate constant for the nickel(II) ion incorporation. The thermodynamic and kinetic parameters are obtained as follows: $\Delta H^\circ = 14.4 \pm 1.3 \text{ kJ mol}^{-1}$ at 20.5 MPa, $\Delta S^\circ = 133 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ at 20.5 MPa and $\Delta V^\circ = 15 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ at 333.3 K for the pre-equilibrium; $\Delta H^\ddagger = 110 \pm 5 \text{ kJ mol}^{-1}$ at 20.5 MPa, $\Delta S^\ddagger = 22 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$ at 20.5 MPa, and $\Delta V^\ddagger = 81 \pm 8 \text{ cm}^3 \text{ mol}^{-1}$ at 333.3 K for the rate-determining step. The positive change in enthalpy and volume and significant positive change in entropy strongly indicate that the outer-sphere association is derived from the desolvation of reactants in $scCO_2$.

Supercritical fluids (SCFs) have been used as a solvent for liquid chromatography and extraction in the field of analytical chemistry, as one of the new reaction media for the preparation of new chemical compounds in the chemical industry, and as a unique solvent with a wide-ranging variation in density for the kinetic study in the field of physical chemistry.^{1–10} The promising applications of SCFs have been successfully developed in various fields, such as biotechnology¹¹ and material processing.¹² Among the supercritical fluids, attention has particularly focused on supercritical carbon dioxide ($scCO_2$) since it is inert, nontoxic, environmentally acceptable, inexpensive, nonflammable, noncorrosive and has a low critical temperature (31.1 °C) and a moderate critical pressure (7.28 MPa).

Supercritical fluid extraction (SFE) using an extractant- $scCO_2$ mixture has been recognized to be promising as an advanced method for the separation of metals from a liquid for the purpose of analytical pretreatment or hydrometallurgy.^{13,14} Therefore, quantitative investigation concerning the complexation and ligand-substitution reactions of metal ions in $scCO_2$ must be important.

The metalloporphyrin formation reaction is one of the important processes from both analytical and bioinorganic points of view.^{15–18} The kinetics of the metalloporphyrin formation

has been extensively studied for many kinds of metal ions in a variety of solvents in order to clarify the metalation mechanism of porphyrins.^{19–29} However, there is no report about the metalation mechanism of porphyrins in supercritical fluids except for the preliminary results of our study.³⁰

On the other hand, in 1960, Fleischer and Wang³¹ first proposed the so-called sitting-atop (SAT) complex of the proto-porphyrin dimethyl ester in chloroform on the basis of visible spectra, infrared spectra, and composition of the SAT complex. After this report, the reports on the detection of the SAT complex have been very limited, occurring only in peculiar systems. We think that a crucial point to form the SAT complex is to guarantee the thermodynamic and kinetic retardation of the dissociation of protons on the pyrrole rings in the SAT complex. Therefore, we must select solvents with a very low Brønsted basicity. Acetonitrile has a very low Brønsted basicity and is a coordinating and aprotic solvent with the significantly high dielectric constant of 36, which is favorable for coordination ability and solubility. In fact, we succeeded in the detection of the sitting-atop (SAT) copper(II) complex of TPP (5,10,15,20-tetraphenylporphyrin) in acetonitrile, where two pyrrolenine nitrogen atoms in the Cu(II)-SAT complex coordinate to the metal ion and two protons on the pyrrole nitrogen still remain.²⁹ The structure parameters around the copper(II) ion in the Cu(II)-SAT complex, determined by a fluorescent XAFS method, have shown an axially elongated and equatorially distorted six-coordinate geometry.³² We

[#] On leave from the Department of Chemistry, Xiangtan University, China

measured the rates of the formation reaction of the SAT complexes for a series of transition metal(II) ions in acetonitrile, using the stopped-flow technique, and we proposed the mechanism where there is a rapid deformation equilibrium of the porphyrin ring prior to the rate-determining step of the bond rupture of a coordinated solvent molecule on the metal(II) ion.³² Furthermore, we measured the rates of the deprotonation reaction of the Cu(II)-SAT complex by some Brønsted bases and indicated that the rate-determining step is the attack of the base to the proton on the pyrrole nitrogen in the SAT complex.³³ Finally the unified mechanism relevant to the porphyrin metalation mechanism has been proposed.^{34,35}

The solubility of metal complexes and porphyrins in scCO₂ is usually very low. However, the fluorinated metal β -diketonates and fluorinated porphyrins possessed excellent solubility in scCO₂.^{36–39} In this context, in order to clarify the metalation mechanism of porphyrins in scCO₂ as a specific solvent, we have investigated the kinetics for the Ni(II) ion incorporation reaction into 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H₂tpfpp) with diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)nickel(II), [Ni(hfac)₂(H₂O)₂], in scCO₂. In addition, the effect of water added as a cosolvent has been examined.

Experimental

Reagents. H₂tpfpp and [Ni(hfac)₂] $\cdot$ nH₂O were obtained from the Aldrich Co. H₂tpfpp (Anal. Calcd: C, 54.22%; H, 1.04%; N, 5.75%; Found: C, 54.20%; H, 1.04%; N, 5.78%) was used without further purification. The scCO₂ solvent was prepared using liquid carbon dioxide (99.99%, Showa Tansan). The commercial reagent of [Ni(hfac)₂] $\cdot$ nH₂O was recrystallized from an acetone/water (50% volume) solution and dried overnight at 70 °C before use. [Ni(tpfpp)] was prepared as follows: nickel(II) acetate tetrahydrate (Wako, 58.5 mg, 0.235 mmol) was added to a DMF (Wako, 30 cm³) solution of H₂tpfpp (Aldrich, 31.4 mg, 0.032 mmol). The mixture was refluxed for 12 h and then added to 100 cm³ of water containing NaCl (5 g). The precipitate was collected by filtration and washed well with water. Recrystallization from ethanol/water gave a red powder product. Anal. Calcd for [Ni(tpfpp)]: C, 51.24; H, 0.78; N, 5.43%. Found: C, 50.98; H, 1.30; N, 5.28%. The absorbance peaks of the UV-vis spectra of [Ni(tpfpp)] appeared at 396, 521, and 555 nm in scCO₂, and at 404, 524 and 558 nm in hexane.

Measurements. Thermal gravity analysis (TGA) was carried out with a Mettler-Toledo TGA/SDTA 851 instrument. Infrared (IR) spectra (KBr pellets) were recorded on a Nicolet AVATAR 36-FT-IR spectrophotometer. Magnetic susceptibilities were measured at room temperature using an MSB-AUTO magnetic susceptibility balance. A CA-07 moisture meter (Mitsubishi) was used to determine the water content of the solid sample by dissolving the sample in acetonitrile.

Kinetic Measurements. The details of the measurements of the reaction rates in scCO₂ using the spectrophotometric cell, the scCO₂-stopped-flow instrument, and the scCO₂ measurement system were previously described.^{30,39} In this study, a newly constructed spectrophotometric supercritical fluid cell with a volume of 3.43 cm³ and an optical path length of 0.991 cm was used in the UV-1600 spectrophotometer (Shimadzu) for the kinetic measurements. The cell has two sapphire windows, which are transparent over the range of 250–800 nm. The pressure in the

cell was controlled to within ± 0.2 MPa for at least 24 h, and the temperature of the cell was constant within ± 0.2 K.

Sampling was carried out as follows. A certain amount of H₂tpfpp solution in hexane was first introduced into the cell. After complete vaporization of the hexane by heating the cell at 338 K, the desired amount of [Ni(hfac)] $\cdot$ nH₂O powder was then introduced, and the cell was heated at 343 K for several tens of minutes. In order to replace the air inside the system, 0.1 MPa CO₂ gas was introduced into the cell after closing the outlet stop valve, and then was slowly released by opening the outlet valve. This procedure was done three times. After a given temperature was established, the cell was filled with CO₂ to the desired pressures, the contents of the cell were stirred by a Teflon-coated steel bar, and then the absorption spectra of the reaction system were recorded as a function of reaction time.

Results and Discussion

Characterization of [Ni(hfac)₂] $\cdot$ nH₂O. The water content was unknown for the commercially available reagent [Ni(hfac)₂] $\cdot$ nH₂O. A TGA of the commercially available reagent and recrystallized reagent showed three weight loss steps at about 353 K, 423 K, and 473 K, respectively. The first one started at about 343 K and ended at about 363 K with a 3.5% weight loss for the commercial reagent and 5.6% weight loss for the recrystallized reagent. When the commercial and recrystallized reagents were dried at 343 K overnight under atmospheric pressure, only two weight loss steps at about 423 K and 473 K were observed in the TGA of the dried reagent. The results of the Karl Fischer method showed that the water content is (10.2 $\pm$ 0.2)% in the commercially available reagent and (7.1 $\pm$ 0.2)% in the dried reagent. The IR spectra at 3465 cm⁻¹ clearly indicated the existence of water in both the commercially available and the dried reagent. It is obvious that there are two kinds of water in [Ni(hfac)₂] $\cdot$ nH₂O; one is the coordinated water which directly binds to the nickel(II) ion and remains after heating at 343 K, and the other is the uncoordinated water which releases at 343 K. These results, accompanied by the results of the elemental analysis, support the compositions of [Ni(hfac)₂(H₂O)₂] $\cdot$ H₂O for the commercially available reagent (Calcd: H₂O, 10.25%; C, 22.77%; H, 1.52%; Found: H₂O, 10.2%; C, 22.73%; H, 1.31%) and [Ni(hfac)₂(H₂O)₂] for the dried reagent (Calcd: H₂O, 7.07%; C, 23.58%; H, 1.18%; Found: H₂O, 7.1%; C, 22.64%; H, 1.13%). The latter was used for the kinetic measurements.

The magnetic measurement indicated that [Ni(hfac)₂(H₂O)₂] is paramagnetic in the solid state with the moment of 2.86 B.M. at 300 K. The UV-visible spectra of [Ni(hfac)₂(H₂O)₂] in scCO₂ (315 and 645 nm at 343.8 K and 20.5 MPa, similar to that in chloroform at 315 and 641 nm) suggested that this species is a monomer with an octahedral structure in scCO₂.^{40–42}

Nickel(II) complexes with a number of pentane-2,4-dione derivatives having alkyl substituents in the 3-position have been prepared, and the substituents in the 3-position of the 2,4-diketonates have a significant influence on the tendency of the nickel(II) complex to adopt either a monomeric or a trimeric structure as the result of the electronic effects associated with the substituent.⁴³ Both the mono- and trimeric deriva-

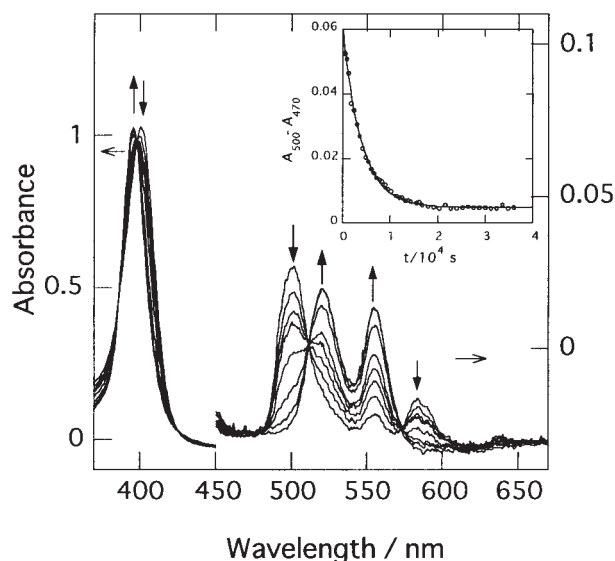


Fig. 1. Spectral change for the reaction system of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]\}$ in scCO_2 at 333.3 K and 20.5 MPa, $2.17 \times 10^{-4} \text{ mol dm}^{-3}$ of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$, and $4.75 \times 10^{-6} \text{ mol dm}^{-3}$ of H_2tpfpp . The spectra at $t = 10, 20, 30, 40, 60, 120, 240$, and 480 min were depicted. In the inset, the absorbances at 500 nm (A_{500}) referred A_{470} versus the reaction time (t) were plotted.

tives of nickel(II) readily form monomeric adducts with ethanol, where the nickel atom has an octahedral environment, with the four oxygen atoms of the pentadionato fragment lying in the equatorial plane and two ethanol oxygen atoms in the axial positions.⁴⁴ In fact, $[\text{Ni}(\text{hfac})_2]$ readily forms octahedral complexes in the presence of coordinating ligands including the donating solvents such as water.^{45–48} As a result, the two waters in $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ are expected to be in the trans position.

Kinetics of Metalloporphyrin Formation between $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and H_2tpfpp . An example of the observed change in the UV-vis absorption spectrum is shown in Fig. 1. The spectral change in Fig. 1 was characteristic for the formation of a metalloporphyrin, and the final absorption spectrum of the reaction product was very consistent with that of $[\text{Ni}(\text{tpfpp})]$, which was independently prepared. All the kinetic measurements in scCO_2 were carried out under the pseudo-first order conditions where $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ is in large excess relative to H_2tpfpp . The absorbance at 500 nm (A_{500}) corresponding to the decrease in H_2tpfpp was found to change as an exponential function, whereas there is almost no absorbance at 500 nm for $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{tpfpp})]$. The change in A_{500} (referred to A_{470}) as a function of the reaction time (t) was then analyzed by a non-linear least-squares calculation according to the following equation:

$$A_{500} = A_{\infty} - (A_{\infty} - A_0) \exp(-k_{\text{obs}}t) \quad (1)$$

where A_{∞} and A_0 are the absorbance at $t = \infty$ and 0, respectively, and k_{obs} is the conditional first-order rate constant.

At 333.3 K and 30.0 MPa, the average value of k_{obs} was $(3.94 \pm 0.20) \times 10^{-4} \text{ s}^{-1}$ for six runs at a constant $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ concentration ($C_{\text{Ni}} = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$) and the varied concentrations of H_2tpfpp from 2.90×10^{-6}

Table 1. The Experimental Values of k_{obs} for the Reaction System of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]\}$ in scCO_2 at 20.5 MPa and Various Temperatures. The Concentration of H_2tpfpp is $4.8 \times 10^{-6} \text{ mol dm}^{-3}$

T/K	$C_{\text{Ni}}/10^{-4} \text{ mol dm}^{-3}$	$x_{\text{Ni}}/10^{-5}$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$
328.3	1.45	0.839	0.889 ± 0.033
	2.19	1.27	1.15 ± 0.03
	3.76	2.17	1.64 ± 0.04
	4.81	2.78	2.05 ± 0.03
	7.02	4.05	2.15 ± 0.04
	9.58	5.53	2.53 ± 0.06
	13.0	7.47	2.54 ± 0.05
	15.8	9.13	2.63 ± 0.14
333.3	1.14	0.687	1.64 ± 0.06
	1.27	0.765	1.63 ± 0.06
	1.60	0.961	1.92 ± 0.06
	2.17	1.31	2.58 ± 0.05
	3.80	2.28	3.59 ± 0.08
	4.86	2.92	3.87 ± 0.08
	6.99	4.20	4.55 ± 0.09
	9.23	5.55	5.25 ± 0.07
	11.2	6.75	4.90 ± 0.09
	13.3	7.99	5.13 ± 0.07
338.6	16.2	9.74	5.23 ± 0.12
	1.07	0.673	2.79 ± 0.09
	2.14	1.35	4.95 ± 0.09
	3.24	2.04	7.27 ± 0.15
	4.41	2.78	8.28 ± 0.23
	9.51	5.98	10.2 ± 0.1
	13.3	8.36	10.4 ± 0.3
343.8	16.1	10.1	10.6 ± 0.1
	0.623	0.411	3.08 ± 0.14
	0.685	0.452	3.87 ± 0.13
	0.897	0.592	5.03 ± 0.20
	1.09	0.718	6.15 ± 0.15
	1.17	0.772	6.49 ± 0.17
	2.14	1.41	10.1 ± 0.3
	3.77	2.49	12.8 ± 0.2
	4.76	3.14	14.0 ± 0.2
	4.81	3.17	15.1 ± 0.6
	6.94	4.58	15.2 ± 0.5
	9.53	6.29	15.4 ± 0.6
	9.68	6.39	17.1 ± 0.2
	12.5	8.24	16.8 ± 0.2
	14.4	9.52	18.1 ± 0.6

to $14.30 \times 10^{-6} \text{ mol dm}^{-3}$. The rate for the formation of the metalloporphyrin, $[\text{Ni}(\text{tpfpp})]$, was confirmed to be first order in porphyrin.

The k_{obs} values were determined at a constant concentration of H_2tpfpp ($4.8 \times 10^{-6} \text{ mol dm}^{-3}$) by varying the total concentration of C_{Ni} at various temperatures (Table 1) and various pressures (Table S1: Supplementary data). The k_{obs} values are plotted in Fig. 2 versus the mole fraction (x_{Ni}) of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$, which is independent of temperature and pressure. The plots at various temperatures (Fig. 2A) and various pressures (Fig. 2B) indicated the curvature and eventual

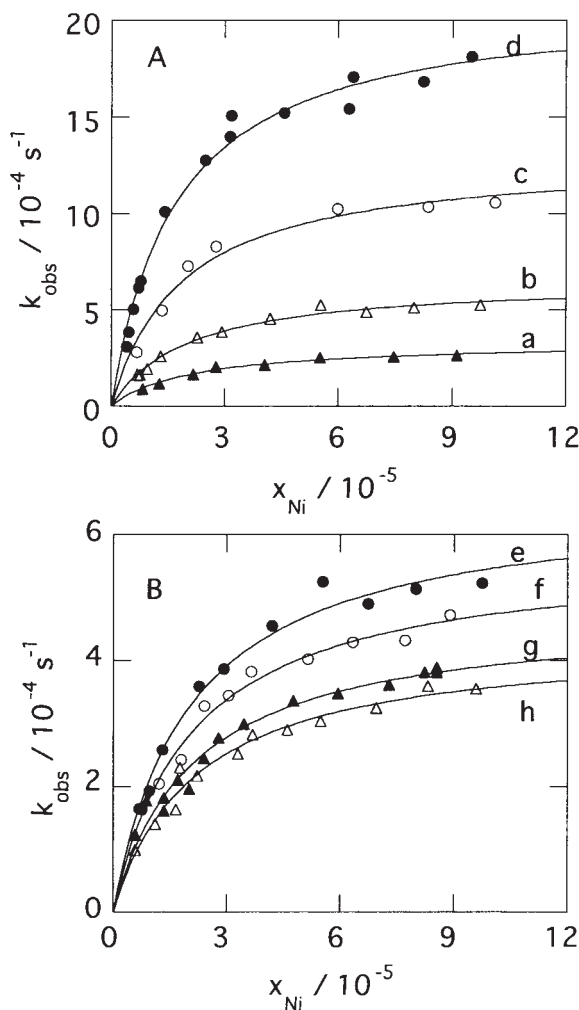
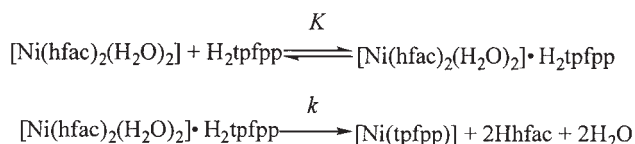


Fig. 2. Dependence of the conditional rate constants (k_{obs}) on the mole fraction (x_{Ni}) of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ for the reaction system of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]\}$ in scCO_2 . In A were given the k_{obs} values at 20.5 MPa and various temperatures, (a): 328.3 K, (b): 333.3 K, (c): 338.6 K, and (d): 343.8 K. In B were given the k_{obs} values at 333.3 K and various pressures, (e): 20.5 MPa, (f): 25.0 MPa, (g): 30.0 MPa, and (h): 35.0 MPa. The solid curves were calculated using the obtained K and k values which are given in Table 2.



Scheme 1.

saturation. Such a saturation dependence invokes Scheme 1 for the reaction between H_2tpfpp and $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$. In Scheme 1, K is the equilibrium constant for the fast preequilibrium to form the outer-sphere association intermediate, $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{tpfpp}$, and k is the first-order rate constant for the rate-determining formation of the metalloporphyrin product, $[\text{Ni}(\text{tpfpp})]$. The k_{obs} value is then expressed in terms of K , k , and x_{Ni} by the following equation:⁴⁹

Table 2. The Obtained Values of K and k for the Reaction System of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]\}$ in scCO_2 at Various Temperatures and Pressures

T/K	P/MPa	$K^{\text{a)}/10^4$	$k^{\text{b)}/10^{-4} \text{ s}^{-1}}$
328.3	20.5	4.61 ± 0.61	3.34 ± 0.15
333.3	20.5	4.89 ± 0.50	6.58 ± 0.23
333.3	25.0	4.79 ± 0.58	5.72 ± 0.23
333.3	30.0	4.65 ± 0.51	4.77 ± 0.18
333.3	35.0	4.53 ± 0.57	4.36 ± 0.19
338.6	20.5	5.34 ± 0.89	13.0 ± 0.7
343.8	20.5	5.87 ± 0.57	21.1 ± 0.7

a) Evaluated thermodynamic parameters: $\Delta H^\circ = 14.4 \pm 1.3 \text{ kJ mol}^{-1}$ at 20.5 MPa, $\Delta S^\circ = 133 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ at 20.5 MPa, and $\Delta V^\circ = 15 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ at 333.3 K. b) Evaluated kinetic parameters: $\Delta H^\ddagger = 110 \pm 5 \text{ kJ mol}^{-1}$ at 20.5 MPa, $\Delta S^\ddagger = 22 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$ at 20.5 MPa, and $\Delta V^\ddagger = 81 \pm 8 \text{ cm}^3 \text{ mol}^{-1}$ at 333.3 K.

$$k_{\text{obs}} = Kkx_{\text{Ni}}/(1 + Kx_{\text{Ni}}) \quad (2)$$

The dissociation of H_2O in the preequilibrium step can be ruled out, because the absorbance changes were reproduced by an exponential function within the error level of the absorbance measurements even at the lowest C_{Ni} ($6.23 \times 10^{-5} \text{ mol dm}^{-3}$). If H_2O is dissociated at the pre-equilibrium step, the observed absorbance changes should not obey the exponential function, because the concentration of H_2O increases with the progress of the reaction. Moreover, if the inner-sphere complex, such as the so-called sitting-atop $[(\text{H}_2\text{tpfpp})\text{Ni}(\text{hfac})_2]$, is formed, and two H_2O molecules are dissociated at the preequilibrium step, the interaction in $[(\text{H}_2\text{tpfpp})\text{Ni}(\text{hfac})_2]$ must be strong, then $[(\text{H}_2\text{tpfpp})\text{Ni}(\text{hfac})_2]$ should give a spectrum which is different from the free H_2tpfpp and metalloporphyrin, $[\text{Ni}(\text{tpfpp})]$. However, we did not observe such a spectrum during the reaction.

The experimental values of k_{obs} at a constant temperature and pressure listed in Table 1 and Table S1 were analyzed by a least-squares calculation according to Eq. 2, and the obtained K and k values at various temperatures and pressures are summarized in Table 2.

Under the isobaric conditions, the K value is related to the changes in enthalpy (ΔH°) and entropy (ΔS°) by Eq. 3 for the chemical equilibrium, and k is related to the activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) by Eq. 4 for the chemical reaction.

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (3)$$

$$\ln(kh/k_{\text{B}}T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad (4)$$

where h is Planck's constant and k_{B} is Boltzmann's constant. The obtained values of K and k at 20.5 MPa listed in Table 2 were analyzed by a least-squares calculation using Eqs. 3 and 4, respectively. The thermodynamic and kinetic parameters were evaluated as $\Delta H^\circ = 14.4 \pm 1.3 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 133 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H^\ddagger = 110 \pm 5 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = 22 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$ at 20.5 MPa.

Furthermore, the pressure dependence of K and k at a constant temperature, which are given in pressure-independent

units, i.e., mole fraction units, is expressed by Eqs. 5 and 6.

$$\partial \ln K / \partial P = -\Delta V^\circ / RT \quad (5)$$

$$\partial \ln k / \partial P = -\Delta V^\ddagger / RT \quad (6)$$

where ΔV° is the change in volume for the preequilibrium (K), and $\Delta V^\ddagger$ is the activation volume for the rate-determining step (k). The obtained values of K and k at 333.3 K listed in Table 2 were analyzed by a least-squares calculation using Eqs. 5, and 6, respectively. The determined values are $\Delta V^\circ = 15 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta V^\ddagger = 81 \pm 8 \text{ cm}^3 \text{ mol}^{-1}$ at 333.3 K.

As is apparent from the relation shown in Fig. 2, just after starting the reaction, the outer-sphere association intermediate, $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{tpfpp}$, is almost quantitatively (ca. 82%) formed at the high concentration of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ as much as $C_{\text{Ni}} = 1.7 \times 10^{-3} \text{ mol dm}^{-3}$ ($x_{\text{Ni}} = 9.82 \times 10^{-4}$) at 328.3 K and 20.5 MPa. Under such conditions, the measured spectrum for the reaction system of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]\}$ within 10 min just after starting the reaction is shown to be almost the same as the sum of the two spectra of H_2tpfpp and $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$. This finding indicates that the interaction in the outer-sphere association is not strong enough to change the absorption spectrum of the free porphyrin. The $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ molecule is almost planar because two waters in $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ are in the trans position. Since the porphyrin core of H_2tpfpp also has a planar structure, H_2tpfpp and $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ molecules may interact between their molecular planes in the outer-sphere association complex.

Kinetics of Metalloporphyrin Formation between $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and H_2tpfpp in the Presence of a Large Amount of Added Water. The addition of a large amount of water to the reaction system made the reaction rate of the metalloporphyrin formation much slower, and the absorbance change during the reaction was observed as an exponential function. The conditional first-order rate constants (k_{obs}) at 343.8 K and 20.5 MPa were determined by the nonlinear least-squares calculation according to Eq. 1 (given in Table S2). Figure 3 shows the relation between the value of k_{obs} and the concentration of added water (C_{w}). The relation of the retardation of the metalloporphyrin formation rate indicates the production of unreactive water adduct species that are formed by the interaction between water molecules and $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$.

It has been reported that $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ has the ability to form a bis-adduct by hydrogen bonding between the aqua ligand and the nitrogen in the adduct ligand.⁵⁰ The composition of $[\text{Ni}(\text{hfac})_2] \cdot 5\text{H}_2\text{O}$ has also been reported.⁴⁸ As a result, the hydrogen bonding between the aqua ligand in $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and the oxygen of H_2O in the outer sphere is expected to form the water adduct, $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, in scCO_2 . Therefore, in the presence of a large excess of added water, we can propose the reactions in Scheme 2, where β_1 and β_2 are the equilibrium constants for the water adduct in the outer sphere. According to Scheme 2, if C_{Ni} is the sum of the concentrations of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$, $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, and $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, we have the following relation:

$$k_{\text{obs}} = kKC_{\text{Ni}} / (1 + \beta_1 C_{\text{w}} + \beta_2 C_{\text{w}}^2 + KC_{\text{Ni}}) \quad (7)$$

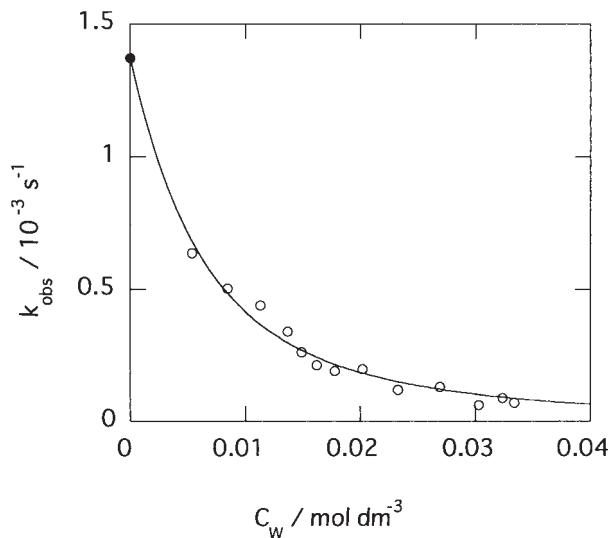
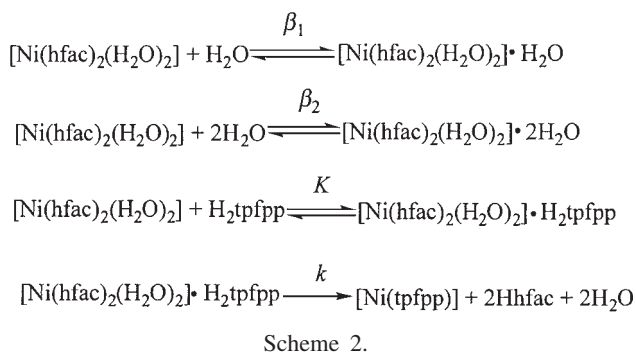


Fig. 3. Dependence of the conditional rate constants (k_{obs}) on the concentrations of H_2O (C_{w}) for the reaction system of $\{\text{H}_2\text{tpfpp} + [\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2] + \text{H}_2\text{O}\}$ in scCO_2 at 20.5 MPa and 343.8 K. The concentrations of $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and H_2tpfpp are $4.9 \times 10^{-4} \text{ mol dm}^{-3}$ and $4.8 \times 10^{-6} \text{ mol dm}^{-3}$, respectively. The point at $C_{\text{w}} = 0$ (filled circle) was obtained from the known values of K and k using Eq. 2. The solid curve is calculated using the obtained values.



With the knowledge of the values of $K = (3.87 \pm 0.38) \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ and $k = (2.11 \pm 0.07) \times 10^{-3} \text{ s}^{-1}$ at 343.8 K and 20.5 MPa determined according to Eq. 2, we can estimate the values of $\beta_1 = (4.0 \pm 0.7) \times 10^2 \text{ mol}^{-1} \text{ dm}^3$ and of $\beta_2 = (2.6 \pm 0.6) \times 10^4 \text{ mol}^{-2} \text{ dm}^6$ at 343.8 K and 20.5 MPa by the least-squares fitting.

Mechanism of Metalloporphyrin Formation in scCO_2 . CO_2 has a modest polarizability, no dipole moment, and a large quadrupole moment. Usually fluorinated compounds are more soluble relative to hydrogenated molecules. Recently, Dardin et al.⁵¹ have presented NMR evidence for specific solute-solvent interactions between CO_2 and fluorinated compounds in scCO_2 which come from the van der Waals interaction between the fluorinated sites in the solute and carbon dioxide. Interestingly, the strong face-to-face stacking interaction of benzene and hexafluorobenzene is explained by a reversal of the quadrupole moment of hexafluorobenzene because of the electron-withdrawing fluorine substituents, allowing a net electrostatic attraction between the π -faces to occur.⁵² In ad-

dition, the solubility of H₂tpfpp in scCO₂ has been shown to increase with the increasing density of scCO₂.³⁹

In the present case, the H₂tpfpp and [Ni(hfac)₂(H₂O)₂] molecules are solvated by the solvent CO₂ molecules in scCO₂. The solvation of two separate molecules of H₂tpfpp and [Ni(hfac)₂(H₂O)₂] may be more oriented than that in one associated molecule due to the larger molecular surface. The outer-sphere association by the interaction between H₂tpfpp and [Ni(hfac)₂(H₂O)₂] leads to the desolvation of the solvated molecules. Therefore, the positive change in enthalpy (14.4 kJ mol⁻¹) and the large positive value for the entropy change (133 J mol⁻¹ K⁻¹) of the pre-association equilibrium will be expected. As described above, the outer-sphere association complex for the pre-equilibrium is not a SAT complex. Furthermore, it is reasonable that the formation of the water adduct, [Ni(hfac)₂(H₂O)₂]·H₂O and [Ni(hfac)₂(H₂O)₂]·2H₂O, between [Ni(hfac)₂(H₂O)₂] and water molecules by hydrogen bonding strongly inhibits the interaction between H₂tpfpp and [Ni(hfac)₂(H₂O)₂]. The decrease in the equilibrium constant (*K*) with the increase in the density of scCO₂ is expressed by the positive value of 15 cm³ mol⁻¹ for the volume change. The formation of the outer-sphere association will become more difficult when more CO₂ molecules are involved in the solvation shell and surround the solute molecules.

According to the recent investigations on the metalation reaction of porphyrins,^{29,32–34} it has been concluded that the nucleophilic attack of the first pyrroline nitrogen of the porphyrin is the rate-determining step for the overall metal ion incorporation. Therefore, during the activation process of the present Ni(II) ion incorporation into H₂tpfpp, it is expected that the nucleophilic attack of the pyrroline nitrogen of H₂tpfpp to the central metal ion occurs together with the dissociation of a water at the axial position. At the same moment, the dissociation of the donating oxygen of the β-diketonate ligand with a negative charge should accompany the abstraction of a pyrrole amine proton of H₂tpfpp, because the charged species is quite unstable in scCO₂ that has a low dielectric constant.

For the rate-determining step, there are two components for the activation volume: a repulsive or intrinsic part due to the change in occupied volume between the reactants and the transition state, and a part due to attractive solute-solvent forces.^{53–55} For the unimolecular decomposition reaction, the repulsive part of the activation volume is usually positive due to an increase in the bond length as bonds are broken.⁵³ The attractive part due to solute-solvent forces is, however, dependent on the isothermal compressibility of supercritical fluids and the polarities of transition state and reactants. This part may be a large negative value⁵⁴ or a negligible value.⁵⁵

In the present case, since CO₂ is a non-coordinating solvent and the experimental conditions are far from the critical point, we can assume that the activation volume for the rate-determining step is dominated by the repulsive contribution in the outer-sphere association complex, [Ni(hfac)₂(H₂O)₂]·H₂tpfpp. This assumption suggests that the release of H₂O and the dissociation of the donating oxygen of the β-diketonate ligand in the transition state cause the large repulsive contribution, which accounts for the positive Δ*V*[‡] value (81 cm³ mol⁻¹) and the large positive value of the activation en-

thalpy (110 kJ mol⁻¹).

Tables S1 and S2 as supplementary data are available by a request to the authors.

This work was supported by Grants-in-Aid for Scientific Research (Nos. 11354009, 11554030, and 12874094) from the Ministry of Education, Science, Sports and Culture. S. L. is a postdoctoral fellow of the Japan Society for the Promotion of Science for foreign researchers in Japan.

References

- 1 K. P. Johnston and J. M. L. Penninger, "Supercritical Fluid Science and Technology," American Chemical Society, Washington (1989).
- 2 F. V. Bright and M. E. P. McNally, "Supercritical Fluid Technology: Theoretical and Applied Approaches in Analytical Chemistry," American Chemical Society, Washington (1992).
- 3 E. Kiran and J. F. Brennecke, "Supercritical Fluid Engineering Science: Fundamentals and Applications," American Chemical Society, Washington (1993).
- 4 P. G. Jessop, T. Ikariya, and R. Noyori, *Science*, **269**, 1065 (1995).
- 5 E. Kiran, P. G. Debenedetti, and C. J. Peters, "Supercritical Fluids: Fundamentals and Applications," Kluwer Academic Publishers, Dordrecht (1998).
- 6 T. Clifford, "Fundamentals of Supercritical Fluids," Oxford University Press, Oxford (1999).
- 7 S. B. Hawthorne, *Anal. Chem.*, **62**, 633A (1990).
- 8 R. M. Smith, "Supercritical Fluid Chromatography," The Royal Society of Chemistry, Cambridge (1993).
- 9 M. D. L. de Castro, M. Valcarcel, and M. T. Tena, "Analytical Supercritical Fluid Extraction," Springer-Verlag, New York (1994).
- 10 L. T. Taylor, "Supercritical Fluid Extraction," John Wiley & Sons, New York (1996).
- 11 E. J. Beckman, *Science*, **271**, 613 (1996).
- 12 D. J. Dixon, G. Luna-Barcenas, and K. P. Johnston, *Polymer*, **35**, 3998 (1994).
- 13 F. Dehghani, T. Wells, N. J. Cotton, and N. R. Foster, *J. Supercrit. Fluids*, **9**, 263 (1996).
- 14 H. Wu, Y. Lin, N. G. Smart, and C. M. Wai, *Anal. Chem.*, **68**, 4072 (1996).
- 15 D. K. Lavalley, *Mol. Struct. Energ.*, **9**, 279 (1988).
- 16 D. K. Lavalley, "The Chemistry and Biochemistry of N-Substituted Porphyrins," VCH, New York (1987).
- 17 M. E. Blackwood, Jr., T. S. Rush, III, A. Medlock, H. A. Dailey, and T. G. Spiro, *J. Am. Chem. Soc.*, **119**, 12170 (1997).
- 18 M. M. Conn, J. R. Prudent, and P. G. Schultz, *J. Am. Chem. Soc.*, **118**, 7012 (1996).
- 19 P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, **96**, 3123 (1974).
- 20 M. J. Bain-Ackerman and D. K. Lavalley, *Inorg. Chem.*, **18**, 3358 (1979).
- 21 J. Turay and P. Hambright, *Inorg. Chem.*, **19**, 562 (1980).
- 22 S. Funahashi, K. Saito, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **54**, 2695 (1981).
- 23 R. F. Pasternack, G. C. Vogel, C. A. Skowronek, R. K. Harris, and J. G. Miller, *Inorg. Chem.*, **20**, 3763 (1981).
- 24 S. Funahashi, Y. Yamaguchi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **57**, 204 (1984).

- 25 S. Funahashi, Y. Yamaguchi, and M. Tanaka, *Inorg. Chem.*, **23**, 2249 (1984).
- 26 L. R. Robinson and P. Hambright, *Inorg. Chim. Acta*, **185**, 17 (1991).
- 27 J. Takeda, T. Ohya, and M. Sato, *Inorg. Chem.*, **31**, 2877 (1992).
- 28 M. Inamo, A. Tomita, Y. Inagaki, N. Asano, K. Suenaga, M. Tabata, and S. Funahashi, *Inorg. Chim. Acta*, **256**, 77 (1997).
- 29 Y. Inada, Y. Sugimoto, Y. Nakano, Y. Itoh, and S. Funahashi, *Inorg. Chem.*, **37**, 5519 (1998).
- 30 Y. Inada, H. Sato, T. Horita, T. Nagamura, and S. Funahashi, *J. Supercrit. Fluids*, **21**, 205 (2001).
- 31 E. B. Fleischer and J. H. Wang, *J. Am. Chem. Soc.*, **82**, 3498 (1960).
- 32 Y. Inada, Y. Nakano, M. Inamo, M. Nomura, and S. Funahashi, *Inorg. Chem.*, **39**, 4793 (2000).
- 33 Y. Inada, T. Yamaguchi, H. Sato, and S. Funahashi, *Inorg. React. Mech.*, **2**, 277 (2000).
- 34 M. Inamo, N. Kamiya, Y. Inada, M. Nomura, and S. Funahashi, *Inorg. Chem.*, **40**, 5636 (2001).
- 35 S. Funahashi, Y. Inada, and M. Inamo, *Anal. Sci.*, **17**, 917 (2001).
- 36 J. A. Darr and M. Poliakoff, *Chem. Rev.*, **99**, 495 (1999).
- 37 A. F. Lagalante, B. N. Hansen, and T. J. Bruno, *Inorg. Chem.*, **34**, 5781 (1995).
- 38 M. Ashraf-Khorassani, M. T. Combs, and L. T. Taylor, *Talanta*, **44**, 755 (1997).
- 39 H. Sato, Y. Inada, T. Nagamura, and S. Funahashi, *J. Supercrit. Fluids*, **21**, 71 (2001).
- 40 F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).
- 41 J. P. Fackler, Jr. and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).
- 42 J. P. Fackler, Jr., M. L. Mittleman, H. Weigold, and G. M. Barrow, *J. Phys. Chem.*, **72**, 4631 (1968).
- 43 A. Dohring, R. Goddard, P. W. Jolly, C. Kruger, and V. R. Polyakov, *Inorg. Chem.*, **36**, 177 (1997).
- 44 V. R. Polyakov and M. Czerwinski, *Inorg. Chem.*, **40**, 4798 (2001).
- 45 A. Caneschi, D. Gatteschi, J. P. Renard, P. Rey, and R. Sessoli, *Inorg. Chem.*, **28**, 2940 (1989).
- 46 M. H. Dickman, *Acta Crystallogr., Sect. C*, **56**, 58 (2000).
- 47 L. C. Porter, M. H. Dickman, and R. J. Doedens, *Inorg. Chem.*, **27**, 1548 (1988).
- 48 K. Arakawa and K. Tanikawa, *Bunseki Kagaku*, **16**, 812 (1967).
- 49 R. G. Wilkins, "The Study of Kinetics and Mechanism of Reaction of Transition Metal Complexes," Allyn and Bacon, Boston (1974). As pointed out in page 28 in Ref. 49, the same kinetic behavior as in Eq. 2 is observed if the complex was viewed as a "dead-end" intermediate in rapid equilibrium and if the reaction proceeded bimolecularly between $[\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2]$ and H_2tpfpp . Kinetics alone will not distinguish between these two mechanisms. Arguments over which of the two is preferred must then be based on the chemical considerations. As discussed later, the mechanism expressed by Eq. 2 must be plausible. A related subject has been reported: Ref. 27.
- 50 D. Luneau, P. Rey, J. Laugier, E. Belorizky, and A. Cogne, *Inorg. Chem.*, **31**, 3578 (1992).
- 51 A. Dardin, J. M. DeSimone, and E. T. Samulski, *J. Phys. Chem. B*, **102**, 1775 (1998).
- 52 A. P. Jr. West, S. Mecozzi, and D. A. Dougherty, *J. Phys. Org. Chem.*, **10**, 347 (1997).
- 53 S. D. Hamann and R. S. Bradley, "High-Pressure Physics and Chemistry," Vol. 2, Academic Press, London and New York (1963).
- 54 K. P. Johnston and C. Haynes, *AIChE J.*, **33**, 2017 (1987).
- 55 Q. Ji, C. R. Lloyd, E. M. Eyring, and R. van Eldik, *J. Phys. Chem. A*, **101**, 243 (1997).