A stronger donor such as $(CH_3)_3P$ gave an insoluble precipitate; thus no evidence of donor–acceptor interactions could be gleaned from potential phosphorus–phosphorus couplings.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work and T. Brisbane for assistance with the NMR spectroscopy.

Registry No. $CH_3(CF_3)_3PO_2CN(CH_3)_2$, 65013-32-3; CO_2, 124-38-9; $CH_3(CF_3)_3PN(CD_3)_2$, 85650-39-1; $HN(CD_3)_2$, 14802-36-9; $CH_3(CF_3)_3PN(CH_3)_2$, 63715-49-1; $(CH_3)_3SiCl$, 75-77-4; $^{13}CO_2$, 1111-72-4; $CH_3(CF_3)_3PO_2{}^{13}CN(CH_3)_2$, 85650-40-4; Me_3N, 75-50-3.

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Mechanism of Iron(III) Complex Formation. Activation Volumes for the Complexation of the Iron(III) Ion with Thiocyanate Ion and Acetohydroxamic Acid

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Activation volumes (ΔV^*) for the complexation of the iron(III) ion with thiocyanate (SCN^-) and acetohydroxamic acid (Hahx) were determined by a high-pressure stopped-flow technique. The values of ΔV^* for reaction of Fe^{3+} are -6.1 ± 1.0 cm^3 mol^{-1} for SCN^- and -10.0 ± 1.4 cm^3 mol^{-1} for Hahx, whereas the ΔV^* values of the $FeOH^{2+}$ ion are 8.5 ± 1.2 cm^3 mol^{-1} for SCN^- and 7.7 ± 0.6 cm^3 mol^{-1} for Hahx. Complexation of $FeOH^{2+}$ is dissociatively activated but that of Fe^{3+} associatively. No apparent parallel relationship is observed between ΔV^* and corresponding ΔS^* values.

Introduction

The sign of activation volumes has been demonstrated to be useful for distinction between reaction pathways for iron(III) complexation with proton ambiguity.[1] The activation volumes so far available for iron(III) complex formation are relatively few,[2] and additional data are required to ascertain the general possibility of this criterion.

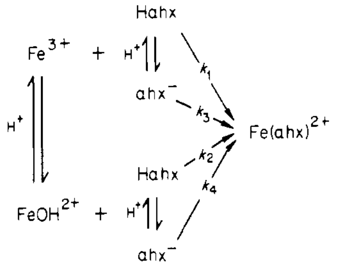
The reaction of the iron(III) ion with thiocyanate has no proton ambiguity. Although activation volumes for thiocyanate are available, the reported values do not agree with each other.[2b,d] Thus we decided to reexperiment by using a high-pressure stopped-flow technique. Moreover, in order to review a relationship between activation volume and activation entropy, we selected the reaction for which the value of activation entropy is the smallest among the available values and investigated the pressure effect on the iron(III) complexation with acetohydroxamic acid.

Experimental Section

Reagents. The solutions of iron(III) perchlorate and sodium perchlorate were prepared as described previously.[1] Reagent grade sodium thiocyanate was twice recrystallized from distilled water. The thiocyanate solution was standardized by the Volhard method.[3] Acetohydroxamic acid, $CH_3CONHOH$ (Aldrich Chemical Co., Inc.), was recrystallized three times from ethyl acetate and dried in vacuo at room temperature.

Measurements. All the measurements were carried out in a room thermostated at 25 ± 0.5 °C. The temperature of the reaction solution was kept to within ±0.1 °C by using a thermoelectric circulating bath. Ionic strength was maintained with sodium perchlorate and perchloric acid at 1.00 mol dm^{-3} for the system of acetohydroxamic acid (AHX or Hahx) and at 1.50 mol dm^{-3} for the thiocyanate system. Solutions were prepared at 25 °C in molar (mol dm^{-3} ≡ M) concentration scale. The molar concentrations were converted to the pressure-independent molal (mol kg^{-1} ≡ *m*) scale, when necessary. Rates at high pressure were measured by a high-pressure stopped-flow apparatus with spectrophotometric detection.[1,4] Reactions were followed mainly at 500 nm in the AHX system and at 460 nm in the NaSCN system. Hydrogen ion concentrations were varied from 0.17 to 0.66 M for the AHX system and from 0.038 to 0.43 M for the SCN^- system.

Scheme I



Results

Reaction rates for the iron(III) complex formation were measured under the pseudo-first-order conditions where the concentration of the ligands was in large excess over that of the iron(III) ion. The backward reactions were completely negligible. In both systems the formation of higher complexes than the 1:1 iron(III) complex was observed. It was confirmed experimentally that the rate of the forward reactions was first order with respect to the respective total concentrations of iron(III) ion and ligands over the following concentration ranges: in the AHX system, $C_{Fe} = 2.8 \times 10^{-4}$–$1.4 \times 10^{-3}$ M, $C_{AHX} = 0.08$–0.62 M; in the SCN system, $C_{Fe} = 2.6 \times 10^{-5}$–$3.9 \times 10^{-5}$ M, $C_{SCN} = 0.20$–0.54 M. Some experiments were also performed under excess iron(III) conditions where only the 1:1 complex was formed. The rate constants obtained were identical with those under the conditions of excess ligand concentrations. Thus, the step of the 1:1 complex should be rate limiting, and the formation of higher complexes must be faster.

Kinetics of Formation of the (Acetohydroxamato)iron(III) Complex. The rate of the formation reaction of the (aceto-

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(1) Ishihara, K., Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 194.

(2) (a) Hasinoff, B. B. *Can. J. Chem.* **1979**, *57*, 77. (b) Jost, A. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 316. (c) Hasinoff, B. B. *Can. J. Chem.* **1976**, *54*, 1820. (d) Heremans, K.; Snauwaert, J.; Rijkenberg, J. *High-Pressure Sci. Technol., AIRAPT Conf., 6th*, **1977**, 646.

(3) Welcher, F. J., Ed. "Standard Methods of Chemical Analysis", 6th ed.; Van Nostrand: Princeton, NJ, 1963; Vol. 2, Part A.

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0020-1669/83/1322-2070$01.50/0

Table I. Rate Constants and Activation Volumes for the Reactions of Fe(III) Ions with Hahx and SCN^- [a]

	Hahx		SCN^-	
	k at 25 °C	$\Delta V^{\ddagger}/cm^3\ mol^{-1}$	k at 25 °C	$\Delta V^{\ddagger}/cm^3\ mol^{-1}$
$k_1{}^0/m^{-1}\ s^{-1}$	6.37 ± 0.33	$-10.0 \pm 1.4\ (\Delta V_1{}^{\ddagger})$	$73.4 \pm 2.2^{b-d}$	$-6.1 \pm 1.0^{b-d}\ (\Delta V_1{}^{\ddagger})$
$k_2{}^0K_{FeOH}{}^0/s^{-1}$	8.76 ± 0.13	$8.5 \pm 0.5\ (\Delta V_2{}^{\ddagger} + \Delta V_{FeOH}{}^{\circ})$	$9.50 \pm 0.27^{b-d}$	$(9.3,^b\ 9.4,^c\ 9.5^d) \pm 1.1\ (\Delta V_2{}^{\ddagger} + \Delta V_{FeOH}{}^{\circ})$
$k_2{}^0/m^{-1}\ s^{-1}$	$(4.92 \pm 0.07) \times 10^3\ ^e$	$7.7 \pm 0.6^e\ (\Delta V_2{}^{\ddagger})$	$(5.86 \pm 0.17) \times 10^3\ ^{b-d}$	$8.5 \pm 1.2,^b\ 7.8 \pm 1.2,^c\ 6.5 \pm 1.6^d\ (\Delta V_2{}^{\ddagger})$

[a] Errors are standard deviation. [b] Computed by fixing $K_{FeOH} = 1.62 \times 10^{-3}\ m$ and $\Delta V_{FeOH}{}^{\circ} = 0.8 \pm 0.1\ cm^3\ mol^{-1}$ [17] in the least-squares fitting. [c] Computed by fixing $K_{FeOH} = 1.62 \times 10^{-3}\ m$ and $\Delta V_{FeOH}{}^{\circ} = 1.6 \pm 0.1\ cm^3\ mol^{-1}$ [2a] in the least-squares fitting. [d] Computed by fixing $K_{FeOH} = 1.62 \times 10^{-3}\ m$ and $\Delta V_{FeOH}{}^{\circ} = 3.0 \pm 0.5\ cm^3\ mol^{-1}$ [2b] in the least-squares fitting. [e] The following values were used: $K_{FeOH} = 1.78 \times 10^{-3}\ m$[6a] and $\Delta V_{FeOH}{}^{\circ} = 0.8 \pm 0.1\ cm^3\ mol^{-1}$.

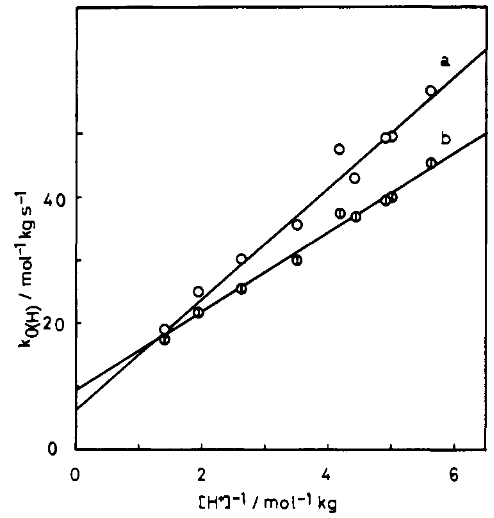

Figure 1. Hydrogen ion concentration dependence of $k_{0(H)}$ at 1 kg cm^{-2} (a) and 1000 kg cm^{-2} (b) in the Fe(III)–AHX system at 25 °C. Each point in Figures 1–4 is the average of several determinations.

hydroxamato)iron(III) complex ($Fe(ahx)^{2+}$: chelated tetraaqua species) is expressed by eq 1, where [Fe′] and [AHX′]

$$d[Fe(ahx)^{2+}]/dt = k_{0(H)}[Fe'][AHX'] \qquad (1)$$

denote the total concentration of all the species of iron(III) not combined with AHX and that of AHX not combined with iron(III), respectively, and $k_{0(H)}$ refers to the conditional second-order rate constant involving hydrogen ion concentration. Under the present experimental conditions, there exist several potential reactants such as hexaaquairon(III) ion (Fe^{3+}), pentaaquahydroxoiron(III) ion ($FeOH^{2+}$), neutral acetohydroxamic acid (Hahx), and deprotonated acetohydroxamate ion (ahx^-). Thus the four possible reaction paths presented in Scheme I should be taken into consideration. The rate of formation of $Fe(ahx)^{2+}$ is then given by eq 2.

$$d[Fe(ahx)^{2+}]/dt = k_1[Fe^{3+}][Hahx] + k_2[FeOH^{2+}] \times [Hahx] + k_3[Fe^{3+}][ahx^-] + k_4[FeOH^{2+}][ahx^-] \qquad (2)$$

Using $K_{FeOH} = [FeOH^{2+}][H^+]/[Fe^{3+}]$ and $K_a = [ahx^-][H^+]/[Hahx]$, we obtain eq 3.

$$d[Fe(ahx)^{2+}]/dt = [Fe^{3+}][Hahx] \times (k_1 + k_2K_{FeOH}/[H^+] + k_3K_a/[H^+] + k_4K_aK_{FeOH}/[H^+]^2) \qquad (3)$$

Since $1 \gg K_{FeOH}/[H^+]$ and $1 \gg K_a/[H^+]$,[5] we obtain eq 4.

$$k_{0(H)} = k_1 + (k_2K_{FeOH} + k_3K_a)/[H^+] + k_4K_aK_{FeOH}/[H^+]^2 \qquad (4)$$

Plots of the values of $k_{0(H)}$ obtained at a constant pressure against $1/[H^+]$ lie on a straight line with a constant intercept, as shown in Figure 1. Figure 1 indicates no contribution of the k_4 path. The value of the slope at 1 kg cm^{-2} corresponds to $k_2K_{FeOH} + k_3K_a = 8.76\ s^{-1}$. If k_3 were to contribute significantly (>1%) to this term, it would have to be at least $1 \times 10^8\ M^{-1}\ s^{-1}$. Since rate constants for Fe^{3+} reactions are expected to be in the range 2–$10^2\ M^{-1}\ s^{-1}$,[1] the contribution of the k_3 path can be ruled out. Consequently, $k_{0(H)}$ can be expressed by eq 5.

$$k_{0(H)} = k_1 + k_2K_{FeOH}/[H^+] \qquad (5)$$

Values of k_1 and k_2K_{FeOH} were obtained from the intercept and the slope of a plot such as Figure 1. Since the plots of ln k_1 and ln k_2 obtained at different pressures against pressure showed linear relationships, the activation volumes for the k_1 and k_2 path were found to be independent of pressure. Thus we can rewrite eq 5 as eq 6 where $k_1{}^0$, $k_2{}^0$, and $K_{FeOH}{}^0$ are constants at zero pressure.

$$k_{0(H)} = k_1{}^0 \exp(-\Delta V_1{}^{\ddagger}PR^{-1}T^{-1}) + k_2{}^0K_{FeOH}{}^0 \exp[-(\Delta V_2{}^{\ddagger} + \Delta V_{FeOH}{}^{\circ})PR^{-1}T^{-1}]/[H^+] \qquad (6)$$

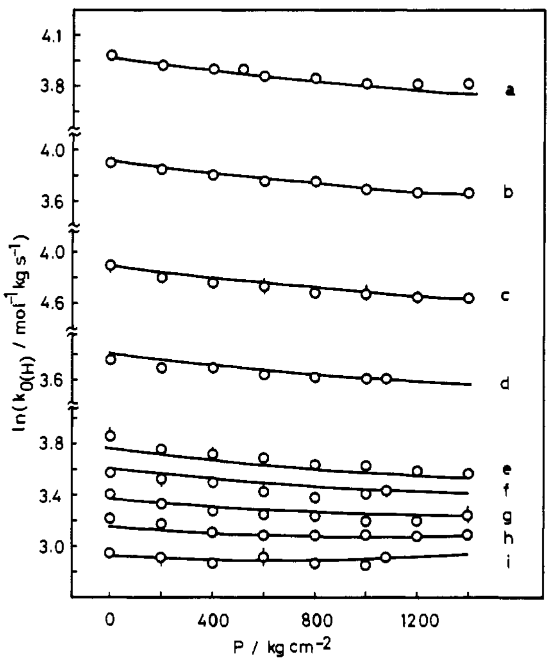

Figure 2. Pressure dependence of conditional second-order rate constants for the reaction of iron(III) ions with Hahx at different hydrogen ion concentrations (at 25 °C and I = 1.07–1.09 m). $[H^+]$ = 0.178 m (a), 0.200 m (b), 0.204 m (c), 0.226 m (d), 0.240 m (e), 0.286 m (f), 0.381 m (g), 0.519 m (h), and 0.716 m (i).

Pressure dependence of $k_{0(H)}$ at a constant concentration of hydrogen ion was shown in Figure 2. Values of $k_1{}^0$, $k_2{}^0$, $\Delta V_1{}^{\ddagger}$, and $\Delta V_2{}^{\ddagger} + \Delta V_{FeOH}{}^{\circ}$ were obtained by a nonlinear least-squares fit to all nine sets of data (226 data points).[7] Values of $k_1{}^0$ and $k_2{}^0$ were revealed to be essentially the same as

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(5) $[Fe'] = [Fe^{3+}](1 + K_{FeOH}/[H^+])$ and $[AHX'] = [Hahx](1 + K_a/[H^+])$, where $K_{FeOH} = 1.65 \times 10^{-3}$ M at 25 °C and I = 1.0 M[6a] and $K_a = 10^{-9.02}$ M at 25 °C and I = 2.00 M.[6b]

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(7) Supplementary material.

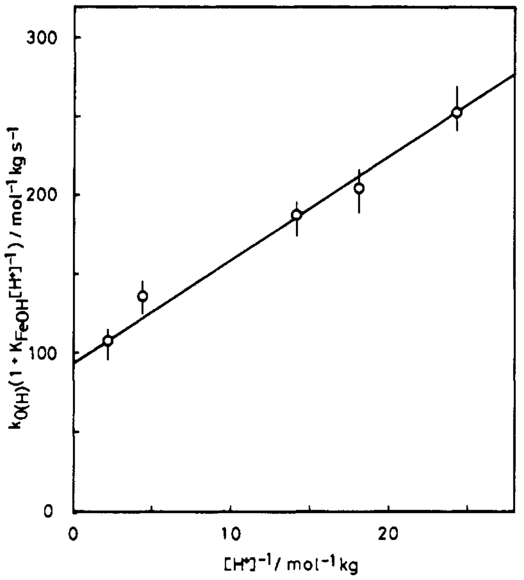

Figure 3. Hydrogen ion concentration dependence of $k_{0(H)}$ at 25 °C and 1000 kg cm^{-2} in the Fe(III)–SCN system.

corresponding values obtained at atmospheric pressure. The solid lines in Figure 2 were depicted by using the constants obtained. The obtained parameters are tabulated in Table I.

Kinetics of Formation of the (Isothiocyanato)iron(III) Complex. The rate of formation of $Fe(NCS)^{2+}$ is given by

$$d[Fe(NCS)^{2+}]/dt = k_1[Fe^{3+}][SCN^-] + k_2[FeOH^{2+}][SCN^-] \quad (7)$$

Therefore, the conditional second-order rate constant $k_{0(H)}$ has the relationship

$$k_{0(H)}(1 + K_{FeOH}/[H^+]) = k_1 + k_2K_{FeOH}/[H^+] \quad (8)$$

The plot of $k_{0(H)}(1 + K_{FeOH}/[H^+])$ against $1/[H^+]$ was a straight line (see Figure 3). Pressure dependence of $k_{0(H)}$ is illustrated in Figure 4. Values of $\ln k_1$ and $\ln k_2$ varied linearly with increasing pressure. Thus we can express the pressure dependence of $k_{0(H)}$ by eq 9. Values of k_1^0, $k_2^0K_{FeOH}^0$,

$$k_{0(H)}[1 + K_{FeOH}^0 \exp(-\Delta V_{FeOH}^0 PR^{-1}T^{-1})/[H^+]] = k_1^0 \exp(-\Delta V_1^{*}PR^{-1}T^{-1}) + k_2^0K_{FeOH}^0 \times \exp[-(\Delta V_2^{*} + \Delta V_{FeOH}^0)PR^{-1}T^{-1}] \quad (9)$$

ΔV_1^{*}, and $\Delta V_2^{*} + \Delta V_{FeOH}^0$ were determined by a nonlinear least-squares fit to all five sets of data (140 data points)[7] with fixed values of $\Delta V_{FeOH}^0 = 0.8 \pm 0.1$ cm^3 mol^{-1},[17] 1.6 ± 0.1 cm^3 mol^{-1},[2a] and 3.0 ± 0.5 cm^3 mol^{-1}.[2b] All the values of parameters obtained are summarized in Table I.

Discussion

It is now generally accepted[8] that complex formation reactions of metal ions proceed by a mechanism in which the rate-determining step is the reaction from the outer-sphere complex to the inner-sphere complex, preceded by the formation of the outer-sphere complex between metal ion and ligand. The observed second-order rate constant k_f is given by the product of the formation constant of the outer-sphere complex and the first-order rate constant ($k_f = K_{os}k^{*}$). Therefore, the overall activation volume is given by $\Delta V^{*} = \Delta V_{os}^0 + \Delta V^{**}$, where ΔV_{os}^0 and ΔV^{**} are the reaction volume for K_{os} and the activation volume for k^{*}, respectively. The volume of activation ΔV^{**} is generally considered[9] the combination of an intrinsic contribution and a solvation contri-

Table II. Activation Volumes for Complexation of Iron(III) Ions So Far Studied

	Fe^{3+}			$FeOH^{2+}$				
ligand	$\Delta V^{\ddagger a}$ ($\Delta V^{*\ddagger b}$)/ cm^{-3} mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	$\Delta V^{\ddagger a}$ ($\Delta V^{*\ddagger b}$)/ cm^{-3} mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	conditions[c]	ref
H_2O[d]	−5.4 ± 0.4[e] (−5.4)	64.0 ± 2.5[f]	12 ± 7[f]	7.0 ± 0.5 (7.0)	42.43 ± 1.46[f]	5.27 ± 3.98[f]	$I = 6.0m$ (Na^+, H^+, ClO_4^-), $[H^+] = 0.3–6.0\ m$[g]	17
Hipt[h]	−8.7 ± 0.8 (−8.7)	59.5 ± 3.0	−19.8 ± 3.0	4.1 ± 0.6 (4.1)	29.2 ± 3.6	−72.3 ± 5.0	$I = 1.00$ M (Na^+, H^+, ClO_4^-), $[H^+] = 0.21–0.98$ M	1
Cl^-	−4.5 ± 1.1 (−6.5)	67 ± 20[i]	4 ± 71[i]	7.8 ± 1.0 (6.2)	46 ± 8[i]	−10 ± 30[i]	$I = 1.5$ M (Na^+, H^+, Cl^-, ClO_4^-), $[H^+] = 0.412, 0.612, 0.812$ M	2c
Br^-	−8 ± 5 (−9.6)	50 ± 8[i]	−42 ± 30[i]		30 ± 8[i]	−75 ± 30[i]	$I = 2.0$ M (Na^+, H^+, Br^-, ClO_4^-), $[H^+] = 0.525, 1.925$ M	2a
NCS^-	−12			8.8			I varied, $[H^+] = 0.02–0.3$ M	2d
NCS^-	~0 (−3.4)			7.1 ± 1.0 (4.4)			$I = 0.2\ m$ ($NaClO_4$), $[H^+] = 2 \times 10^{-3}–1.5 \times 10^{-2}\ m$	2b
NCS^-	−6.1 ± 1.0 (−8.1)	54.4 ± 5.9[j]	−20 ± 20[j]	8.5 ± 1.2 (6.9)	42[j]	−32[j]	$I = 1.5$ M (Na^+, H^+, SCN^-, ClO_4^-), $[H^+] = 0.038–0.43$ M	this work
Hahx	−10.0 ± 1.4 (−10.0)	38[6b]	−100[6b]	7.7 ± 0.6 (7.7)	20 ± 2[6b]	−110 ± 4[6b]	$I = 1.00$ M (Na^+, H^+, ClO_4^-), $[H^+] = 0.17–0.66$ M	this work

[a] Observed activation volume disregarding any initial ion pairing. [b] Intrinsic activation volume taking into consideration the contribution of outer-sphere formation according to eq 11. [c] At 298.2 K unless otherwise indicated. [d] Water exchange. [e] Error limits as given by original authors except for this work in which errors are standard deviations. [f] Cited from: Grant, M.; Jordan, R. B. *Inorg. Chem.* 1981, *20*, 55. [g] At 382.8 K. [h] Hipt ≡ 4-isopropyltropolone. [i] Cited from: Yasunaga, T.; Harada, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2165. [j] Cited from: Below, J. F., Jr.; Connick, R. E.; Coppel, C. P. *J. Am. Chem. Soc.* 1958, *80*, 2961.

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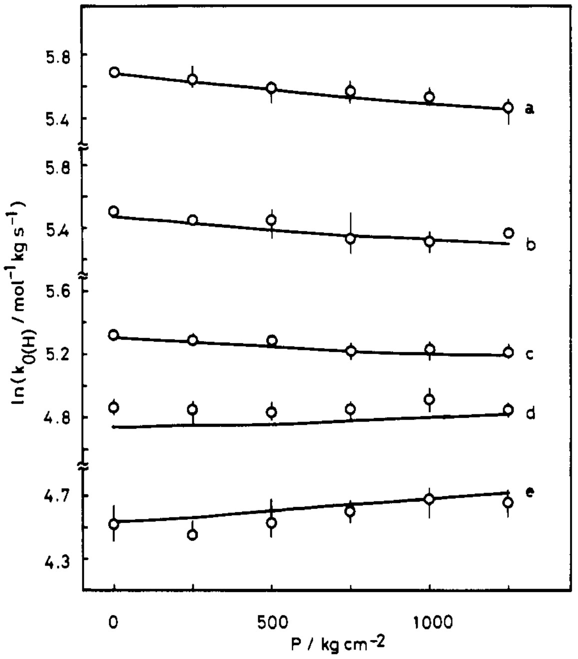

Figure 4. Pressure dependence of conditional second-order rate constants for the reaction of iron(III) ions with SCN^- at different hydrogen ion concentrations (at 25 °C and $I = 1.61$ *m*). $[H^+] = 0.0411$ *m* (a), 0.0554 *m* (b), 0.0708 *m* (c), 0.229 *m* (d), and 0.461 *m* (e).

bution: $\Delta V^{**} = \Delta V^{*}_{intr} + \Delta V^{*}_{solv}$; ΔV^{*}_{intr} is the change in partial molar volume caused by bond making or bond breaking in the activation process, and ΔV^{*}_{solv} is the change in volume with variation of solvation. Since no net change in charge occurs in the activation process from the outer-sphere complex to the inner-sphere complex, negligible solvational changes are expected and $\Delta V^{*}_{solv} \simeq 0$ cm^3 mol^{-1}; i.e., $\Delta V^{**} \simeq \Delta V^{*}_{intr}$.

The equilibrium constant K_{os} for the formation of the outer-sphere complex can be calculated approximately according to Eigen[10] and Fuoss[11] by using eq 10. In these

$$K_{os} = \frac{4\pi N_A a^3}{3000} e^{-U(\epsilon)/kt}$$

$$U(\epsilon) = \frac{z_M z_L e^2}{a\epsilon} - \frac{z_M z_L e^2 \kappa}{\epsilon(1 + \kappa a)} \qquad \kappa^2 = \frac{8\pi N_A e^2 I}{1000\epsilon k T} \tag{10}$$

equations N_A is the Avogadro constant, a is the distance of closest approach of the two ions, k is the Boltzmann constant, $z_M e$ and $z_L e$ are the charges of the metal ion and ligand, respectively, ϵ is the bulk dielectric constant, and I is the ionic strength. The reaction volume, $\Delta V_{os}°$, of the outer-sphere complex is obtained by differentiation of eq 10 with respect to pressure:

$$\Delta V_{os}° = -RT[(\partial \ln K_{os}/\partial P)_T + \beta] \tag{11}$$

where β is the solution compressibility. In the Hahx system, since Hahx has no formal charge, if any, its dipole may be small; $\Delta V_{os}°$ should be substantially zero. In the SCN^- system, at $I = 1.50$ mol dm^{-3} and 25 °C, $\Delta V_{os,Fe}°$ and $\Delta V_{os,FeOH}°$ are estimated to be 2.0 and 1.6 cm^3 mol^{-1}, respectively, from eq 11. In this calculation we used the following values: (1) The value of a was taken to be about 5×10^{-8} cm, which is assumed to be independent of pressure. (2) The value of β is -3.6×10^{-5} kg^{-1} cm^2 at 25 °C and $I = 1.5$ mol dm^{-3} ($NaClO_4$).[12,13] (3) The value of $(\partial\epsilon/\partial P)_T$ was estimated to be 3.62×10^{-3} kg^{-1} cm^2 from the pressure dependence of the dielectric constant of water.[14-16]

In Table II, available values of activation volume for iron(III) complexation are summarized together with our results. As apparent from the values in Table II, the ΔV_{Fe}^{**} values for Fe^{3+} are negative and the ΔV_{FeOH}^{**} for $FeOH^{2+}$ are positive.

The positive ΔV^{*} value corresponds to the increase in its own volume, intrinsic volume, due to lengthening of a bond at the transition state, and the negative value of ΔV^{*} indicates the volume decrease by the formation of an additional bond. Recently Swaddle and Merbach[17] have reported that the activation volumes for water exchange on $FeOH^{2+}$ and Fe^{3+} are 7.0 and −5.4 cm^3 mol^{-1}, respectively, and concluded that water exchange on $FeOH^{2+}$ is dissociatively activated but that on Fe^{3+} associatively. Their findings are similar to ours. As apparent from Table II, ΔV^{*} values for different ligands are not so much different although the ligands are very different in size. This indicates that the extent of insertion of the donor atom of entering ligands to the inner sphere is almost the same.

We observed hardly parallel relations between ΔV^{*} and ΔS^{*} for such ligands as used in the present study, for which a clear isokinetic relationship is observed (see Table II). In principle, the activation volume corresponds to inferred change in nuclear positions between reactants and transition state. This reflects a structural aspect that should be intrinsically simpler than the alternative concept of activation entropy, which depends on change in both the nuclear positions and energy. It seems likely that ΔS^{*} values reflect important contributions from the solvent interaction.[18] In conclusion, the interpretation of ΔS^{*} in terms of mechanism is likely to be complicated by solvent-interaction effects, whereas the sign of ΔV^{*} is useful for diagnosing the mechanism, dissociative or associative.

Note Added in Proof. After the submission of the present paper, the attention of the authors was kindly drawn to the following paper: Doss, R.; van Eldik, R.; Kelm, H. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 925. In this paper +6.7 and ~0 cm^3 mol^{-1} of activation volume were reported for the NCS^- complexation with Fe^{3+} and $Fe(OH)^{2+}$, respectively. This result does not agree with ours. They worked in the nitrate medium and at iron(III) concentration and pH both higher than those in our case. We wonder if the formation of a nitrato iron complex(es) and polymerized hydroxo species possibly makes the reaction system complicated and different from ours. For nitrato and hydroxo complexes of iron(III), see: "Stability Constants of Metal-Ion Complexes"; The Chemical Society: London; Spec. Publ. No. 17.

Registry No. Iron, 7439-89-6; thiocyanic acid, 463-56-9; acetohydroxamic acid, 546-88-3.

Supplementary Material Available: Listings of rate constants for formation of the (acetohydroxamato)iron(III) complex (Table SI) and the (isothiocyanato)iron(II) complex (Table SII) under various conditions (7 pages). Ordering information is given on any current masthead page.

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