This agreement for Re–Re bonds demonstrates the applicability of the method to bonds between d-block atoms, and even though reliable values of k_e for the group 6B metals are not at hand, these can easily be generated by variation of the constant a to ensure the best fit between calculated and observed values of r_e and D_e for the higher order bonds.

Results

The Morse constants, a, were varied in each case within limits established by analogy with approximate values of the corresponding double-bond force constants estimated from diatomic molecular spectra. This produced reasonable values of multiple-bond lengths and dissociation energies, in fair agreement with available experimental values. The results for all calculations are summarized in Table I and illustrated graphically in Figure 1.

The major defect of the comparison is the dearth of reliable experimental values for the quantities of interest. Clearly, erroneous definition of the single bond produces poor predictions of the properties of the higher order bonds. Evaluation of the agreement should hence not be too strict. In view of this, the agreement between calculated and observed bond properties is excellent, especially for the Re$\overset{n}{-}$Re and Mo$\overset{n}{-}$Mo bonds.

Discussion

A common problem in the field of metal–metal bonding is the assignment of exact bond orders. In many cases bond orders actually appear to be fractional rather than integral. This is not always easy to rationalize in terms of the established models of multiple bonding. In terms of the screening mechanism proposed here, it presents no problem. In fact, bonds of exactly integral order would be the exception rather than the rule insofar as eq 1 relates bond order to electron density in the region between atomic cores. This electron density must be sensitive to the nature of any ligands attached to the bonded atoms. In a variety of compounds, one therefore expects metal–metal bond orders spanning the whole region from 1 to 4 instead of well-defined integral bond orders only. In many ways this agrees with experience.

In view of recent criticism[10] of Cotton's formulation of quadruple bonds, the present results have additional significance. It provides independent evidence of a heuristic nature to support Cotton's model. Starting from eq 1, together with characteristic single-bond properties, one predicts the properties of multiple bonds, in good agreement with the most reliable experimental values. In the sense of the bond order concept as commonly applied to bonds between p-block atoms, bond order 4 is therefore seen to occur with the homonuclear bonds of Cr, Mo, W, and Re.

The present approach does not stipulate the electronic distribution of the higher order bonding electrons, but in order to satisfy the requirements of the Pauli principle for the internuclear region, molecular orbitals of the type proposed by Cotton would clearly be required.

Future work will be directed toward the characterization of bond orders for the large number of intermediate-type bonds that occur in metal clusters.

Acknowledgment. Generous support from the Council for Scientific and Industrial Research is gratefully acknowledged.

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Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

Mechanistic Difference of the Iron(III) Ion Complexation in Different Solvents

KOJI ISHIHARA, SHIGENOBU FUNAHASHI, and MOTOHARU TANAKA*

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The activation volumes ($\Delta V^{\ddagger}$) for the complexation of the iron(III) ion with acetohydroxamic acid, 4-isopropyltropolone, and thiocyanate ion in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO) were determined by a high-pressure stopped-flow technique. Values of $\Delta V^{\ddagger}$ for the formation of the (acetohydroxamato)iron(III) and (isopropyltropolonato)iron(III) complexes are −0.8 ± 0.2 and 5.0 ± 0.4 $cm^3\ mol^{-1}$, respectively, in DMF and 3.0 ± 0.3 and 10.9 ± 1.7 $cm^3\ mol^{-1}$ in Me_2SO, respectively. For the formation and dissociation of the 1:1 (isothiocyanato)iron(III) complex in Me_2SO, the $\Delta V^{\ddagger}$ values are 3.3 ± 0.6 and −8.5 ± 1.4 $cm^3\ mol^{-1}$, respectively. The change in the sign of $\Delta V^{\ddagger}$ is interpreted on the basis of relative bulkiness of both the entering ligand and the coordinated solvent molecule.

Introduction

The mechanism of the complexation of the iron(III) ion and the solvent exchange on the iron(III) ion has been studied in acidic aqueous solution at high pressures.[1-3] It has been concluded from the sign of the activation volumes ($\Delta V^{\ddagger}$) that the hexaaquairon(III) ion reacts through an associative interchange (I_a) mechanism but the pentaaquahydroxoiron(III) ion via a dissociative interchange (I_d) mechanism. Recently we have concluded that all the formation and dissociation of the 1:1 nickel(II) complex and the solvent exchange on the nickel(II) ion in various solvents can be accommodated within the framework of a similar I_d mechanism.[4]

Recently, interesting data on activation volumes for the nonaqueous solvent exchange on the Fe(III) ion were reported by Merbach et al.[5] Values of $\Delta V^{\ddagger}$ for the solvent exchange on the Fe(III) ion in Me_2SO (−3.1 ± 0.3 $cm^3\ mol^{-1}$) and in DMF (−0.9 ± 0.2 $cm^3\ mol^{-1}$) are less negative in comparison

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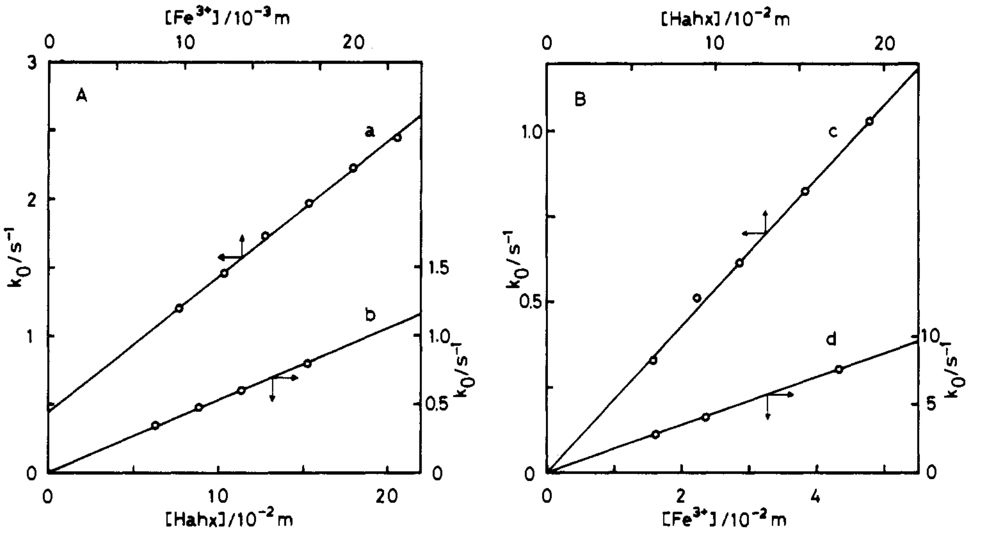

Figure 1. Concentration dependence of k_0. (A) In Me_2SO: (a) for the SCN system at 25 °C and [NaSCN] = 1.28×10^{-4} *m*; (b) for the AHX system at 40 °C and $[Fe(ClO_4)_3] = 2.2 \times 10^{-4}$ *m*. (B) In DMF: (c) for the AHX system at 25 °C and $[Fe(ClO_4)_3] = (2.7–2.8) \times 10^{-4}$ *m*; (d) for the IPT system at 25 °C and [Hipt] = $(3.1–6.3) \times 10^{-5}$ *m*.

with that in water (-5.4 ± 0.4 cm^3 mol^{-1}). We anticipated that the mechanism of iron(III) ion complexation would be less associative in bulky solvents. It was thus decided to measure the volumes of activation for the complexation of the iron(III) ion in DMF and Me_2SO in order to compare them with the corresponding values in water.[1,2] We selected the thiocyanate ion as a simple charged ligand and acetohydroxamic acid (AHX) and 4-isopropyltropolone (IPT) as neutral ligands because AHX is comparable to DMF and Me_2SO in their size while IPT is larger than DMF and Me_2SO.

Experimental Section

Solvents. Reagent grade dimethyl sulfoxide (Me_2SO) (Wakojunyaku, Osaka, Japan) was dried over 3-Å molecular sieves for 1 day and then it was distilled three times under vacuum; the first and second distillations were carried out in the presence of calcium hydride (4 g dm^{-3}) and the last in the absence of any drying agent. The purified Me_2SO was used within 2 days. Reagent grade *N*,*N*-dimethylformamide (DMF) (Wakojunyaku) dried over 3-Å molecular sieves for a few days was distilled three times at ca. 26 °C under vacuum. The last middle fraction was used within 24 h.

Reagents. $[Fe(H_2O)_6](ClO_4)_3$. A 5.6-g portion of spongelike iron (99.99%, Wakojunyaku) was dissolved in 100 cm^3 of 60% $HClO_4$ (super special grade, Wakojunyaku) by heating. The resultant solution was concentrated by evaporation. The pale purple crystals were filtered and recrystallized from 60% $HClO_4$. Absence of chloride ion was checked by silver nitrate.

$[Fe(Me_2SO)_6](ClO_4)_3$. The following procedure for preparation of hexakis(solvento)iron(III) perchlorate was employed.[6-8] When fresh Me_2SO was added to the acetone solution of the hexahydrate ($[Fe(H_2O)_6](ClO_4)_3$), the yellowish green precipitate appeared. The precipitate was collected on a G3 glass filter and was recrystallized from Me_2SO solution by adding acetone, washed with hot acetone several times, and dried under vacuum at room temperature.

$[Fe(DMF)_6](ClO_4)_3$. Diethyl ether was added to the acetone solution of the hexahydrate. When phase separation occurred, a suitable amount of acetone and/or diethyl ether was added to get a uniphase solution. Fresh DMF was added to the homogeneous solution. Light yellow crystals slowly precipitated from the solution. The crystals were recrystallized from DMF solution by adding acetone and diethyl ether and dried under vacuum at room temperature.

The concentration of the iron(III) solution in Me_2SO and DMF prepared by weighing respective hexakis(solvento)iron(III) perchlorate agreed excellently with that determined by a replacement titration with the Cu–TAR–EDTA system.[9]

Acetohydroxamic acid (AHX or Hahx) (Aldrich Chemical Co., Inc.) was recrystallized three times from ethyl acetate at ca. 80 °C. Since the acid is hygroscopic, it was dried under vacuum at room temperature just before use. 4-Isopropyltropolone (IPT or Hipt) (Takasago Perfumery Co., Ltd., Tokyo, Japan) was recrystallized three times from ligroin below 50 °C and dried under vacuum. Sodium thiocyanate and sodium perchlorate anhydride were prepared as described previously.[2]

Measurements and Results

All solutions were 0.20 M (M ≡ mol dm^{-3}) in sodium perchlorate. Measurements were carried out at 25 ± 0.1 °C in DMF and at 40 ± 0.1 °C in Me_2SO (Me_2SO freezes at pressure higher than ca. 500 kg cm^{-2} (1 kg cm^{-2} = 0.098 067 MPa) at 25 °C). Rates were followed at 500 nm for the Fe^{3+} + AHX reaction (AHX system), at 440 nm for the Fe^{3+} + IPT reaction (IPT system), and at 460 nm for the Fe^{3+} + SCN^- reaction (SCN system) by the high-pressure stopped-flow spectrophotometer (Type FIT-3[4,10]). In order to ensure pseudo-first-order conditions, excess ligand concentration was employed for the AHX system and for the IPT and SCN systems metal ions were in excess. For the AHX system [Hahx] = 0.06–0.19 *m* (*m* ≡ mol kg^{-1}) and $[Fe(ClO_4)_3] = 2.2 \times 10^{-4}–2.8 \times 10^{-4}$ *m*, for the IPT system $[Fe(ClO_4)_3]$ = 0.015–0.043 *m* and [Hipt] = $2.6 \times 10^{-5}–3.1 \times 10^{-4}$ *m*, and for the SCN system $[Fe(ClO_4)_3] = 2.8 \times 10^{-3}–0.026$ *m* and [NaSCN] = $5.9 \times 10^{-5}–1.3 \times 10^{-4}$ *m*. Pseudo-first-order plots showed very good linearity at least up to 90% reaction. The dissociation of the Fe(III) complex is not appreciable for the AHX and IPT systems under the experimental conditions.

The reactions studied in this work are expressed by eq 1–3.

$$Fe^{3+} + Hahx \xrightarrow{k_f} Fe(ahx)^{2+} + H^+ \qquad (1)$$

$$Fe^{3+} + Hipt \xrightarrow{k_f} Fe(ipt)^{2+} + H^+ \qquad (2)$$

$$Fe^{3+} + SCN^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Fe(NCS)^{2+} \qquad (3)$$

The conditional first-order rate constants (k_0) were linearly related with the excess reactant concentrations in all systems (see Figure 1). Thus, the formation of the 1:1 complex should

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Table I. Activation Volumes for the Complexation of the Iron(III) Ion[a]

	$\Delta V^{\ddagger}_{f}$/cm^3 mol^{-1}		SCN$^-$ [d]		
solvent	Hahx[b]	Hipt[c]	$\Delta V^{\ddagger}_{f}$/cm^3 mol^{-1}	$\Delta V^{\ddagger}_{d}$/cm^3 mol^{-1}	$\Delta V^{\ddagger}_{ex}$[e]/cm^3 mol^{-1}
Me_2SO	3.0 ± 0.3	10.9 ± 1.7	3.3 ± 0.6	−8.5 ± 1.4	−3.1 ± 0.3
DMF	−0.8 ± 0.2	5.0 ± 0.4			−0.9 ± 0.2
H_2O	−10.0 ± 1.4[f] (−10.0)[i]	−8.7 ± 0.8[g] (−8.7)[i]	−6.1 ± 1.0[f] (−8.1)[i]	−15.0 ± 1.2[h]	−5.4 ± 0.4

[a] Errors are standard deviations; at 25 °C in DMF and H_2O and at 40 °C in Me_2SO. [b] $[NaClO_4] = 0.19$ *m* in Me_2SO, $[NaClO_4] = 0.216$ *m* in DMF, and $I = 1.07$-1.09 *m* in H_2O. [c] $[NaClO_4] = 0.186$ *m* in Me_2SO, $[NaClO_4] = 0.214$ *m* in DMF, and $I = 1.05$ *m* in H_2O. [d] $[NaClO_4] = 0.186$ *m* in Me_2SO and $I = 1.61$ *m* in H_2O. [e] Activation volume for solvent exchange taken from ref 3 and 5. [f] Reference 2. [g] Reference 1. [h] Reference 12 and see the text. [i] Estimated $\Delta V^{*\ddagger}_{f,intr}$ values.

be rate determining. The proton released during the reaction brought about no complexity to the reaction because of a negligible contribution of the backward reaction. Thus, the conditional first-order rate constants (k_0) are expressed as follows: for the AHX system (excess ligand)

$$k_0 = k_f[\mathrm{Hahx}] \qquad (4)$$

for the IPT system (excess Fe^{3+})

$$k_0 = k_f[\mathrm{Fe}^{3+}] \qquad (5)$$

and for the SCN system (excess Fe^{3+})

$$k_0 = k_f[\mathrm{Fe}^{3+}] + k_d \qquad (6)$$

The observed numerical values are tabulated in Table S1 (supplementary material).[11] The second-order rate constants k_f and the volumes of activation ΔV^{*}_{f} for the AHX and IPT systems were obtained from the slopes of the linear plots of ln k_f vs. pressure as depicted in Figure 2. k_f and ΔV^{*}_{f} for the AHX system were determined to be 5.31 ± 0.04 m^{-1} s^{-1} and 3.0 ± 0.3 cm^3 mol^{-1} in Me_2SO at 40 °C and $[NaClO_4] = 0.19$ *m* and 5.42 ± 0.06 m^{-1} s^{-1} and −0.8 ± 0.2 cm^3 mol^{-1} in DMF at 25 °C and $[NaClO_4] = 0.216$ *m*. The k_f and ΔV^{*}_{f} values for the IPT system are 49.3 ± 2.4 m^{-1} s^{-1} and 10.9 ± 1.7 cm^3 mol^{-1} in Me_2SO at 40 °C and $[NaClO_4] = 0.186$ *m* and 171 ± 3 m^{-1} s^{-1} and 5.0 ± 0.4 cm^3 mol^{-1} in DMF at 25 °C and $[NaClO_4] = 0.214$ *m*. The values of activation volume for the complexation (ΔV^{*}_{f}) and dissociation (ΔV^{*}_{d}) in the SCN system were refined by applying nonlinear least-squares fitting to eq 7, after confirmation of the pressure independence

$$k_0 = k_f^0 \exp(-\Delta V^{*}_{f}R^{-1}T^{-1}P)[\mathrm{Fe}^{3+}] + k_d^0 \exp(-\Delta V^{*}_{d}R^{-1}T^{-1}P) \qquad (7)$$

of ΔV^{*}_{f} and ΔV^{*}_{d},[4] where k_f^0 and k_d^0 refer to rate constants at zero pressure. The refined values for the formation and dissociation are $k_f^0 = 289 \pm 5$ m^{-1} s^{-1}, $\Delta V^{*}_{f} = 3.3 \pm 0.6$ cm^3 mol^{-1}, $k_d^0 = 1.00 \pm 0.05$ s^{-1}, and $\Delta V^{*}_{d} = -8.5 \pm 1.4$ cm^3 mol^{-1} in Me_2SO at 40 °C and $[NaClO_4] = 0.186$ *m*. The obtained values reproduce very nicely the experimental results (see Figure 3). The activation volumes obtained in this work are summarized in Table I along with related data.

Discussion

We have measured dilatometrically the reaction volumes (ΔV°) for the reaction of Fe^{3+} with the thiocyanate ion in Me_2SO and water.[12] The ΔV° value obtained in Me_2SO is 12.4 ± 0.6 cm^3 mol^{-1}, which agrees with 11.8 ± 2.0 cm^3 mol^{-1} estimated from the difference between the activation volumes ($\Delta V^{\circ} = \Delta V^{*}_{f} - \Delta V^{*}_{d}$). The ΔV° in water was determined to be 8.9 ± 0.2 cm^3 mol^{-1}. Thus, the value of ΔV^{*}_{d} is evaluated to be −15.0 ± 1.2 cm^3 mol^{-1} with knowledge of ΔV^{*}_{f} (Table I).

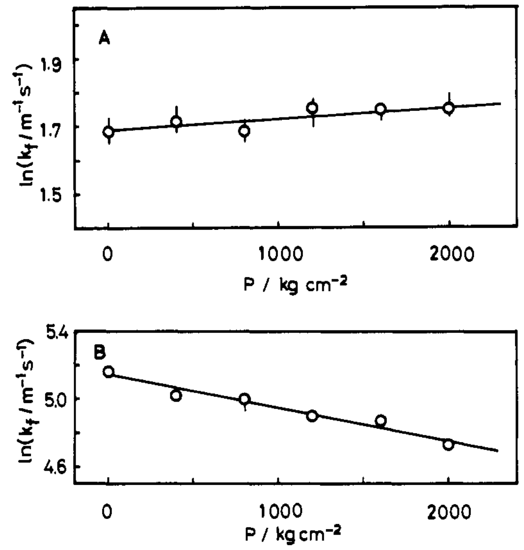

Figure 2. Pressure dependence of k_f for the Fe^{3+} complexation in DMF at 25 °C: (A) for the AHX system including 41 data points; (B) for the IPT system including 21 data points.

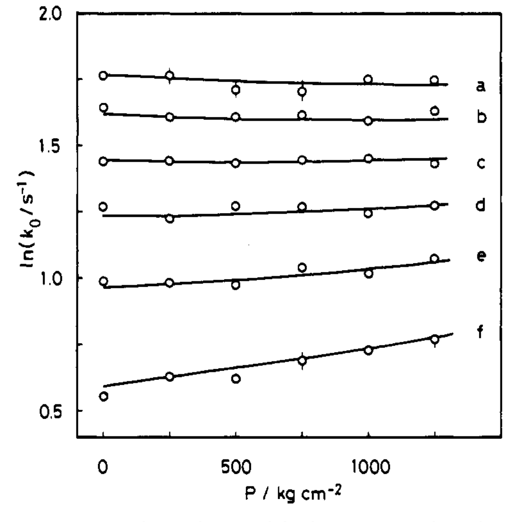

Figure 3. Pressure dependence of k_0 for the complexation of Fe^{3+} with SCN^- in Me_2SO at 40 °C including 72 data points: $[Fe(ClO_4)_3]/m = 1.68 \times 10^{-2}$ (a), 1.40×10^{-2} (b), 1.12×10^{-2} (c), 8.42×10^{-3} (d), 5.61×10^{-3} (e), 2.81×10^{-3} (f).

Reactions for the AHX and IPT systems are described by eq 8. Fe^{3+} forms first the outer-sphere complex with the

$$\mathrm{Fe}^{3+} + \mathrm{HL} \overset{K_{os}}{\rightleftharpoons} \mathrm{Fe}^{3+}\cdots\mathrm{HL} \xrightarrow{k_f^*} \mathrm{FeL}^{2} + \mathrm{H}^{+} \qquad (8)$$

bidentate ligand HL (Hahx or Hipt). This complex turns to the tetraaquamonoligandoiron(III) complex (FeL^{2+}) through an activated complex followed by fast deprotonation and ring closure.[13] K_{os} and k_f^* represent the formation constant of the

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[12] Sengoku, K.; Funahashi, S.; Tanaka, M., unpublished results.

outer-sphere complex and the first-order rate constant in the rate-determining step, respectively. Thus, the observed second-order rate constant k_f for complex formation is equal to $K_{os}k_f^*$. The observed activation volume $\Delta V^{\ddagger}_f$ for the formation is the sum of volume changes ($\Delta V^{\circ}_{os} + \Delta V^{*\ddagger}_f$). Since there is no formal charge on the entering ligand (HL), ΔV°_{os} would contribute negligibly to $\Delta V^{\ddagger}_f$. Furthermore, $\Delta V^{*\ddagger}_f$ is regarded as a composite value of $\Delta V^{*\ddagger}_{f,solv}$ and $\Delta V^{*\ddagger}_{f,intr}$, which are solvational and intrinsic volume changes in the activation process.[14] $\Delta V^{*\ddagger}_{f,solv}$ would be negligible when both entering and leaving ligands are uncharged. After all, the $\Delta V^{\ddagger}_f$ obtained for the AHX and IPT systems corresponds to $\Delta V^{*\ddagger}_{f,intr}$, which reflects the volume change by bond making or bond breaking in the activation process.

The SCN system is represented by eq 9. k_d is the first-order

$$Fe^{3+} + NCS^- \xrightleftharpoons{K_{os}} Fe^{3+}\cdots NCS^- \xrightleftharpoons[k_d]{k_f^*} Fe(NCS)^{2+} \quad (9)$$

rate constant for the dissociation of the $Fe(NCS)^{2+}$ complex. The observed second-order rate constant k_f is also written as $k_f = K_{os}k_f^*$. Therefore, the observed $\Delta V^{\ddagger}_f$ for formation is given by the sum of ΔV°_{os} and $\Delta V^{*\ddagger}_f$, of which the ΔV°_{os} value is significant for the SCN system because the outer-sphere complex formation will involve the substantial charge neutralization and resultant release of electrostriction. The approximate ΔV°_{os} values can be estimated by differentiation of the Fuoss equation with respect to pressure when the pressure dependence of solvent dielectric constant (ϵ) is known.[2,15] For example, in the case of the reaction between Fe^{3+} and SCN^- at ionic strength I = 0.2 M and 25 °C, ΔV°_{os} is evaluated to be 3.4 cm^3 mol^{-1} in H_2O (ϵ = 78.5 and $\partial\epsilon/\partial P$ = 3.62 × 10^{-3} kg^{-1} cm^2 at 1 kg cm^{-2} [16,17]) with a = 5 × 10^{-8} cm assumed for the closest approach distance and 8.9 cm^3 mol^{-1} in CH_3CN (ϵ = 36.0 and $\partial\epsilon/\partial P$ = 4.02 × 10^{-3} kg^{-1} cm^2 at 1 kg cm^{-2} [18]) with a = 7 × 10^{-8} cm. Unfortunately the pressure coefficient of the dielectric constant is not available for Me_2SO. However, since for the SCN system in Me_2SO the ΔV°_{os} value should be positive and $\Delta V^{*\ddagger}_{f,solv}$ possibly has a small positive value, the $\Delta V^{*\ddagger}_{f,intr}$ will be smaller than $\Delta V^{\ddagger}_f$ (3.3 cm^3 mol^{-1}).

On the basis of the $\Delta V^{*\ddagger}_{f,intr}$ values estimated above, we consider the reaction mechanisms for complex formation of the iron(III) ion. The activation volumes for complexation of the hexaaquairon(III) ion in aqueous solution are all negative.[1,2] On the basis of negative activation volume, an associative interchange (I_a) mechanism has been assigned. In contrast, as apparent from Table I, the activation volumes change in sign in different solvents. This mechanistic change would be explained in terms of relative bulkiness of coordinated solvent and entering molecules. It should be sterically difficult for the donor atom in a bulky entering ligand to approach to the central ferric ion hexacoordinated by a bulky solvent such as DMF and Me_2SO. Thus, in such a case a metal–solvent bond should be lengthened in the activation process in order to accommodate the entering ligand: a less associative mode of activation should be operative. The degree of the bond lengthening depends on steric bulkiness of both the entering ligand and the coordinated solvent.

The values of $\Delta V^{\ddagger}$ for the formation in all the systems gradually increase in the order H_2O < DMF < Me_2SO. For the AHX system $\Delta V^{\ddagger}$ is more negative than for the IPT system in all solvents. Judging from models of the hexakis(solvento)iron(III) ion, $Fe(Me_2SO)_6^{3+}$ is the most sterically crowded for the penetration of the entering ligand and the order of such a steric hindrance is Me_2SO > DMF > H_2O. It is also clear that IPT is larger and bulkier than AHX. Thus, more extensive bond lengthening should be required to accommodate bulkier IPT. Correspondingly, $\Delta V^{\ddagger}_f$ is larger for IPT than for AHX (Table I): $\Delta V^{\ddagger}$ values reflect the bulkiness of both the entering ligand and the coordinated solvent.

In organic solvents much bulkier than water, it may be difficult to pack an extra molecule of the entering ligand around a metal ion to generate the transition state for an associative process. The comparison of rates of ligand substitution (including solvent exchange) at Ni^{2+} and at Fe^{3+} lends some support to the idea of steric effects playing an important role. Since such a steric effect is not significant for the hexaaquairon(III) ion in aqueous solution, the complexation of this cation is associatively activated. However, in bulky solvents the mechanism of the reaction may change from an associative to a dissociative process, depending on the steric factors. On the other hand, since the activation mode of the nickel(II) ion complexation is dissociative in water and the mechanism is less dependent on the steric factor, its activation mode is dissociative even in bulky solvents. Consequently, all the substitution reactions at the nickel(II) ion in various solvents can be accommodated within the framework of a similar I_d mechanism.[4]

The dissociation of the $Fe(NCS)^{2+}$ complex in solvent (S) should be similar to the solvent exchange and the complex formation:

$$FeS_5(NCS)^{2+} + S^* \xrightleftharpoons{K_{os}} FeS_5(NCS)^{2+}\cdots S^* \xrightarrow{k_d^*} FeS_5S^{*3+} + NCS^- \quad (10)$$

In this case the measured k_d equals $k_d^*K_{os}[S]/(1 + K_{os}[S])$. Since $1 << K_{os}[S]$, under the present conditions we obtain $k_d = k_d^*$. Since solvational volume change ($\Delta V^{*\ddagger}_{d,solv}$) possibly has a small negative value, the intrinsic volume change ($\Delta V^{*\ddagger}_{d,intr}$) would be somewhat less negative than the observed $\Delta V^{\ddagger}_d$. Thus, the $\Delta V^{*\ddagger}_{d,intr}$ values in Me_2SO and water may be comparable to the corresponding $\Delta V^{\ddagger}_{ex}$ values (−3.1 and −5.4 cm^3 mol^{-1}).

Several authors have correlated kinetic parameters of ligand substitution reactions with solvent parameters (fluidity,[19a,c] enthalpy of evaporation,[19b,c,20a,c] donor number,[20b,d,21,22] solubility parameter,[20b,d] etc.). As is obvious from this paper, the mechanism may be different from solvent to solvent especially for reactions with an associative mode of activation in water. Therefore, care should be taken in correlating the rate and activation parameters with solvent parameters.

Registry No. Iron, 7439-89-6; acetohydroxamic acid, 546-88-3; thiocyanate, 302-04-5; 4-isopropyltropolone, 499-44-5; *N,N*-dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

Supplementary Material Available: A listing of rate constants for the complexation of the Fe(III) ion with acetohydroxamic acid, 4-isopropyltropolone, and thiocyanate in DMF (at 25 °C) and Me_2SO (at 40 °C) under high pressure (Table S1) (3 pages). Ordering information is given on any current masthead page.

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(13) The rate constant of deprotonation of HL can be calculated with the available pK_a and the estimated rate constant of the protonation of L (nearly diffusion controlled). The rate of deprotonation is indeed much faster than that of the complexation. In the aqueous solution we observe an isokinetic relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the Fe^{3+} complexation with various ligands including Hahx, Hipt, and some other monodentate ligands (see Table II in ref 2). Thus, it may be safely said that both the deprotonation and the ring closure are not the rate-determining step.

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