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Kinetic Studies of the Complex Formation of Iron(III) with 4-Isopropyltropolone by a High-Pressure Stopped-Flow Technique. Mechanistic Difference between the Hexaaquairon(III) Ion and the Pentaaquahydroxoiron(III) Ion in Their Complexation

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The formation rate of the 1:1 iron(III) complex with 4-isopropyltropolone (Hipt) has been studied spectrophotometrically in aqueous solution of low pH at various temperatures and pressures by a stopped-flow technique. The rate law is expressed as $d[\mathrm{Fe(ipt)}^{2+}]/dt = (k_1 + k_2K_{\mathrm{FeOH}}[\mathrm{H}^+]^{-1})(1 + K_{\mathrm{H}}[\mathrm{H}^+])^{-1}[\mathrm{Fe}^{3+}][\mathrm{Hipt}]$, with $k_1 = 21.7 \pm 1.1$ M^{-1} s^{-1} and $k_2 = (6.30 \pm 0.31) \times 10^3$ M^{-1} s^{-1} at 25 °C and $I = 1.00$ M at atmospheric pressure. The activation parameters for the reaction of $\mathrm{Fe(OH_2)_6}^{3+}$ (k_1 path) and the reaction of $\mathrm{Fe(OH_2)_5OH}^{2+}$ (k_2 path) are as follows: $\Delta H^{*}_1 = 59.5 \pm 3.0$ kJ mol^{-1}, $\Delta S^{*}_1 = -19.8 \pm 3.0$ J mol^{-1} K^{-1}, $\Delta V^{*}_1 = -8.7 \pm 0.8$ cm^3 mol^{-1}; $\Delta H^{*}_2 = 29.2 \pm 3.6$ kJ mol^{-1}, $\Delta S^{*}_2 = -72.3 \pm 5.0$ J mol^{-1} K^{-1}, $\Delta V^{*}_2 = 4.1 \pm 0.6$ cm^3 mol^{-1}. Associative- and dissociative-interchange mechanisms are most probably operative for the k_1 and k_2 paths, respectively.

Introduction

There are more than 50 papers on the complex formation of iron(III).[1,2] These studies lead to a common conclusion that the rate constant of the reaction of the pentaaquahydroxoferric ion ($\mathrm{Fe(OH_2)_5OH^{2+}}$ or $\mathrm{FeOH^{2+}}$) is about three orders of magnitude larger than that of the hexaaquaferric ion ($\mathrm{Fe(OH_2)_6}^{3+}$ or $\mathrm{Fe^{3+}}$). Because of such higher reactivity of $\mathrm{FeOH^{2+}}$ in comparison with $\mathrm{Fe^{3+}}$, there are many reports for $\mathrm{FeOH^{2+}}$, but there are not so many works on $\mathrm{Fe^{3+}}$. Although the complex formation of $\mathrm{FeOH^{2+}}$ appears to have been accepted to proceed through a dissociative process,[2] a paper that asserts its associative activation has been published recently.[3] The complex formation of $\mathrm{Fe^{3+}}$ has been claimed to proceed via an associative transition state on the basis of the values of activation volume obtained by using a high-pressure temperature-jump apparatus.[4] The recent NMR study by Grant and Jordan[5] has provided activation parameters for the exchange of solvent water at $\mathrm{Fe^{3+}}$ and at $\mathrm{FeOH^{2+}}$. These values should be useful as a measure to compare with activation parameters of the ligand substitution on these ions and to determine the mechanism. Despite this knowledge, the reaction mechanism of iron(III) complexation does not appear to have been proved decisively.

In this paper we present the mechanistic difference between $\mathrm{Fe^{3+}}$ and $\mathrm{FeOH^{2+}}$ in their complexation on the basis of the values of activation volume obtained by a high-pressure stopped-flow technique.[6,7] 4-Isopropyltropolone (Hipt or IPT), which was termed hinokitiol or β-tujaplicin, was used as a ligand. The ligand forms a stable 1:1 Fe(III) complex[8] with a high absorption coefficient of 2.1×10^3 M^{-1} cm^{-1} (M ≡ mol dm^{-3}) at 440 nm.

Isopropyltropolones are contained in *Chamaecyparis taiwanensis* Masamune et Suzuki and *Thuja plicata* D. Don.[9-12] Their antibacterial and antifungal activities have been demonstrated.[9-11] Since in recent years there have been endeavors to make clear the reaction mechanisms of heavy-metal ions in vivo,[13] the present work should contribute also to the biological field.

After this paper had been prepared for publication, an interesting paper by Swaddle and Merbach[14] appeared, which describes the kinetics of solvent water exchange on iron(III) under high pressure. Their high-pressure NMR study has provided data consistent with the dissociative activation for substitution on $\mathrm{FeOH^{2+}}$ and the associative activation for $\mathrm{Fe^{3+}}$.

Experimental Section

Reagents. Iron(III) Perchlorate. The reagent grade iron(III) chloride was dissolved in perchloric acid, and hydrochloric acid was expelled by evaporation. The absence of chloride ion was checked by silver nitrate. The iron(III) perchlorate was recrystallized twice from 60% perchloric acid solution. The stock solution of iron(III) ion contained 2.57×10^{-2} M Fe(III) ion and 0.844 M perchloric acid. Its concentration was determined both by an EDTA titration with Variamine Blue B base as an indicator[15] and by a replacement titration with the Cu-TAR-EDTA system.[16] The acidity of the stock solution was determined by means of the Gran plot.[17]

4-Isopropyltropolone. Crystalline 4-isopropyltropolone (Takasago Perfumery Co., Ltd., Tokyo, Japan) was recrystallized three times from ligroin. The crystal was dried in vacuo.

Solutions of sodium perchlorate and sodium hydroxide were prepared as described previously.[18] Perchloric acid of special purity (Wakojunyaku) was used without further purification.

Measurements. All measurements were carried out in a room thermostated to within ±0.5 °C. Temperature of the reaction solution was controlled to within ±0.1 °C by using a thermoelectric circulating bath. Ionic strength was maintained at 1.00 M with sodium perchlorate and perchloric acid. Solutions of Fe(III) and IPT were prepared at 25 °C in molar concentration scale. The molar concentrations were converted to the pressure-independent molal (mol kg^{-1} ≡ *m*) scale when necessary.

The protonation constant of IPT was determined spectrophotometrically at 360 nm. The absorbance was measured with a spectrophotometer (Model 1 PMQ II, Karl Zeiss). We used excess Fe(III) ion, with which IPT forms quantitatively the 1:1 Fe(III)-IPT complex. Reaction rates of complex formation at atmospheric pressure were followed as a function of time at 440 nm, a wavelength of maximum absorption of the 1:1 Fe(III)-IPT complex, by a stopped-flow spec-

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Table I. Rate Constants and Activation Parameters for Reactions of Fe(III) Ions with IPT

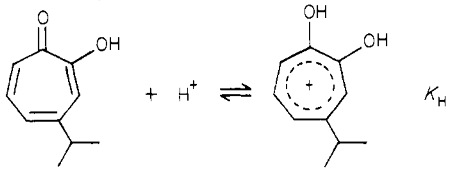
rate constant	k(25 °C) value	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
k_1/M^{-1} s^{-1}	21.7 ± 1.1	59.5 ± 3.0	−19.8 ± 3.0	−8.7 ± 0.8 ($\Delta V^{\ddagger}{}_1$)
k_2K_{FeOH}/s^{-1}	10.4 ± 0.5	71.9 ± 3.6	15.6 ± 5.0	5.7 ± 0.5 ($\Delta V^{\ddagger}{}_2 + \Delta V^{\circ}{}_{FeOH}$)
$k_2{}^a$/10^3 M^{-1} s^{-1}	6.30 ± 0.31	29.2 ± 3.6	−72.3 ± 5.0	4.1 ± 0.6 ($\Delta V^{\ddagger}{}_2$)
$k_4K_HK_{FeOH}$/M^{-1} s^{-1}	21.7 ± 1.1	59.5 ± 3.0	−19.8 ± 8.0	−8.7 ± 0.8 ($\Delta V^{\ddagger}{}_4 + \Delta V^{\circ}{}_H + \Delta V^{\circ}{}_{FeOH}$)
$k_4{}^a$/10^3 M^{-1} s^{-1}	7.74 ± 0.39	23.2 ± 3.0	−91.7 ± 8.0	−10.0 ± 1.2 ($\Delta V^{\ddagger}{}_4$)

[a] The following values were used for estimation of k_2 and k_4: $K_{FeOH} = 1.65 \times 10^{-3}$ M,[19] $\Delta V^{\circ}{}_{FeOH} = 1.6$ cm^3 mol^{-1},[21] $K_H = 1.70$ M^{-1}, $\Delta V^{\circ}{}_H = -0.3$ cm^3 mol^{-1}.

trophotometer (Type RA 1100, Union Giken Co., Osaka, Japan) or highly sensitive spectrophotometer (Type SM 401, Union Giken) with a sample-mixing device (Type MX 7, Union Giken). The high-pressure stopped-flow apparatus that we have constructed[6,7] was used for measurement of the rates of complex formation at high pressures.

Results

Protonation Constant of IPT. The protonation of Hipt is expressed as



(1)

Hipt H$_2$ipt$^+$

where H$_2$ipt$^+$ is a protonated species of IPT and K_H = [H$_2$ipt$^+$][Hipt]$^{-1}$[H$^+$]$^{-1}$. Visible absorption spectra of IPT solutions with various hydrogen ion concentrations ((1.35 × 10^{-2})–0.944 M) have distinct isosbestic points at 341 nm. The apparent molar absorption coefficient $\bar{\epsilon}$ of IPT at 360 nm is expressed as $\bar{\epsilon} = (\epsilon_2K_H[H^+] + \epsilon_1)(K_H[H^+] + 1)^{-1}$, where ϵ_1 and ϵ_2 are the molar absorption coefficients of Hipt and H$_2$ipt$^+$, respectively. The values of K_H/M^{-1} at I = 1.00 M were determined to be as follows: 1.78 ± 0.02 at 20 °C; 1.70 ± 0.02 at 25 °C; 1.64 ± 0.02 at 30 °C. The thermodynamic parameters were evaluated as $\Delta H^{\circ} = 6.1 \pm 0.2$ kJ mol^{-1} and $\Delta S^{\circ} = 16 \pm 2$ J mol^{-1} K^{-1}.

Rate of Complex Formation of Fe(III) with IPT. The reaction of Fe(III) with IPT was studied in the presence of Fe(III) (C_{Fe} = (1.03–7.04) × 10^{-3} M) in excess over IPT (C_{IPT} = (2.00 × 10^{-5})–(1.18 × 10^{-4}) M) at the hydrogen ion concentration 0.21–0.98 M. With the formation constant[8] taken into account, only the (4-isopropyltropolonato)iron(III) (Fe(ipt)$^{2+}$) ion is formed quantitatively under our experimental conditions. The formation rate of the Fe(ipt)$^{2+}$ complex is proportional to the total concentrations of the uncomplexed Fe(III) and IPT ([Fe(III)′] and [IPT′], respectively). Thus the rate is expressed by eq 2, where $k_{0(H)}$ is a conditional

$$d[Fe(ipt)^{2+}]/dt = k_{0(H)}[Fe(III)'][IPT'] \qquad (2)$$

second-order rate constant involving hydrogen ion concentration.

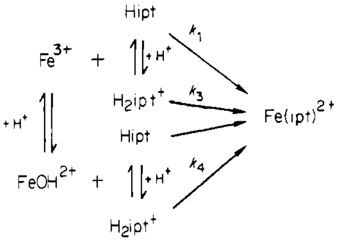
Under the present experimental conditions there are four possible paths as shown in Scheme I. Therefore, the rate of the overall complex formation is expressed by eq 3, where

$$\begin{aligned} d[Fe(ipt)^{2+}]/dt &= k_1[Fe^{3+}][Hipt] + k_2[FeOH^{2+}] \times \\ &[Hipt] + k_3[Fe^{3+}][H_2ipt^+] + k_4[FeOH^{2+}][H_2ipt^+] = \\ &[Fe(III)'][IPT'](k_1 + k_2K_{FeOH}[H^+]^{-1} + k_3K_H[H^+] + \\ &k_4K_HK_{FeOH})(1 + K_H[H^+])^{-1}(1 + K_{FeOH}[H^+]^{-1})^{-1} \qquad (3) \end{aligned}$$

K_{FeOH} = [FeOH^{2+}][H$^+$][Fe^{3+}]$^{-1}$, [Fe(III)′] = [Fe^{3+}](1 + K_{FeOH}[H$^+$]$^{-1}$), and [IPT′] = [Hipt](1 + K_H[H$^+$]). Comparing eq 2 with eq 3, we obtain eq 4, because K_{FeOH}[H$^+$]$^{-1}$ is negligible against unity at high acidity.

$$\begin{aligned} k_{0(H)}(1 + K_H[H^+]) &= \\ k_1 + k_2K_{FeOH}[H^+]^{-1} &+ k_3K_H[H^+] + k_4K_HK_{FeOH} \qquad (4) \end{aligned}$$

Scheme I



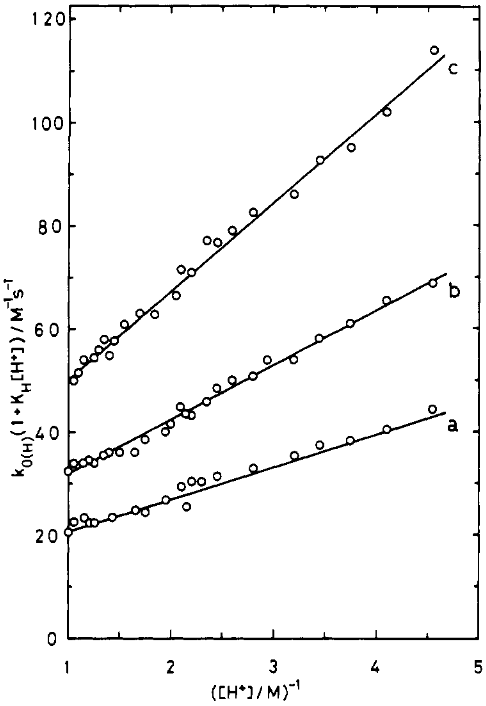


Figure 1. Hydrogen ion dependence of $k_{0(H)}$ at atmospheric pressure and I = 1.00 M: (a) 20 °C; (b) 25 °C; (c) 30 °C.

Values of $k_{0(H)}$(1 + K_H[H$^+$]) obtained at various hydrogen ion concentrations are plotted as a function of [H$^+$]$^{-1}$ in Figure 1. The plots clearly indicate that the k_3 path is negligible. At this stage, however, we can not decide which path is responsible for the reaction, the k_1 path or the k_4 path. In order to postulate which of the two paths is really relevant, we now evaluate values of the rate constants and corresponding activation parameters. Here we used the values of hydrolysis constants of Fe^{3+} reported by Milburn and Vosburgh.[19] The values obtained are given in Table I.

Formation Rate of Fe(III) Complexes at High Pressure. The conditional second-order rate constants $k_{0(H)}$ were measured at various pressures by a high-pressure stopped-flow technique.

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(19) K_{FeOH} = 1.65 × 10^{-3} M (25 °C); the values at 20 and 30 °C were estimated by using the values of ΔH° (42.7 kJ mol^{-1}) and ΔS° (89.9 J mol^{-1} K^{-1}): Milburn, R. M.; Vosburgh, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 1352.

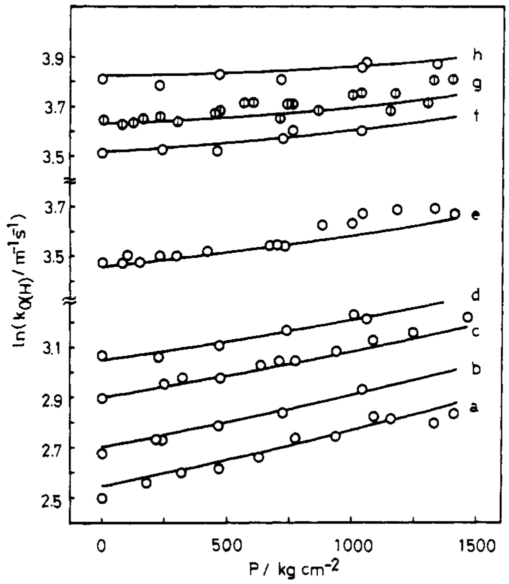

Figure 2. Pressure dependence of $k_{0(H)}$ at different hydrogen ion concentrations (25 °C, I = 1.05 *m*): (a) 0.954 *m*; (b) 0.793 *m*; (c) 0.631 *m*; (d) 0.530 *m*; (e) 0.411 *m*; (f) 0.302 *m*; (g) 0.264 *m*; (h) 0.211 m. Each point is the average of three or more determinations. The solid curves were calculated by using the rate constants and activation volumes obtained.

Plots of the values of ln $k_{0(H)}$ at a given [H$^+$] against pressure P are shown in Figure 2. With the assumption that activation volume $\Delta V^{\ddagger}$ and molar volume change ΔV° are independent of pressure, $k_{0(H)}$ is expressed as eq 5, where k^0 and K^0 represent rate and equilibrium constants, respectively, at zero pressure, and $\Delta V^{\circ}{}_{H}$ and $\Delta V^{\circ}{}_{FeOH}$ refer to volume changes for the protonation of IPT and for the hydrolysis reaction of Fe^{3+}, respectively. In the case where the k_4 path is much more important than the k_1 path, $k_1{}^0$ and $\Delta V^{\ddagger}{}_1$ in eq 5 should be replaced by $k_4{}^0K_H{}^0K_{FeOH}{}^0$ and $\Delta V^{\ddagger}{}_4 + \Delta V^{\circ}{}_H + \Delta V^{\circ}{}_{FeOH}$, respectively. Contribution of the k_4 path will be ruled out (see Discussion). The values of rate constant, activation volume, and molar volume change were obtained by a nonlinear least-squares fit to all the data (454 points) simultaneously.[20] Values of $k_1{}^0$ and $k_2{}^0$ agree with corresponding values obtained at atmospheric pressure within the experimental uncertainties. The $\Delta V^{\circ}{}_H$ value was determined to be −0.3 ± 0.2 cm^3 mol^{-1}. The values obtained are summarized in Table I. The value of $\Delta V^{\circ}{}_{FeOH}$, 1.6 cm^3 mol^{-1}, was used to estimate k_2 and k_4 values.[21] With knowledge of the value of $\Delta V^{\circ}{}_H$, the plot according to eq 4 is possible. An example of such plots is demonstrated in Figure 3. As shown in Figure 4, the plots of k_1 and k_2K_{FeOH} vs. pressure gave straight lines within the experimental error. Thus $\Delta V^{\ddagger}{}_1$ and $\Delta V^{\ddagger}{}_2$ are in fact independent of pressure.

$$k_{0(H)}\{1 + K_H{}^0[H^+]\exp(-\Delta V^{\circ}{}_H PR^{-1}T^{-1})\} = k_1{}^0\exp(-\Delta V^{\ddagger}{}_1 PR^{-1}T^{-1}) + k_2{}^0K_{FeOH}{}^0 \exp\{-(\Delta V^{\ddagger}{}_2 + \Delta V^{\circ}{}_{FeOH})PR^{-1}T^{-1}\} \quad (5)$$

Discussion

According to the formation now generally accepted for complex formation reactions of metal ions, the reactions for k_1 and k_2 paths are given by eq 6 and 7, where K_{os} is the formation constant for the outer-sphere complex and k^* is the first-order rate constant for the reaction from the outer-sphere complex to the inner-sphere complex as the rate-determining step (step II). Step III is the process of chelate ring closure, which is usually much faster than step II. The observed second-order rate constant k_f is given by $k_f = K_{os}k^*$. Therefore, the overall activation volume is given by $\Delta V^{\ddagger} = \Delta V^{\circ}{}_{os} + \Delta V^{*\ddagger}$, where $\Delta V^{\circ}{}_{os}$ and $\Delta V^{*\ddagger}$ are the reaction volume for K_{os} and the activation volume for k^*, respectively.

$$Fe(OH_2)_6{}^{3+} + Hipt \underset{I}{\overset{K_{os}(1)}{\rightleftharpoons}} Fe(OH_2)_6{}^{3+}\cdots Hipt \xrightarrow[II]{k^*{}_1} Fe(OH_2)_5(Hipt)^{3+} + H_2O \xrightarrow[III]{fast} Fe(OH_2)_4(ipt)^{2+} + 2H_2O + H^+ \quad (6)$$

$$Fe(OH_2)_5(OH)^{2+} + Hipt \underset{I}{\overset{K_{os}(2)}{\rightleftharpoons}} Fe(OH_2)_5(OH)^{2+}\cdots Hipt \xrightarrow[II]{k^*{}_2} Fe(OH_2)_4(OH)(Hipt)^{2+} + H_2O \xrightarrow[III]{fast} Fe(OH_2)_4(ipt)^{2+} + 2H_2O \quad (7)$$

The volume of activation $\Delta V^{*\ddagger}$ is generally expressed as $\Delta V^{*\ddagger} = \Delta V^{\ddagger}{}_{intr} + \Delta V^{\ddagger}{}_{solv}$. $\Delta V^{\ddagger}{}_{intr}$ is the change in partial molar volume caused by bond making or bond breaking in the activation process, and $\Delta V^{\ddagger}{}_{solv}$ is the change in volume with variation of solvation. Since there is substantially no change in the electric charge density in the activation process from the outer-sphere complex to the inner-sphere complex, we may consider $\Delta V^{\ddagger}{}_{solv} \simeq 0$, i.e., $\Delta V^{*\ddagger} \simeq \Delta V^{\ddagger}{}_{intr}$. Since Hipt has no formal charge, if any, its dipole may be little and $\Delta V^{\circ}{}_{os}(1)$ and $\Delta V^{\circ}{}_{os}(2)$ should be substantially zero.[22] Consequently, the total volume of activation should correspond to $\Delta V^{\ddagger}{}_{intr}$.

The rate constant k_2 is about two orders of magnitude larger than k_1. The difference of rate constants between Fe^{3+} and FeOH^{2+} would be considered to reflect their reactivity, since the ligand is the same neutral Hipt in both cases. The different sign of values of activation volume strongly indicates that their mechanisms differ from each other distinctly. When one water molecule coordinated in the inner sphere of FeOH^{2+} dissociates to the outer sphere, the partial molar volume increases,[23] while, when the ligand (or donor atom) enters into the inner sphere

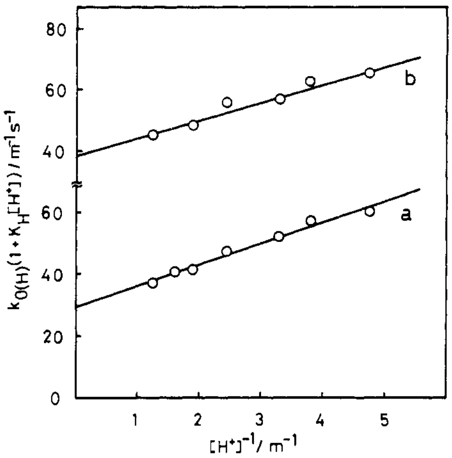

Figure 3. Hydrogen ion dependence of $k_{0(H)}$ at constant pressure: (a) 230 kg cm^{-2}; (b) 1040 kg cm^{-2}.

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[20] Nakagawa, T.; Oyanagi, Y. Program Library SALS (Statistical Analysis with Least-Squares Fitting), Nagoya University Computation Center, Nagoya, Japan, 1981.

[21] $\Delta V^{\circ}{}_{FeOH}$ values: ref 4a, 1.6 ± 0.1 cm^3 mol^{-1} at 24.2 °C and I = 1.5 M; ref 4b, 3 ± 0.5 cm^3 mol^{-1} at 25 °C and I = 0.2 *m*; ref 4c, −1 cm^3 mol^{-1}.

[22] Hemmes, P. *J. Phys. Chem.* **1972**, *76*, 895.

[23] Swaddle has pointed out that the transfer of water from the first coordination sphere of Cr^{3+} to bulk water at 298 K causes a volume change of about 9.0 cm^3 mol^{-1}: Swaddle, T. W. *Inorg. Chem.* **1980**, *19*, 3203.

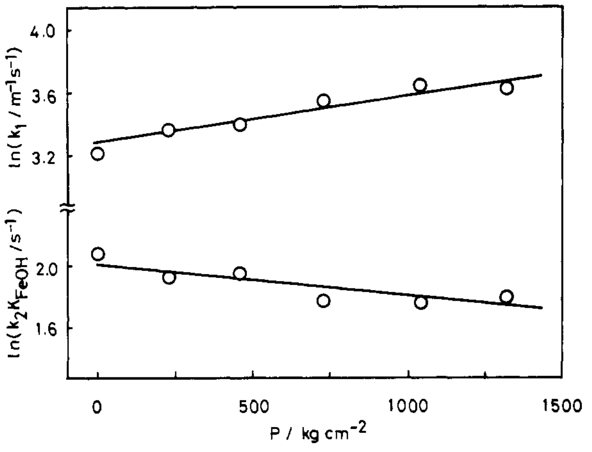

Figure 4. Pressure dependence of k_1 and k_2K_{FeOH}.

of Fe^{3+}, the volume at the transition state decreases. The value $\Delta V^{\ddagger}_1$ = −8.7 cm^3 mol^{-1} reflects that a decrease in volume brought about by the movement of the coordination atom of Hipt into the inner sphere of Fe^{3+} is partially canceled by an increase in volume invoked by extension of the bond of a water molecule occupied in the inner sphere. The value $\Delta V^{\ddagger}_2$ = 4.1 cm^3 mol^{-1} indicates that a volume increase caused by lengthening of the bond of a water molecule coordinated in the inner sphere of $FeOH^{2+}$ is partially compensated by a volume decrease due to the entering of the donor atom of Hipt into the inner sphere. Consequently, associative- and dissociative-interchange mechanisms[24] are most probably operative for the k_1 and k_2 paths, respectively.

Ambiguity exists in interpreting the experimental kinetic data owing to the existence of the two kinetically indistinguishable paths, k_1 and k_4. The rate constant k_4 and its activation parameters can be easily estimated with knowledge of the protonation constant of Hipt and the first hydrolysis constant of Fe^{3+} (see Table I).

Previously two criteria have been proposed for distinction between reaction paths with proton ambiguity.[25,26] For the Fe^{3+} ion in the formation of a series of iron(III) complexes, rate constants all lie in the range 2–10^2 M^{-1} s^{-1}. This range of rate constants is substantially lower than that for the $FeOH^{2+}$ ion, for which rate constants are in the range (5 × 10^3)–(3 × 10^5) M^{-1} s^{-1}. The similarity in the rate constants allows us to decide which is the predominant path leading to the complex formation (criterion 1). An additional criterion takes into account available values of the activation parameters for the dissociation (aquation) of the iron(III) complexes[25,26] (criterion 2). In the present system it is impossible to distinguish between the k_1 path and the k_4 path on the basis of criterion 1, since values of rate constants are reasonable for both paths (see Table I). Since we have no data of aquation of the Fe(III)–IPT complex, criterion 2 is now not applicable.

Now, let us consider that the k_4 path differs from the k_2 path with respect to protonation of the ligand. The value of k_4 is comparable to that of k_2, for which the mechanism has been proven to be dissociative (vide supra). It is reasonable to expect that k_4 for the reaction of $FeOH^{2+}$ with a positive ligand H_2ipt^+ should be smaller than k_2 for the reaction with a neutral ligands Hipt. However, in fact, the former value is a little larger than the latter value. Therefore, we exclude the k_4 path.

In Table II, available values of activation volume for the iron(III) complex formation are summarized together with ours. The activation volume for Fe^{3+} is negative, and the activation volume for $FeOH^{2+}$ is positive. Since the activation volume $\Delta V^{\ddagger}_4$ for the k_4 path is calculated to be negative, the k_4 path can be ruled out and the k_1 path should be relevant.

Table II. Activation Volumes[a] for Complexation of Iron(III) Ions

	$\Delta V^{\ddagger}$/cm^3 mol^{-1}		
ligand	Fe^{3+}	$FeOH^{2+}$	ref
Cl^-	−4.5 ± 1.1	7.8 ± 1.0	4c
NCS^-	−12	8.8	28
NCS^-	~0	7.1 ± 1.0	4b
Br^-	−8 ± 4		4a
H_2O	−5.4 ± 0.4	7.8 ± 0.2	14
Hipt	−8.7 ± 0.8	4.1 ± 0.6	this work

[a] Disregarding any initial ion pairing.

The results and consideration described above provide further support for the view that the sign of activation volumes may be taken as a useful tool for choosing between kinetically indistinguishable paths 1 and 4. Thus we may add the following as the third criterion: the higher the pressure, the faster Fe^{3+} undergoes complexation but the slower $FeOH^{2+}$ reacts (criterion 3).

Most recently, Swaddle and Merbach[14] have reported that the volumes of activation for water exchange on Fe^{3+} and $FeOH^{2+}$ are −5.4 and 7.8 cm^3 mol^{-1}, respectively, and concluded that water exchange on Fe^{3+} is associatively activated but that on $FeOH^{2+}$ is dissociatively activated. Their findings are similar to the corresponding volumes of activation observed for complexation of Fe(III) ions in this work.

The primary criterion for a "normal" dissociative mechanism is that the rate constant k^* should be similar to the rate constant for solvent exchange, k_{ex}. Actually, the two quantities should have the relation

$$k_f = K_{os}k^* = fK_{os}k_{ex} \qquad (8)$$

where f is a statistical factor.[27] This simple relation will be valid only if the solvent exchange of the dissociative mode of activation is not influenced by the proximity of the ligand in the outer sphere. Let us compare formally the present results with the data[29] of water exchange, according to eq 8. As K_{os} is expected to be 0.3 M^{-1} at 25 °C and I = 1.0 M for both the Fe^{3+} + Hipt and the $FeOH^{2+}$ + Hipt reactions, rate constants for water exchange are about 10 times larger than the corresponding values for complexation of Hipt, k^*_1 and k^*_2. This is thought to result from the nondissociative mechanism, which is compatible with the previous conclusion. The large decrease in activation entropy is reflected in the decrease in rate for complexation. It should be noted that in both cases, for Fe^{3+} of the I_a mechanism and for $FeOH^{2+}$ of the I_d mechanism, the values of activation enthalpy for complexation are lower than those for water exchange. It has been stated previously that the less dissociative the reaction mechanism, the lower the activation enthalpy.[30] It may thus be said that the bond making is a little more important in the complexation of Fe^{3+} and $FeOH^{2+}$ than in the water exchange at these ions. In fact, the volume of activation is only a little but definitely smaller in the complexation of Fe^{3+} and $FeOH^{2+}$ than in the water exchange at these ions. Since the strength of the metal–water bond is weakened by the entering of a

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ligand into the inner sphere in the interchange mechanism, both enthalpy and entropy of activation are lowered.

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Halometal Derivatives of $W_{12}PO_{40}^{3-}$ and Related ^{183}W NMR Studies

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$(Bu_4N)_4ClTiW_{11}PO_{39}$, $(Bu_4N)_3(H)ClTiW_{11}PO_{39}$, $(Bu_4N)_4ClSnW_{11}PO_{39}$, and $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$ have been prepared. The first was converted to $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$ and to salts of $TiW_{11}PO_{40}^{5-}$. ^{183}W NMR spectra were obtained for $ClTiW_{11}PO_{39}^{4-}$, $CpFe(CO)_2SnW_{11}PO_{39}^{5-}$, and $TiW_{11}PO_{40}^{5-}$, and a detailed assignment of the resonances was made for $TiW_{11}PO_{40}^{5-}$ on the basis of spin–spin couplings.

Introduction

Derivatives of Keggin-structure heteropolytungstates that have aquo, oxo, hydroxo, organic, or organometallic ligands on a peripheral heteroatom have been reported.[1–4] This paper adds halogen and alkoxyl to the list by describing derivatives of $W_{12}PO_{40}^{3-}$ that have chlorine bonded to a peripheral titanium, tin, or aluminum heteroatom and conversion of the chlorotitanium derivative to a methoxytitanium analogue. Related tungsten NMR studies are also presented, including unambiguous assignments of the tungsten resonances in the spectrum of $TiW_{11}PO_{40}^{5-}$, a hydrolysis product of $ClTiW_{11}PO_{39}^{4-}$. These assignments differ from those that would have been made on the basis of an existing scheme[6a] for assigning tungsten resonances in derivatives of $W_{12}PO_{40}^{3-}$.

Preparation and Properties

Treatment of $(Bu_4N)_4H_3W_{11}PO_{39}$[2] with titanium tetrachloride, aluminum chloride, or stannic chloride gives $(Bu_4N)_4ClTiW_{11}PO_{39}$, $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$, and $(Bu_4N)_4ClSnW_{11}PO_{39}$. While the first two preparations proceed satisfactorily in dichloroethane, the use of anhydrous media in the preparation of $(Bu_4N)_4ClSnW_{11}PO_{39}$ gives erratic results. Unidentified mixtures containing excess tin and chlorine are frequently obtained. These problems are avoided by the use of slightly moist acetonitrile as the solvent for this reaction; good yields of $(Bu_4N)_4ClSnW_{11}PO_{39}$ are then obtained reproducibly.

Charge considerations suggest that basicity should increase in the order $W_{12}PO_{40}^{3-} < ClTiW_{11}PO_{39}^{4-} < ClAlW_{11}PO_{39}^{5-}$. Accordingly, we observed no reaction of hydrogen chloride with $W_{12}PO_{40}^{3-}$ in dichloroethane, reversible protonation of $ClTiW_{11}PO_{39}^{4-}$ under the same conditions, and have isolated $ClAlW_{11}PO_{39}^{5-}$ *only* as the protonated salt $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$.

$(Bu_4N)_4ClTiW_{11}PO_{39}$ reacts smoothly with sodium methoxide in methanol/acetonitrile to form $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$ and with tetrabutylammonium hydroxide in acetonitrile to give the previously reported[2] $TiW_{11}PO_{40}^{5-}$ anion. The latter anion was also prepared from $TiCl_4$ and $W_{11}PO_{39}^{7-}$ in buffered aqueous solution.

The infrared spectra of the new salts described above all closely resemble the spectrum of $(Bu_4N)_3W_{12}PO_{40}$ in the 700–1000-cm^{-1} region, except for slight changes in band positions. The asymmetric phosphate stretching region is of more interest. It has been noted[3a,5] that the triply degenerate phosphate stretch in the spectrum of $W_{12}PO_{40}^{3-}$ is frequently split into two bands because of loss of tetrahedral symmetry when a WO^{4+} group is replaced by a hetero group. The degree of splitting varies with the nature of the hetero group and the strength of the bond between it and its associated phosphate oxygen. Thus, $CpTiW_{11}PO_{39}^{4-}$ displays two bands in this region (1088, 1060 cm^{-1}), while $C_6H_5SnW_{11}PO_{39}^{4-}$ has only one.[3a,b] For the unprotonated halogenated derivatives and $CH_3OTiW_{11}PO_{39}^{4-}$, the situation is reversed. The titanium species exhibit only one phosphate stretch (1075 cm^{-1}) while $ClSnW_{11}PO_{39}^{4-}$ displays two (1055, 1080 cm^{-1}). The protonated anions $(H)ClTiW_{11}PO_{39}^{3-}$ and $(H)ClAlW_{11}PO_{39}^{4-}$ have a relatively broad band in this region with unresolved shoulders.

^{183}W NMR Spectra

The ^{183}W NMR spectrum of $(Bu_4N)_5TiW_{11}PO_{40}$ in CH_3CN/CD_3CN at 30 °C (Figure 1) provides support for the monosubstituted C_s structure because of the observed six resonances, five of relative intensity 2 and one of relative intensity 1. Peaks are labeled alphabetically in sequence from low to high field for use in later discussion, and it is seen they are in a 2:2:1:2:2:2 order. In contrast, the ^{183}W NMR spectrum of $CpTiW_{11}PO_{40}^{4-}$ has been shown by Gansow, Ho, and Klemperer[6a] to have the multiplets in a 2:1:2:2:2:2 order. Assignments were made for these resonances by using a charge distribution scheme which would require that the spectra of *all* $RMW_{11}PO_{39}^{n-}$ species, wherein RM has a charge less than 4, should have at least four resonances of intensity 2 upfield of the resonance of intensity 1. Since we observe only three

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