Kinetics of Axial Substitution of the Iron(II) Complex of 2,3,9,10-Tetraphenyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradeca-tetraene in Acetonitrile. Evidence for a Dissociative-Interchange Mechanism

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The reaction of the iron(II) complex of 2,3,9,10-tetraphenyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene ([FeL(CH₃CN)₂]²⁺, 1) with imidazole and thiocyanate ion in acetonitrile has been investigated spectrophotometrically at various temperatures and pressures. The axial substitution of 1 with imidazole is first order with respect to the concentration of the iron(II) complex and imidazole and the rate constant and the activation parameters are obtained as k (25.0 °C)=0.69 mol⁻¹ kg s⁻¹, $\Delta H^{\neq}$=76±4 kJ mol⁻¹, $\Delta S^{\neq}$=7±13 J mol⁻¹ K⁻¹, $\Delta V^{\neq}$=13.7±0.9 cm³ mol⁻¹. It has been demonstrated that at higher concentration of imidazole there exists self-associated imidazole which does not react directly with the complex. The axial substitution of 1 with thiocyanate ion proceeds through the ion-association between 1 and SCN⁻ prior to the rate-determining step from the outer-sphere complex to the inner-sphere complex. The activation parameters for the rate-determining step were determined as follows: k^0 (25.0 °C and 0.1 MPa)=2.35 s⁻¹, ΔH^*=86±2 kJ mol⁻¹, ΔS^*=51±6 J mol⁻¹ K⁻¹, ΔV^*=10.1±0.2 cm³ mol⁻¹. The positive activation volumes strongly indicate a dissociative character of the activation process.

Transition-metal complexes containing macrocyclic ligands have been investigated as models for biological molecules.[1,2] One particular interest in these model studies has been to elucidate mechanisms of solvent exchange and ligand substitution at the axial coordination site of metal complexes with macrocyclic ligands from biological interests.[3,4] There are a number of kinetic studies on axial ligand substitution reactions in six-coordinated iron(II) complexes with macrocyclic ligands,[5–21] including phthalocyanine[5–11] and porphyrins.[12–14] In such complexes the equatorial positions are occupied by four nitrogen atoms of the macrocyclic ligands and the axial sites by the ligands taking part in the relevant rate processes. Despite numerous studies, the reaction mechanism of axial substitution of iron complexes does not appear to have been proved decisively and there seems to be no mechanistic approach on the basis of the activation volumes.

We present here the results of a kinetic study on the substitution of axial acetonitrile by imidazole(Im) and thiocyanate ion in the iron(II) complex of 2,3,9,10-tetraphenyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetra-

$$[FeL(CH_3CN)_2]^{2+}, 1$$

decatetraene ([FeL(CH₃CN)₂]²⁺, 1) at various temperatures and pressures. The overall reactions are represented by Eqs. 1 and 2.

$$1 + 2Im \rightleftharpoons [FeL(Im)_2]^{2+} + 2CH_3CN \quad (1)$$

$$1 + 2SCN^- \rightleftharpoons FeL(SCN)_2 + 2CH_3CN \quad (2)$$
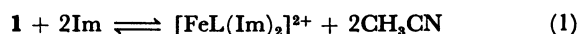
Experimental

Materials. **Acetonitrile:** Reagent grade acetonitrile (Wako Pure Chemical Industries, Ltd.) was refluxed over P₂O₅ (2 g dm⁻³) for longer than 3 h and distilled under dry air. Furthermore, the distilled acetonitrile was refluxed over calcium hydride (Wako) (2 g dm⁻³) in an argon atmosphere for longer than 3 h, distilled under argon, and stored in a dry box. The amount of water contained in acetonitrile was checked by the Karl-Fisher method and it was found to be less than 2×10⁻³ mol dm⁻³.

Imidazole: Imidazole (Wako) was purified by sublimation in vacuo (3 mmHg, 80—100 °C).

Sodium Thiocyanate: Reagent grade sodium thiocyanate (Nakarai Chemicals) was recrystallized from methanol. The crystals were washed with diethyl ether and dried for 6 h under reduced pressure. The amount of water contained in the crystals was determined to be less than 0.015 wt%.

Anhydrous Sodium Perchlorate: A sodium perchlorate solution was prepared by neutralizing reagent grade 60% perchloric acid with reagent grade anhydrous sodium carbonate. Heavy-metal impurities in the sodium perchlorate solution were precipitated as hydroxides together with active carbon at pH 8.5. After concentration of the solution crystals of sodium perchlorate hydrates were obtained by cooling the solution. Sodium perchlorate was then crystallized twice from distilled water. Anhydrous sodium perchlorate was obtained by drying the obtained sodium perchlorate hydrates at 60 °C under reduced
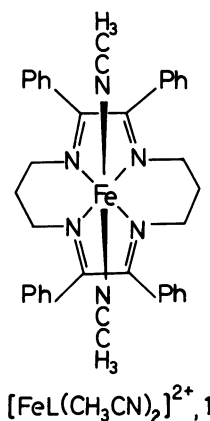
pressure for more than 5 h.

[FeL(CH₃CN)₂](PF₆)₂: This complex was synthesized by a procedure similar to the literature method.[22] All operations were carried out under an argon atmosphere. Yielded dark purple crystals were washed with cold methanol and then with ether. The product was purified further by chromatography (Silica gel 2308, Merck; ϕ45 mm, h 270 mm column; eluent: dry nitromethane). Recrystallization from dry acetonitrile and dry diethyl ether gave purple crystals. Anal. Calcd for $C_{38}H_{38}N_6P_2F_{12}Fe$: C, 49.39; H, 4.14; N, 9.09; Fe, 6.04. Found: C, 49.36; H, 4.08; N, 8.94; Fe, 5.95±0.03. After decomposition of the complex by heating with sodium carbonate, iron was determined by the colorimetry with 1,10-phenanthlorine. ¹H NMR (acetone-d_6, Me₄Si): 1.62 ppm (m, 4H), 2.51 (m, 6H), 4.35 (m, 8H), 7.48 (m, 20H). Visible electronic spectrum (CH₃CN solution): λ_{max} (ε) 551 nm (8.83×10^3 mol⁻¹ dm³ cm⁻¹), 592 nm (1.78×10^4 mol⁻¹ dm³ cm⁻¹). Half-wave potential of Fe^{2+}/Fe^{3+} for the complex 1.48 V (ΔP=64 mV, 100 mV s⁻¹). IR (KBr pellet): 1340(m), 1320(m), 1270(m), 1115(w), 1080(w), 1030(w, axial CH₃CN), 845(s, PF_6^-), 710(s).

Measurement. The reaction was started by mixing the iron(II) complex solution with an imidazole or a thiocyanate ion solution. Reactions at atmospheric pressure were followed by a stopped-flow spectrophotometer (Type RA 401, Union Giken). Reactions at high pressure up to 200 MPa were measured with a high-pressure stopped-flow apparatus with spectrophotometric detection (Type FIT 3).[23,24]

Results

Reaction of 1 with Imidazole. Under conditions with a large excess of imidazole over the bis(acetonitrile) complex, during the reaction after mixing, we observed solutions having visible absorption spectra corresponding to those of the species $[FeL(Im)_2]^{2+}$, but not corresponding to $[FeL(CH_3CN)(Im)]^{2+}$. Moreover, the final change in absorbance was independent of the concentration of imidazole and proportional to the complex concentration. Therefore, under the present experimental conditions the reverse reaction is negligible for the kinetic study and the second ligation is much faster than the first ligation of imidazole. The axial substitution of the complex with imidazole was followed at 592 nm, the maximum wavelength of the complex. The first-order plots were linear at least for 3 half-lives. Rate constants obtained at a constant concentration of imidazole (C_{Im}=0.150 mol kg⁻¹) and various concentrations of the complex (C_{FeL}=2.68—5.91×10⁻⁵ mol kg⁻¹) were independent of the complex concentration. The rate law is thus given by

$$-d[1]/dt = k_{0(Im)}[1], \tag{3}$$

where $k_{0(Im)}$ is a conditional first-order rate constant. Rate constants $k_{0(Im)}$ were obtained at various concentrations of imidazole. The plots of $k_{0(Im)}$
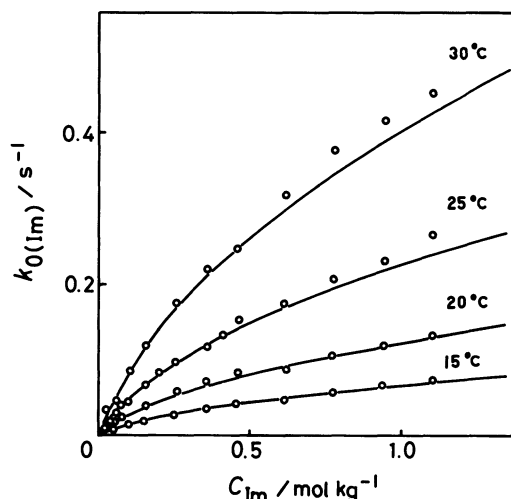

Fig. 1. Imidazole concentration dependence of first-order rate constants under atmospheric pressure at 15.0, 20.0, 25.0, and 30.0 °C. In Figs. 1—6, each point is an average of several runs. In Figs. 1, 3, 5, and 6, the soild lines were calculated by using the values obtained.
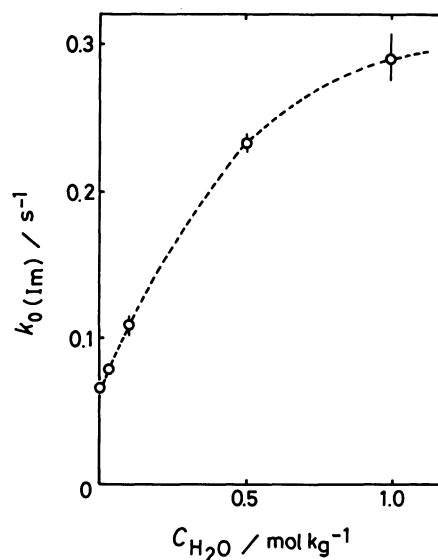

Fig. 2. Water effect on rate. C_{H_2O} is the concentration of added water. The rate constants were obtained at C_{FeL}=5.90 × 10⁻⁵ mol kg⁻¹, C_{Im}=0.150 mol kg⁻¹, and 25.0 °C.

against the total concentrations of imidazole, C_{Im}, are shown in Fig. 1.

The effect of water on the rate was checked by the addition of water (see Fig. 2). Rates drastically increase with increasing water concentration. However since water in the present reaction systems is less than 5×10⁻³ mol dm⁻³, we believe with confidence that the presence of water, if any, does not affect our results. The rate was also not influenced by introduction of sodium perchlorate up to 0.2 mol kg⁻¹. The absence of any salt effect is

consistent with the imidazole reacting as free base.

Conditional first-order rate constants $k_{0(Im)}$ were determined at various temperatures and various pressures and they are shown as a function of imidazole concentrations in Figs. 1 and 3.

Reaction of 1 with Thiocyanate Ion. In a large excess of thiocyanate ion concentrations over the bis(acetonitrile) complex concentration, equilibrium 2 is much favored to the right and the reverse reaction is negligible. Under pseudo-first-order conditions, the axial substitution was followed at 732 nm, the maximum wavelength of the bis(thiocyanato) complex produced. The conditional first-
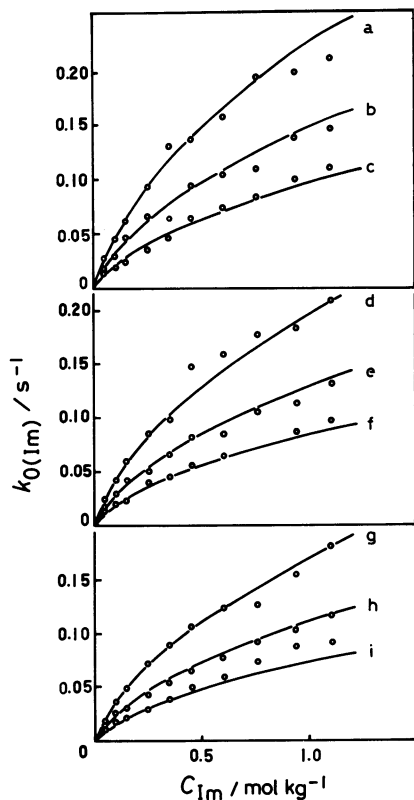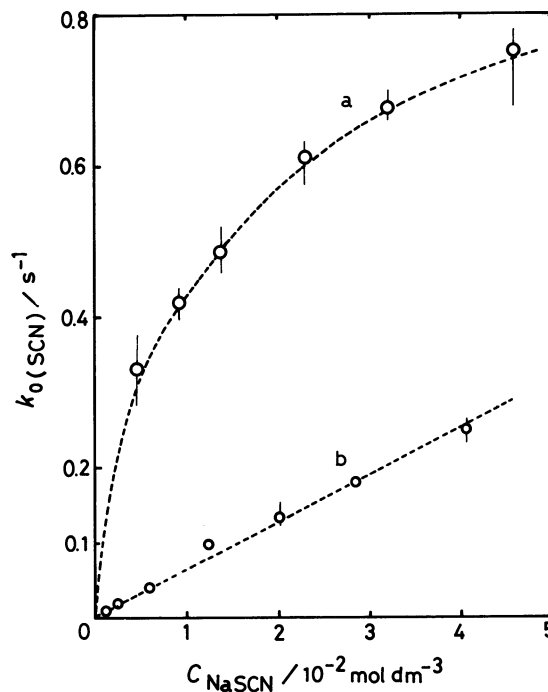

Fig. 3. Imidazole concentration dependence of first-order rate constants at 25.0 °C and nine different pressures. a: 0.1 MPa, b: 73.6 MPa, c: 147 MPa, d: 24.5 MPa, e: 98.1 MPa, f: 172 MPa, g: 49.0 MPa, h: 123 MPa, i: 196 MPa.

Fig. 4. Dependence of rate constant $k_{0(SCN)}$ on the total concentation of sodium thiocyanate (a) in the absence of and (b) in the presence of sodium perchlorate (C_{NaClO_4}=0.20 mol kg^{-1}).
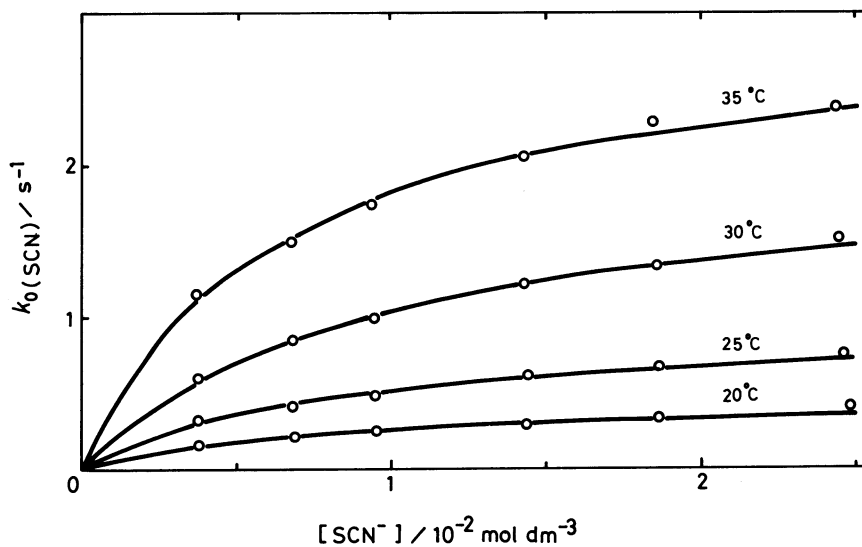

Fig. 5. Thiocyanate-ion concentration dependence of first-order rate constants at 20.0, 25.0, 30.0, 35.0, and 35.0 °C.
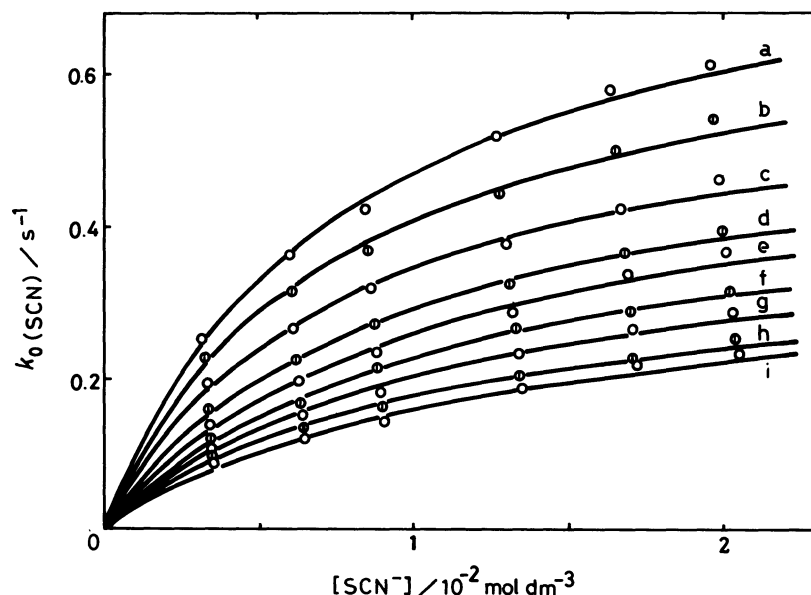
Fig. 6. Thiocyanate-ion concentration dependence of first-order rate constants at nine different pressure. a: 0.1 MPa, b: 24.5 MPa, c: 49.0 MPa, d: 73.6 MPa, e: 98.1 MPa, f: 123 MPa, g: 147 MPa, h: 172 MPa, i: 196 MPa.

order plots were excellently linear and the rate was confirmed to be first order with respect to the bis(acetonitrile) complex. Then we have

$$-\mathrm{d}[1]/\mathrm{d}t = \mathrm{d}[FeL(SCN)_2]/\mathrm{d}t = k_{0(SCN)}[1], \qquad (4)$$

where $k_{0(SCN)}$ is a conditional first-order rate constant involving the concentration of thiocyanate ion. Conditional first-order rate constants were obtained at various concentrations of thiocyanate ion both in the presence and in the absence of sodium perchlorate. As apparent from Fig. 4, in the presence of $NaClO_4$ the plot of $k_{0(SCN)}$ vs. the total concentration of sodium thiocyanate, C_{NaSCN}, gives a straight line through the origin, while in the absence of $NaClO_4$ the plot is leveled out with increasing thiocyanate concentration.
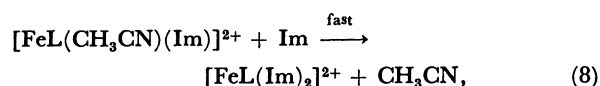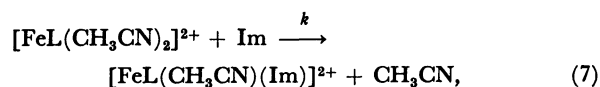
First-order rate constants $k_{0(SCN)}$ were determined as a function of thiocyanate ion concentrations at various temperatures and pressures. In Figs. 5 and 6 values of $k_{0(SCN)}$ are plotted as a function of the concentration of free thiocyanate ion, [SCN$^-$] (not the total concentration of sodium thiocyanate, C_{NaSCN}, see Discussion).

Discussion

In reaction systems showing a leveling of $k_{0(L)}$ with increasing concentration ([L]) of an incoming ligand, the plot of $k_{0(L)}^{-1}$ vs. [L]$^{-1}$ gives sometimes a straight line. In this case $k_{0(L)}$ is expressed as follows:

$$k_{0(L)} = \frac{a[L]}{1+b[L]}. \qquad (5)$$

However, the plot of $k_{0(L)}^{-1}$ vs. [L]$^{-1}$ for the imidazole system in this work did not give a straight line. Data at higher concentration of imidazole were unable to fit to the function of Eq. 5. This behavior may be rationalized in terms of the known tendency for imidazole to make hydrogen bonding strongly with itself.[25,26] If the resulted dimer (Im$_2$) is assumed to be unreactive with the complex, it is possible to express the reaction as follows:

$$2Im \overset{K}{\rightleftharpoons} Im_2, \qquad (6)$$

$$[FeL(CH_3CN)_2]^{2+} + Im \overset{k}{\longrightarrow}$$
$$[FeL(CH_3CN)(Im)]^{2+} + CH_3CN, \qquad (7)$$

$$[FeL(CH_3CN)(Im)]^{2+} + Im \overset{fast}{\longrightarrow}$$
$$[FeL(Im)_2]^{2+} + CH_3CN, \qquad (8)$$

where K refers to the dimerization constant of imidazole (Eq. 6), k is a second-order rate constant for the mono (imidazole) complex formation (Eq. 7), and the second imidazole reaction (Eq. 8) is very rapid. In a case where $C_{Im} \gg C_{FeL}$, we obtain

$$k_{0(Im)} = k\frac{\sqrt{8KC_{Im}+1}-1}{4K}. \qquad (9)$$

The $k_{0(Im)}$'s for a series of imidazole concentrations at 15, 20, 25, and 30 °C were fitted to Eq. 9 by a nonlinear least-squares program. The values of thermodynamic and activation parameters were obtained as follows: $\Delta H^{\ne}$=74±3 kJ mol^{-1}, $\Delta S^{\ne}$=0±9 J mol^{-1} K^{-1}, ΔH=−36±8 kJ mol^{-1}, and ΔS=−100±30 J mol^{-1} K^{-1}.

Since the plots of $\ln k$ and $\ln K$ against pressure showed linear relationships within experimental errors, the activation volume $\Delta V^{\neq}$ and the reaction volume ΔV can be accepted to be independent of pressure. Thus we can express k and K by Eqs. 10 and 11.

$$k = k^0 \exp(-\Delta V^{\neq} P/RT), \qquad (10)$$

$$K = K^0 \exp(-\Delta VP/RT), \qquad (11)$$

where k^0 and K^0 are constants at zero pressure, and then the conditional first-order rate constant is expressed as Eq. 12.

$$k_{0(\mathrm{Im})} =$$
$$k^0 \exp(-\Delta V^{\neq} P/RT)\frac{\sqrt{8K^0\exp(-\Delta VP/RT)C_{\mathrm{Im}}+1}-1}{4K^0\exp(-\Delta VP/RT)}$$
$$(12)$$

Values of k^0, K^0, $\Delta V^{\neq}$, and ΔV were obtained by a nonlinear least-squares fit to all nine sets of data (201 data points): $k^0=0.686\,\mathrm{mol^{-1}\,kg\,s^{-1}}$, $\Delta V^{\neq}=13.6\pm1.4$ $\mathrm{cm^3\,mol^{-1}}$, $K^0=3.7\,\mathrm{mol^{-1}\,kg}$, $\Delta V=1.6\pm4.2\,\mathrm{cm^3\,mol^{-1}}$. The final analysis of data by the least-squares program (SALS)[27] was carried out by applying simultaneously all data (341 data points) obtained at various temperatures and pressures. The parameters obtained are summarized in Table 1. The solid lines in Figs. 1 and 3 were depicted by the obtained values.

The activation volume of $13.7\,\mathrm{cm^3\,mol^{-1}}$ is considerably larger than that found for the CH_3CN exchange at Ni^{2+} ($7.3\,\mathrm{cm^3\,mol^{-1}}$), the most dissociative among solvent exchange reactions of bivalent transition metal ions.[28] Since the entering ligand, imidazole, has no charge, the electrostatic contribution to the volume change due to the interaction between the complex and imidazole is negligible. Therefore $\Delta V^{\neq}$ of $13.6\,\mathrm{cm^3\,mol^{-1}}$ points to a marked dissociative character of the reaction.
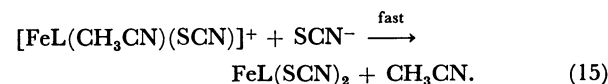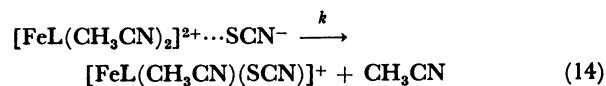
Figures 5 and 6 show also a falling-off of $k_{0(\mathrm{SCN})}$ with increasing concentration of the incoming ligand, $[SCN^-]$. We assume that the reaction of 1 with thiocyanate ion proceeds by the following processes:

$$1 + SCN^- \overset{K_{os}}{\rightleftharpoons} [FeL(CH_3CN)_2]^{2+}\cdots SCN^-, \qquad (13)$$

Table 1. Thermodynamic and Activation Parameters According to Eq. 6, Eq. 7, and Eq. 14[a]

Eq. 6	Eq. 7	Eq. 14
$\Delta H=-23\pm12$	$\Delta H^{\neq}=76\pm4$	$\Delta H^{\neq}=86\pm2$
$\Delta S=-67\pm41$	$\Delta S^{\neq}=7\pm13$	$\Delta S^{\neq}=51\pm6$
$\Delta V=-1.3\pm2.7$	$\Delta V^{\neq}=13.7\pm0.9$	$\Delta V^{\neq}=10.1\pm0.2$

a) Enthalpy, entropy, and volume are given by the unit in $\mathrm{kJ\,mol^{-1}}$, $\mathrm{J\,mol^{-1}\,K^{-1}}$, and $\mathrm{cm^3\,mol^{-1}}$, respectively.

$$[FeL(CH_3CN)_2]^{2+}\cdots SCN^- \overset{k}{\longrightarrow}$$
$$[FeL(CH_3CN)(SCN)]^+ + CH_3CN \qquad (14)$$

$$[FeL(CH_3CN)(SCN)]^+ + SCN^- \overset{fast}{\longrightarrow}$$
$$FeL(SCN)_2 + CH_3CN. \qquad (15)$$

Then, the conditional first-order rate constant is given by Eq. 16.

$$k_{0(\mathrm{SCN})} = \frac{kK_{os}[SCN^-]}{1+K_{os}[SCN^-]} \qquad (16)$$

The rate constant (k) of the unimolecular reaction may not be affected by ionic strength, I, while the association constant of the outer-sphere complex, K_{os}, varies as a function of ionic strength. For computation of K_{os} as described below we used the molar concentration calculated from the molal concentration with knowledge of the density of each solution at a certain temperature and pressure.[29] The ion association constant K_{NaSCN} of sodium thiocyanate in acetonitrile is available: thermodynamic constant $K_{NaSCN}=88\,\mathrm{mol\,dm^{-3}}$ at $I=0\,\mathrm{mol}$ $\mathrm{dm^{-3}}$.[30] The ionic strength dependence of K_{NaSCN} is given by the following relations:[31]

$$K_{NaSCN} = K_{NaSCN}y_{\pm}^2, \quad \log y_{\pm} = -AI/(1+BaI), \qquad (17)$$

where $A=(DT)^{-3/2}\times1.8246\times10^6$, $B=(DT)^{-1/2}\times50.29\times10^8$, $y_{\pm}$ is a mean activity coefficient, D is the specific dielectric constant of acetonitrile of which the temperature and pressure dependence is available,[29] and a is the distance of the closest approach which is accepted to be $4\times10^{-8}\,\mathrm{cm}$. Since, in the absence of sodium perchlorate, sodium thiocyanate exists in a very large excess (up to $5\times10^{-2}\,\mathrm{mol\,dm^{-3}}$), the ionic strength is controlled by the added sodium thiocyanate and then the ionic strength is given by Eq. 18.

$$I = \{-1+(1+4K_{NaSCN}C_{NaSCN})^{1/2}\}/2K_{NaSCN} \qquad (18)$$

The ionic strength for each run was calculated by Eqs. 17 and 18. We have

$$k = \frac{kT}{h}\exp\left(-\frac{\Delta H^{\neq}-T\Delta S^{\neq}}{RT}\right) \qquad (19)$$

K_{os} is given by Eq. 20[32]

$$K_{os} = \frac{4\pi N a^3}{3000}\exp\left\{-\frac{u(a)}{kT}\right\}, \qquad (20)$$

where $u(a)=z_1z_2e^2/aD-z_1z_2e^2\kappa/D(1+\kappa a)$, $\kappa^2=8\pi Ne^2I/1000DkT$, a is the distance of the closest approach, and the other symbols have their usual meanings. The parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, and a) from the data (187 data points) of temperature dependence of $k_{0(\mathrm{SCN})}$ were computed with knowledge of values of variables such as I, $[SCN^-]$, T, and $k_{0(\mathrm{SCN})}$ with use of Eqs. 16, 19, and 20 by a nonlinear least-squares program. We

obtained the following values: $\Delta H^{\neq}=86\pm2$ kJ mol^{-1}, $\Delta S^{\neq}=51\pm6$ J K^{-1} mol^{-1}, and $\hat{a}=(6.1\pm0.3)\times10^{-8}$ cm. With knowledge of values of I, [SCN$^-$], P, and $k_{0(SCN)}$ the parameters of k^0, $\Delta V^{\neq}$, and $\hat{a}$ from the data (162 data points) of pressure dependence of $k_{0(SCN)}$ were estimated with use of Eqs. 10, 16, and 20 by a nonlinear least-squares best fit. The following values were determined: $k^0=2.35\pm0.05$ s^{-1}, $\Delta V^{\neq}=10.1\pm0.2$ cm^3 mol^{-1}, and $\hat{a}=(6.9\pm0.2)\times10^{-8}$ cm. The $\hat{a}$ value of 6—7$\times10^{-8}$ cm is reasonable judging from the molecular model. The fact that the entropy of activation and the activation volume are both positive is consistent with the dissociative character of the reaction.

In the presence of a large excess of sodium perchlorate the values of K_{os} and [SCN$^-$] become smaller than in the absence of sodium perchlorate. Moreover because of the equilibrium Na$^+$+SCN$^-$$\rightleftarrows$ Na$^+$SCN$^-$, [SCN$^-$] is proportional to C_{NaSCN} in the presence of a large excess of sodium perchlorate. Therefore the term K_{os}[SCN$^-$] should be smaller than unity in Eq. 16. In this case, $k_{0(SCN)}$ is, in fact, proportional to the thiocyanate ion concentration as seen in Fig. 4b. We can calculate the ion-association constant, K_{NaClO_4}, of sodium perchlorate in CH$_3$CN from the data at 25.0 °C and 0.1 MPa in Fig. 4. The value of K_{NaClO_4} is evaluated to be 45 ± 5 mol^{-1} dm^3 at $I=0.057\pm0.002$ mol dm^{-3} which is reasonable as compared to the K_{NaSCN} value of 59 mol^{-1} dm^3 at $I=0.057$ mol dm^{-3} obtained from Eq. 17.

Jones and Twigg have pointed out two possible mechanisms for the substitution of axially bound dimethyl sulfoxide (Me$_2$SO) by imidazole at an iron (II) phthalocyanine center in Me$_2$SO.[5] In order to distinguish the two mechanisms they have extended their study to higher concentration range of imidazole up to 1.45 mol dm^{-3},[6] without finding the curvature which we observed in this work. This seems reasonable because imidazole dimerizes to a lesser extent in Me$_2$SO which is much more basic than acetonitrile.[33]

Rates of exchange of acetonitrile solvent on hexasolventoiron(II) ion are available:[28b,34] $k=6.6\times10^5$ s^{-1} (25 °C), $\Delta H^{\neq}=41.4$ kJ mol^{-1}, $\Delta S^{\neq}=5.3$ J K^{-1} mol^{-1}, and $\Delta V^{\neq}=3$ cm^3 mol^{-1}.[28b] The exchange rate is about 6 orders of magnitude higher than that for axial substitution in [FeL(CH$_3$CN)$_2$]$^{2+}$ primarily due to the difference in activation enthalpy. This will result from the different state of the paramagnetic high-spin hexa(acetonitrile)iron(II) and diamagnetic low-spin [Fe(II)L]$^{2+}$ ions. The activation volume for axial substitution of [Fe(II)L]$^{2+}$ is larger than that for solvent exchange and [FeL(CH$_3$CN)$_2$]$^{2+}$ reacts more dissociatively than [Fe(CH$_3$CN)$_6$]$^{2+}$ does.

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