The aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH)^{3-}$ is 2.3×10^4 times faster than that of the corresponding *cis*-$Cr(C_2O_4)_2(N_3)(H_2O)^{2-}$ at 25 °C.[4] This is a result of an increase in ΔS^* from −18.1 to +24.6 cal/(deg mol) and in ΔH^* from +18.4 to +26.2 kcal/mol. These activation parameters imply that the mechanism changed from associative activation to dissociative activation for the aquation reaction.

This contrasts the results for the aquation of *trans*-$Cr(C_2O_4)_2(CH_3COO)H_2O^{2-}$ and for that of the corresponding hydroxy complex.[13] In this system, there is a 60-fold increase in the rate constant. The value of ΔH^* changes from +16.3 to +8.4 kcal/mol and that of ΔS^* from −18.8 to −38.8 cal/(deg mol). This difference in the direction of change of the values of the activation parameters is very hard to rationalize. It might be that the CH_3COO^- ligand is involved in extensive hydrogen bonding in the activated complex.

The labilization of ligation of $Cr(H_2O)_5(OH)^{2+}$ compared to that of $Cr(H_2O)_6^{3+}$ is documented.[5,6] It was concluded that the ligation reactions of $Cr(H_2O)_5(OH)^{2+}$ were more dissociative than those of $Cr(H_2O)_6^{3+}$ and that the coordinated hydroxide stabilized the transition state.

In the aquation reaction of $Cr(H_2O)_5X^{n+}$, where X is Cl^-,[21] Br^-,[22] I^-,[21] N_3^-,[23] NO_3^-,[24] SO_4^{2-},[25] and α-hydroxyalkyl,[26] there is a term in the rate law that is inverse first order in [H^+] and that becomes predominant at higher pH values. Presumably, this term is due to the reaction of $Cr(H_2O)_4(OH)X^+$. However, the rate law is incompletely defined, and hence, no comparisons can be made.

The ligation of $CrTPPS(OH)H_2O^{4-}$ by NCS^-, pyridine, and imidazole is 6100, 350, and 21 times faster than that of $CrTPPS(H_2O)_2^{3-}$ at 25 °C, respectively.[1,27,28] However, the lability of the hydroxy complex compared to that of the aquo complex is not reflected in a monotonic change of the activation parameters. The change in the value of ΔH^* from the aquo to the hydroxy complex, $\Delta(\Delta H^*)$, is −0.1, −13.0, and −4.0 kcal/mol, respectively. The change in the values of $\Delta(\Delta S^*)$ is +16.9, −25.8, and −5.7 cal/(deg mol), respectively. In the ligation reaction of $CrTMpyP(H_2O)_2^{5+}$ by NCS^- this increase is 5880 times.[5,28] However, the reasons for this lability in these two complexes are totally different. In the $CrTPPS(H_2O)_2^{3-}$ system the lability is due to a constant ΔH^* (+16.7 ± 0.1 kcal/mol) and a substantial positive increase in ΔS^* (from −12.8 to +4.1 cal/(deg mol)) whereas in the $CrTMpyP(H_2O)_2^{5+}$ system ΔH^* decreases from +19.8 to +14.6 kcal/mol and ΔS^* decreases from −5.5 to −7.2 cal/(deg mol). These changes are difficult to explain.

A viable explanation of these observations awaits additional work.

Registry No. *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, 18954-99-9; *trans*-$Cr(C_2O_4)_2(OH)(H_2O)^{2-}$, 36444-11-8; *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$, 36444-10-7.

---

(21) Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1965**, *4*, 532.
(22) Guthrie, F. A.; King, E. L. *Inorg. Chem.* **1964**, *3*, 916.
(23) Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1964**, *3*, 234.
(24) Swaddle, T. W. *J. Am. Chem. Soc.* **1967**, *89*, 4338. Ardon, M.; Sutin, N. *Inorg. Chem.* **1967**, *6*, 2268.
(25) Finholt, J. E.; Deming, S. N. *Inorg. Chem.* **1967**, *6*, 1533.
(26) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1984**, *23*, 84.
(27) Ashley, K. R.; Trent, I.; Kuo, J., to be submitted for publication.
(28) $TPPS^{6-}$ = *meso*-tetrakis(*p*-sulfonatophenyl)porphyrinate. $TMpyP^{2+}$ = *meso*-tetrakis(*N*-methylpyridium-4-yl)porphyrin.

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan, and Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Tokyo 152, Japan

Rate and Mechanism of Ligand Exchange of Tris(acetylacetonato)scandium(III) in Acetonitrile

Yoshihiro Hatakeyama,[1a,b] Hiroaki Kido,*[1a] Masayuki Harada,[1c] Hiroshi Tomiyasu,[1c]
and Hiroshi Fukutomi[1c,d]

Received September 11, 1987

Tris(acetylaceotnato)scandium(III) undergoes ligand exchange with the enolate form of acetylacetone in CD_3CN at 30–74 °C. The observed first-order rate constant, obtained by the ^1H NMR method, is expressed by $k_0 = k_1'[\text{enol}] + k_2'$ at [complex] $\simeq$ 0.05 M, [Hacac] = 0.19 − 0.58 M, and [H_2O] = 0.026–0.26 M; $k_1' = 52 \pm 3$ M^{-1} s^{-1} and $k_2' = 1.5 \pm 0.9$ s^{-1} at 56 °C. No water catalysis was observed. The k_2' term is minor in the concentration region. The ΔH^* and ΔS^* values for k_1' are 36 ± 5 kJ mol^{-1} and −105 ± 16 J K^{-1} mol^{-1}, respectively. The deuterium isotope effect $k_1'(H)/k_1'(D)$ was significant (ca. 5). The I_a mechanism is assigned to the rate-determining formation of an intermediate containing a one-ended $acac^-$ and a unidentate Hacac in the enol form.

Introduction

Very little information is available for ligand substitution of tervalent scandium complexes. Only the rate of anation of murexide to the "aqua" complex in aqueous solution (pH 4) was reported by Geier (4.8×10^7 M^{-1} s^{-1} at 12 °C).[2] However, there is some uncertainty in the hydration number of the tervalent ion, which is readily hydrolyzed and dimerized.[3] There have been no kinetic data for verified $[Sc(H_2O)_6]^{3+}$. In trimethyl phosphate (TMP), there is the ion $[Sc(TMP)_6]^{3+}$,[4] for which a valuable result on the rate of the ligand exchange was obtained.[4,5a,b] The A or I_a mechanism was proposed from ΔH^*, ΔS^*, and ΔV^* values.[5b] However, it is uncertain whether the mechanism and the lability are general for $Sc^{III}O_6$-type complexes, since the ligand is rather bulky and the related information on $[M^{III}(TMP)_6]^{3+}$ is restricted to Al^{III}, Ga^{III}, and In^{III}.[5c] It would be essential for an understanding of the kinetic nature of Sc^{III} to compare Sc^{III} with various M^{III}, including transition-metal ions, for a single complex.

---

(1) (a) Tohoku University. (b) Present address: Nippon Petrochemical Co., Ltd., Kawasaki, Japan 210. (c) Tokyo Institute of Technology. (d) Present address: Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan.
(2) Geier, G. *Ber. Bunsen.-Ges. Phys. Chem.* **1965**, *69*, 617–625.
(3) (a) Biedermann, G.; Kilpatrick, M.; Pokras, L.; Sillen, L. G. *Acta Chem. Scand.* **1956**, *10*, 1327–1339. (b) Cole, D. L.; Rich, L. D.; Owen, J. D.; Eyring, E. M. *Inorg. Chem.* **1969**, *8*, 682–685.
(4) Pisaniello, D. L.; Lincoln, S. F.; Williams, E. H. *J. Chem. Soc., Chem. Commun.* **1978**, 1047–1048.
(5) (a) Ammann, C.; Ph.D. Thesis, EPF-Lausanne, 1981. Helm, L.; Ammann, C.; Merbach, A. E., to be submitted for publication (cf. 5b). (b) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479–1493. (c) Ammann, C.; Merbach, A. E. *Inorg. Chim. Acta* **1980**, X98 (Abstracts of Vth International Symposium on Solute-Solute-Solvent Interactions).

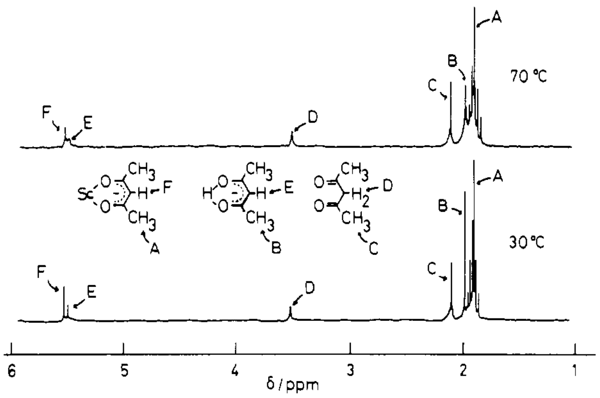

Figure 1. ^1H NMR spectra of a solution containing $[Sc(acac)_3]$ (0.017 M) and Hacac (0.054 M) in CD_3CN at 30 and 70 °C. Peaks without assignment are attributed to the solvent.

Tris(acetylacetonato)scandium, $Sc(acac)_3$, is known to have the $Sc^{III}O_6$ pseudooctahedral core in the solid state.[6] A group of the present authors has studied the ligand exchange of $[M^{III}(acac)_3]$ ($M^{III} = V^{III}, Cr^{III}, Mn^{III}, Fe^{III}, Ru^{III}, Co^{III}, Rh^{III}, Al^{III}$, and Ga^{III}) in organic solvents by the ^{14}C-labeling method.[7a-k] The apparently complicated reaction between bidentates consists of a rather simple substitution process, and the mechanism is identical with that of the substitution for the aqua ligand in $[M^{III}L_5(H_2O)]^{3+}$ ($L = H_2O$ or NH_3) for each M^{III}. A linear free energy relationship (LFER) was found between the first-order rate constants for the acetylacetonato and the aqua complexes.[7l] In other words, the data for $[M^{III}(acac)_3]$ could afford extrapolations for the unknown substitution behavior of $[M^{III}(H_2O)_6]^{3+}$. Another group of the authors has investigated the fast exchange of $[Th^{IV}(acac)_4]$, $[U^{IV}(acac)_4]$, and $[U^{VI}O_2(acac)_2(DMSO)]$ with Hacac in various organic solvents by NMR methods.[8] In this paper, we have studied the title reaction by ^1H NMR for a general understanding of the substitution process of $Sc^{III}O_6$ complexes.

Experimental Section

Materials. $Sc(acac)_3$ was synthesized from Sc_2O_3 by a method similar to that of Stites for $La(acac)_3$.[9] The solution of scandium chloride (0.004 mol in 10 mL of water) was obtained from Sc_2O_3 (0.3 g) and concentrated hydrochloric acid (6 mL) and mixed with the solution containing 1 mL of distilled acetylacetone and 2 mL of concentrated aqueous ammonia (10 mL, pH 7, adjusted with diluted hydrochloric acid). A white precipitate was obtained on slow addition of aqueous ammonia (0.1 M, ca. 50 mL). Colorless crystals (1.2 g) were obtained by recrystallization from a mixture of benzene and acetylacetone (10:1 v/v). Anal. Calcd. for $C_{15}H_{21}O_6Sc$: C, 52.6; H, 6.2. Found: C, 52.5; H, 6.4.

Acetylacetone was dried over anhydrous calcium sulfate and distilled twice. $[3\text{-}^2H_2]$Acetylacetone was prepared by the reported procedure[7e] and purified by distillation; the deuterium content was determined by ^1H NMR. $[^2H_3]$Acetonitrile was distilled in the presence of phosphorous pentoxide.

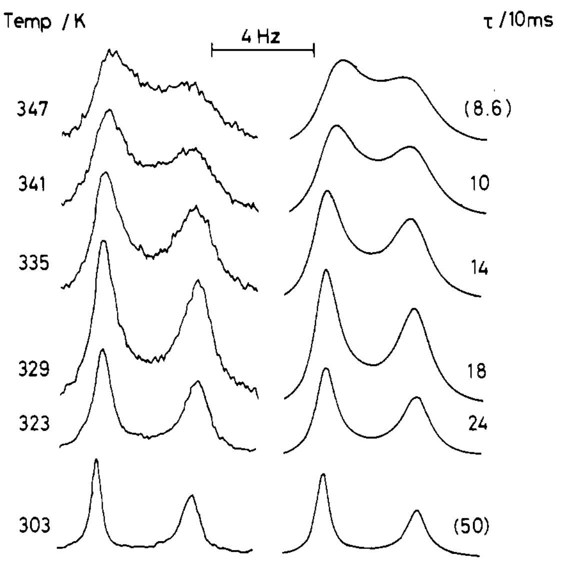

Figure 2. Observed (left) and simulated (right) ^1H NMR shapes in the methylidene region (E and F, Figure 1). [complex] = 0.044 M, [Hacac] = 0.21 M, and $[H_2O]$ = 0.044 M.

Measurement of ^1H NMR Spectra. A JEOL JNM-100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller was used at 100 MHz for ^1H NMR measurements. The reaction mixtures were prepared by mixing a small amount of the complex with the Hacac solution in CD_3CN. The Hacac solution was prepared several days before use to attain tautomeric equilibrium between the keto and the enol forms. They were weighed in 5 mm o.d. NMR tubes with a microbalance. The concentration ratio, [enol]/[keto], was determined by the area measurements of methylidyne proton signals for keto and enol tautomers. Water contents were determined by the Karl Fischer method immediately after NMR measurements. The density of the reaction mixtures was determined by weighing a known volume of the mixture to convert molality into molarity.

Kinetic Analysis. The kinetic analysis was carried out by use of a computer program based on the modified Bloch equation for the two-site exchange as described previously.[8c]

Results

The absorption spectrum of $Sc(acac)_3$ shows a peak at 299 nm with a molar extinction coefficient of $3.6 \times 10^4\ M^{-1}\ cm^{-1}$ in acetonitrile. Hacac also gives a peak at 272 nm ($6900\ M^{-1}, cm^{-1}$) in the solvent after the tautomeric equilibration. The spectrum of the reaction mixture containing $Sc(acac)_3$ and Hacac coincided with the sum of the spectrum of each component in acetonitrile and remained unchanged at least for several hours.

The ^1H NMR spectra of the reaction mixture in CD_3CN show (Figure 1) three methyl proton and two methylidyne proton signals at 30 °C. Two methyl proton signals of $Sc(acac)_3$ (A) and Hacac in the enol form (B) broadened as the temperature was raised but did not coalesce even at 74 °C (CD_3CN, bp 81 °C). A similar behavior was observed in methylidyne proton signals of $Sc(acac)_3$ (F) and Hacac in the enol form (E). The change of the ^1H NMR signals with temperature is shown in the left side of Figure 2. However, no line broadening was observed for the methyl proton signal (C) and the methylidene proton signal (D) of Hacac in the keto form (Figure 1). Therefore, the ligand exchange reaction takes place exclusively between $Sc(acac)_3$ and Hacac in the enol form

$$Sc(acac^*)_3 + \text{Hacac (enol)} \rightleftharpoons Sc(acac)_3 + \text{Hacac}^* \text{ (enol)} \qquad (1)$$

Since signals A and B overlapped with the methyl proton signals of the solvent, the rate analysis was carried out with signals E and F. Line shapes for the best-fit values at each temperature were simulated and are shown in Figure 2. The chemical shift and the line half-width of signals of the solution containing either the complex or the free ligand were constant throughout the

---

(6) Anderson, T. J.; Neuman, M. A.; Melson, G. A. *Inorg. Chem.* **1973**, *12*, 927–930.

(7) (a) Saito, K.; Masuda, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 384–389. (b) Saito, K.; Masuda, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 119–124. (c) Matsuzawa, K.; Saito, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2777–2779. (d) Chatterjee, C.; Matsuzawa, K.; Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2809–2812. (e) Kido, H.; Saito, K. *Inorg. Chem.* **1977**, *16*, 397–400. (f) Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3545–3548. (g) Kido, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 82–87. (h) Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 424–428. (i) Watanabe, A.; Kido, H.; Saito, K. *Inorg. Chem.* **1981**, *20*, 1107–1112. (j) Nagasawa, A.; Kido, H.; Hattori, T. M.; Saito, K. *Inorg. Chem.*, **1986**, *26*, 4330–4333. (k) Kido, H.; Koyama, M.; Saito, K., submitted for publication. (l) Kido, H.; Saito, K., *J. Am. Chem. Soc.*, in press. (m) Kido, H.; Hatakeyama, Y.; Saito, K., submitted for publication.

(8) (a) Fujiwara, N.; Tomiyasu, H.; Fukutomi, H. *Chem. Lett.* **1963**, 377–378. (b) Ikeda, Y.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1060–1066. (c) Fujiwara, N.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1576–1581. (d) Ikeda, Y.; Tomiyasu, H.; Fukutomi, H. *Inorg. Chem.* **1984**, *23*, 1356–1360. (e) Ikeda, Y.; Tomiyasu, H.; Fukutomi, H. *Inorg. Chem.* **1984**, *23*, 3197–3202. (f) Ohno, H.; Fujiwara, N.; Tomiyasu, H.; Fukutomi, H. *34th Symposium on Coordination Chemistry*; Nagaoka, Japan, 1984; Abstr. p 118.

(9) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142–3143.

Table I. Observed First-Order Rate Constants at 50 °C

$[Sc(acac)_3]$/M	[Hacac]/M[a]	$[H_2O]$/M	k_0/s^{-1}
0.044	0.21	0.044	6.3
0.039	0.26	0.124	8.0
0.041	0.19	0.256	6.3
0.045	0.45	0.026	11.3
0.053	0.58	0.044	14.9
0.047	0.27[b]	0.040	3.0
0.042	0.58[b]	0.062	6.3

[a] Enol 62%. [b] Deuterium content of $[3\text{-}^2H_2]$Hacac is 65% in the reaction mixture.

temperature and were used as the limited values in the kinetic analysis. The first-order rate constant, k_0, was calculated from eq 2 and 3, where τ and P with the subscripts c and f are the mean

$$\tau = \tau_c P_f = \tau_f P_c \qquad (2)$$

$$k_0 = 3\tau_c^{-1} \qquad (3)$$

lifetimes and the mole fractions of the coordinated and the free sites, respectively. The data at 30 and 74 °C were excluded from the kinetic analysis since τ's have large errors, which seemed to be caused by the very small difference in the chemical shift and the line half-width at 30 °C from the limited values and by the increased noise at 74 °C because of the temperature close to the boiling point of acetonitrile (81 °C).

The observed first-order rate constants, k_0, are listed in Table I. Plots of k_0 against [enol] at $[H_2O]$ = 0.026–0.044 M gave straight lines with small intercepts (open symbols in Figure 3). When $[H_2O]$ was increased, k_0 did not change (Figure 3). Hence, eq 4 holds. The contribution of k_2' to k_0 is minor in the [enol]

$$k_0 = k_1'[\text{enol}] + k_2' \qquad (4)$$

region studied. The k_1' values are listed in Table II together with the values of activation parameters and k_2'.

When $[3\text{-}^2H_2]$Hacac was used instead of the ordinary Hacac (deuterium content of ca. 65 % in the reaction mixture), k_0 was remarkably decreased, as shown in Table I. The k_1' values are calculated by eq 4 and shown in Table II as $k_1'([3\text{-}^2H_2]\text{Hacac})$. The ratios of the rate constants $k_1'(H)/k_1'(D)$ are listed in Table II, where $k_1'(D)$ is the extrapolated value to a deuterium content of 100%.

Discussion

The ligand exchange reaction, eq 1, proceeds practically via a path governed by k_1' (k_1 path) in the region $[Sc(acac)_3]$ = 0.039–0.053 M, [enol] = 0.12–0.36 M, and $[H_2O]$ = 0.03–0.26 M in acetonitrile. Water did not catalyze the exchange.

Reaction Route of the k_1 Path. It is reasonable to consider for the k_1 path the reaction route illustrated in Figure 4, which was concluded commonly to be that for the exchange of $M^{III}(acac)_3$ previously studied.[7e–j] The intermediate II is formed from $Sc(acac)_3$ (I) and the enol and is converted into II* by the proton transfer from the enol to the enolate. Then II* gives I* and the enol. The first step is the substitution process of the free enol for one end of the chelated enolate (k_a). The second is an intramolecular H^+-transfer process between unidentate ligands in II (k_b). The third is the reverse of the first (k_{-a}). The observations, the first-order dependence of k_0 on [enol] and the deuterium isotope effect, are consistent with the mechanism. The concentration of II is very low as compared with I, for the following reasons: (1) no significant peaks other than those for Hacac and

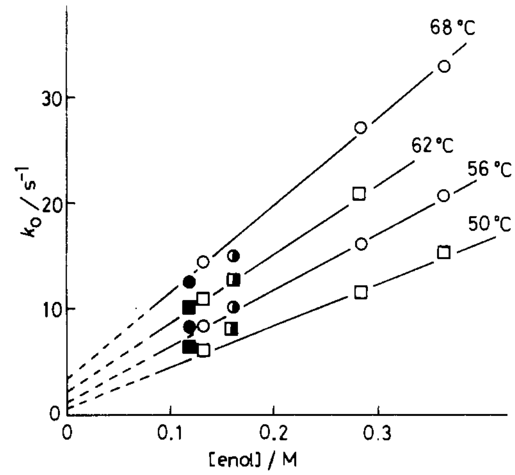

Figure 3. Influence of the free ligand concentration on the ligand exchange rate constant (k_0) of $[Sc(acac)_3]$ in CD_3CN ([complex] = 0.04 M): $[H_2O]$ = 0.026–0.044 M (○, □), 0.12 M (◐, ◧), and 0.26 M (●, ■).

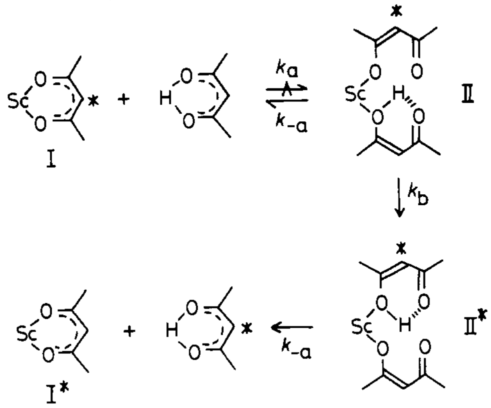

Figure 4. Mechanism of the ligand exchange of $[Sc(acac)_3]$ in acetonitrile. Asterisks denote labeling. Two chelate ligands are omitted for simplicity.

the complex in the NMR spectrum (Figure 1) were observed; (2) a two-site exchange model could be applied to the kinetic analysis; (3) additivity of the absorption spectrum of the reaction mixture was confirmed for Hacac and the complex. Hence $k_a[\text{enol}] \ll k_{-a}$.

If $k_a[\text{enol}] \ll k_b$ is assumed, the k_a step is regarded as being substantially rate-determining. A steady-state approximation to II gives eq 5. A branching ratio, $k_b/(k_{-a} + k_b)$, gives the

$$k_1'[\text{enol}] = k_a[\text{enol}]\frac{k_b}{k_{-a} + k_b} \qquad (5)$$

probability for the exchange from II.

Deuterium Isotope Effect. On the basis of the observed isotope effect $k_1'(H)/k_1'(D)$ (ca. 5, Table II), the ratio of k_b to k_{-a} and the branching ratio can be estimated, provided that only k_b is subject to the effect. A large $k_1'(H)/k_1'(D)$ value, ca. 9, which was found in the ligand exchange of $[Th^{IV}(acac)_4]$ in $CDCl_3$,[8f] is regarded to be very close to the expected maximum isotope effect in the approximate treatment, in which the transition states have

Table II. Rate Constants and Activation Parameters for the Ligand Exchange of $Sc(acac)_3$ in CD_3CN

rate const	temp/°C				$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
	50	56	62	68		
$k_1'/M^{-1}\,s^{-1}$	36 ± 6	52 ± 3	67	78 ± 7	36 ± 5	−105 ± 16
k_2'/s^{-1}	$1._4 \pm 1._6$	$1._5 \pm 0._9$	2	$4._4 \pm 1._9$		
$k_1'^{a}/M^{-1}\,s^{-1}$	18	23	32	41		
$k_1'(H)/k_1'(D)^{b}$ (mean 5.3 ± 1.1)	4.8	7.4	5.1	3.7		

[a] Deuterium content of 65%. [b] Extrapolated to a deuterium content of 100%.

Table III. Branching Ratio and Expected Deuterium Isotope Effect (r_D) on It for k_{-a}/k_b and $k_b/k_b(D)$

		r_D[a]			
k_{-a}/k_b	$k_b/(k_{-a} + k_b)$	$k_b/k_b(D) = 3$	$k_b/k_b(D) = 5$	$k_b/k_b(D) = 7$	$k_b/k_b(D) = 9$
0.001	1.00	1.0	1.0	1.0	1.0
0.01	0.99	1.0	1.0	1.1	1.1
0.1	0.90	1.2	1.4	1.5	1.7
1	0.50	2.0	3.0	4.0	5.0
10	0.09	2.8	4.6	6.5	8.3
100	0.01	3.0	5.0	7.0	9.0
1000	0.001	3.0	5.0	7.0	9.0

[a] $r_D = (k_b/(k_{-a} + k_b))/(k_b(D)/(k_{-a} + k_b(D)))$.

Table IV. Kinetic Parameters and Proposed Mechanisms for the Ligand Exchange of $[M^{III}(acac)_3]$ in Hacac or in CH_3CN[a]

M^{III}	r/pm	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	effect of [Hacac][d]	$k_1(H)/k_1(D)$	mechanism	ref
Co	52.5	152	+80	0	1.0	D or I_d	7f,g
Al	53.0	85	−38	1	1.6	I[f]	7j
Cr	61.5	120	−21	1	1.5	I[f]	7e,f
Ga	62.0	67	−71	1	1.9	I_a	7m
V	64.0	73	−73	1	1.0	I_a	7i
Fe	64.5	60	−92	1	1.0	I_a	7h
Rh	66.5	118	−79		1.4	I_a	7g
Ru	68	115	−61			I_a	7g
Sc	74.5	36[b,c]	−88,[c] −105[b]	1	~5[e]	I_a	this work
In	80.0	47[b,c]	−84,[c] −101[b]	1	~5[e]	I_a	7m

[a] For k_1/s^{-1} in Hacac, except where noted. [b] For $k_1'/M^{-1}\ s^{-1}$ in CH_3CN. [c] For k_1/s^{-1} ($=k_1'$ [enol]) at [enol] = 8 M (extrapolation of [enol] to that in neat Hacac). [d] $k_1[\mathrm{Hacac}]^{0\ \mathrm{or}\ 1}$ in Hacac diluted with CH_3CN ([Hacac] = 2–9.7 M) or presence (1) or absence (0) of the k_1' term in CH_3CN. [e] $k_1'(H)/k_1'(D)$. [f] $I_d - I_a$ borderline.

the same energy for both isotopes and the rate difference lies totally in the ground states.[10] The difference is estimated from the difference in the zero-point energies on the basis of the ratio of stretching frequencies given by the harmonic oscillator equation. For the present system, the maximum $k_b(H)/k_b(D)$ value is calculated to be ca. 8.4, which is almost equal to 9, by using the stretching frequency value of O–H in Hacac (~3000 cm^{-1}). Therefore, it is reasonable to consider that the isotope effect in the present system is in fact close to the maximum value and to assume $k_b(H)/k_b(D)$ is 9. Equation 6 indicates that the observed

$$r_D = \left(\frac{k_b(H)}{k_{-a} + k_b(H)}\right) \Bigg/ \left(\frac{k_b(D)}{k_{-a} + k_b(D)}\right) \qquad (6)$$

$k_1'(H)/k_1'(D)$ should be equal to the ratio of the branching ratios. r_D is calculated for the variation of k_{-a}/k_b and $k_b/k_b(D)$ ((H)'s for k's are omitted when obvious) and listed in Table III, together with the branching ratio. The observed $k_1'(H)/k_1'(D)$ ratio being nearly 5, $k_b/k_b(D) \geq 5$, $k_{-a}/k_b \geq 1$, and $k_b/(k_{-a} + k_b) \geq 0.5$ are required for $r_D = 5$. However, for the most plausible $k_b/k_b(D) \sim 9$, $k_{-a}/k_b \sim 1$ and $k_b/(k_{-a} + k_b) \sim 0.5$ are the most probable.

The resulting estimation $k_{-a} \approx k_b$ is consistent with the assumption $k_a[\mathrm{enol}] \ll k_b$ since $k_a[\mathrm{enol}] \ll k_{-a}$. If otherwise assumed, i.e., where $k_a[\mathrm{enol}] \ll k_b$ is not true, the observed isotope effect could not be interpreted. The relationship $k_a[\mathrm{enol}] \ll k_a \sim k_{-b}$ is also consistent with our previous conclusion that the k_a step substantially governs the ligand exchange rate of $M^{III}(acac)_3$ (M^{III} = V^{III}, Cr^{III}, Mn^{III}, Fe^{III}, Ru^{III}, Co^{III}, Rh^{III}, Al^{III}, and Ga^{III}).[7e–j] The best proof is a linear free energy relationship between the first-order rate constants of the exchange at a constant [Hacac] and of the exchange and/or substitution reactions of unidentates such as H_2O and Cl^- for the aqua ligand in $[M^{III}L_5(H_2O)]^{3+}$ (L = H_2O and/or NH_3) for M^{III} shown above.[11] The present exchange is not exceptional.

Ligand Substitution Mechanism. $\Delta S^\ddagger$ is also regarded to reflect substantially the k_a step (Figure 4). The branching ratio (estimated to be ca. 0.5) could affect $\Delta S^\ddagger$ (eq 5). However, even if the term of the branching ratio affects only $\Delta S^\ddagger$, the contribution is at most only −6 J K^{-1} mol^{-1}, which is estimated by multiplication of logarithm of the probability by the gas constant ($R \ln [k_b/(k_{-a} + k_b)]$). This is very small as compared with the observed value (−105 J K^{-1} mol^{-1}). For the simple substitution process (k_a step), mechanisms have been proposed for $M^{III}(acac)_3$ in Table IV mainly on the basis of the $\Delta S^\ddagger$ values and the rate dependence on [Hacac]. The $\Delta S^\ddagger$'s for M^{III} other than Sc^{III} and In^{III} are less affected by the branching ratio, which is estimated to be close to unity (Table III) because of the modest deuterium isotope effect (Table IV). The present $\Delta S^\ddagger$ is greatly negative, even though it is calculated for the first-order rate constant k_1 that is obtained from k_1'[enol] value extrapolated to [enol] = 8 M (neat) used for the comparison with $\Delta S^\ddagger$'s for k_1 in neat Hacac for other $[M^{III}(acac)_3]$. The participation of [enol] in the rate equation (eq 4) was also confirmed. These facts clearly indicate an associative mechanism for the k_a step. The A mechanism was preferred for the trimethyl phosphate (TMP) exchange of $[Sc(TMP)_6]^{3+}$ in TMP or CH_3NO_2.[5b] We prefer I_a rather than A for the present exchange for the following reasons. The $\Delta S^\ddagger$ of Sc^{III} in Table IV together with that of In^{III} is not distinctly more negative as compared with the $\Delta S^\ddagger$'s of Ga^{III}, V^{III}, Fe^{III}, Rh^{III}, and Ru^{III}, for which the I_a mechanism was previously concluded by an independent comparison of kinetic parameters within each M^{III}. It is within the gradual increase of the negative value with the increase of ionic radius (r)[12] of M^{III}.

An A mechanism was proposed for the exchange of $Th(acac)_4$ on the basis of the existence of a 9-coordinated congenial complex, $Th(tta)_4topo$ (tta = 2-thenoyltrifluoroacetate, topo = trioctylphosphine oxide) and the retardation effect of the rate by bases such as DMSO and H_2O.[8c] The effect was interpreted by the occupation of the ninth coordination site by the bases. However, in the present exchange, the rate was not varied by [H_2O]. Moreover, although a 7-coordinated $Y(acac)_3H_2O$[13] was reported for Y^{III} (r = 90.0 pm), such a species is not known for Sc^{III} (r = 74.5 pm). We tend to think that $Sc(acac)_3$ does not have the capacity to accept the seventh ligand even though Sc^{III} has the

---

(10) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 203–204.

(11) Reference 7l and references cited therein.

(12) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 925–946. (b) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(13) Pope, G. W.; Steinbach, J. F.; Wagner, W. F. *J. Inorg. Nucl. Chem.* **1961**, *20*, 304–313.

largest ionic $\mathrm{M^{III}}$ radius in the first transition series.

Kinetic Features of $\mathrm{Sc^{III}O_6}$ Complexes. The k_1 defined above is calculated to be 80 $\mathrm{s^{-1}}$ at 25 °C by extrapolation of [enol] for the present exchange. The LFER shows that the first-order rate constant, $k_1(\mathrm{H_2O})$, of water exchange and anation of $[\mathrm{M^{III}L_5(H_2O)}]^{3+}$ (L = $\mathrm{H_2O}$ and/or $\mathrm{NH_3}$) are larger than k_1 by about 10^4–10^5 invariably for various $\mathrm{M^{III}}$.[7] The relationship and the present data indicate that $k_1(\mathrm{H_2O})$ for $[\mathrm{Sc^{III}(H_2O)_6}]^{3+}$, if it exists, is most probably 10^6–10^7 $\mathrm{s^{-1}}$, although the hydration number of the ion is still uncertain in spite of a recent X-ray diffraction study on aqueous solutions of $\mathrm{ScCl_3}$ and $\mathrm{Sc(ClO_4)_3}$ (frequency factor of Sc–O 6–8).[14]

It is pointed out that the $\mathrm{Sc^{III}}$ complexes such as $[\mathrm{ScF_6}]^{3-}$, $[\mathrm{Sc(bpy)_3}]^{3+}$, $[\mathrm{ScCl_2(bpy)_2}]^{+}$ (bpy = 2,2′-bipyridine), $[\mathrm{Sc(DMSO)_6}]^{3+}$ (DMSO = dimethyl sulfoxide) exhibit the usual coordination number of 6 and that $\mathrm{Sc^{III}}$ has a greater similarity to $\mathrm{Al^{III}}$ rather than to $\mathrm{Y^{III}}$, $\mathrm{La^{III}}$, and tervalent lanthanides in the physical properties of $\mathrm{Na_3M^{III}F_6}$ crystals and in the stability constant of ethylenediaminetetraacetate complexes in aqueous solution.[15,16] In the present exchange, $\mathrm{Sc^{III}}$ shows a remarkable similarity to $\mathrm{In^{III}}$ rather than $\mathrm{Al^{III}}$ in the ΔH^* and ΔS^* values (Table IV); hence, the k_1' ratio of $\mathrm{Sc^{III}}$ to $\mathrm{In^{III}}$ at 25 °C is only 50. The same tendency has been found in the ligand exchange of $[\mathrm{Sc(TMP)_6}]^{3+}$ and $[\mathrm{In^{III}(TMP)_6}]^{3+}$ in nitromethane, where ΔH^*/kJ $\mathrm{mol^{-1}}$, ΔS^*/J $\mathrm{K^{-1}\,mol^{-1}}$, and ΔV^*/$\mathrm{cm^3\,mol^{-1}}$ values are 21.2, −144, and −18.7 for $\mathrm{Sc^{III}}$ and 32.8, −118, and −22.8 for $\mathrm{In^{III}}$, respectively, and the corresponding ratio of the second-order rate constants is 5.[5b,c] For $[\mathrm{Al^{III}(TMP)_6}]^{3+}$, quite different values of the activation parameters were reported (85.1, +38.2, and +22.5, respectively).[5b,c] Therefore, as for the ligand substitution behavior, $\mathrm{Sc^{III}O_6}$ is concluded to be akin to $\mathrm{In^{III}O_6}$ rather than $\mathrm{Al^{III}O_6}$. Any similar transition metal $\mathrm{M^{III}(acac)_3}$ could not be found in the present exchange (Table IV). The similarity is attributed mainly to the ionic radius (Table IV), which dominates electrostatic interactions between $\mathrm{M^{III}}$ and the ligand in the substitution process, since the ions have $\mathrm{d^0}$ or $\mathrm{d^{10}}$ configurations and are hence unaffected by ligand field change in the activation process.

In conclusion, $\mathrm{Sc^{III}O_6}$ complexes seem to have generally similar features in the ligand substitution process to $\mathrm{In^{III}O_6}$ features in both lability and mechanism because of steric and electronic features of the central metal ions.

Acknowledgment. We are grateful to Professor Kazuo Saito and Dr. Akira Nagasawa for valuable discussions.

Registry No. $\mathrm{Sc(acac)_3}$, 14284-94-7; Hacac, 17272-66-1; $\mathrm{D_2}$, 7782-39-0.

---

(14) Yamaguchi, T.; Ohtaki, H.; Kanno, H. *35th Conference on Coordination Chemistry*; Hiroshima, Japan, 1985; Abstr. p. 46.

(15) Melson, G. A.; Stotz, R. W. *Coord. Chem. Rev.* **1971**, *7*, 133–160.

(16) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: 1984; p 1109.

Contribution from the Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790, Japan,
and Faculty of General Education, Gifu University, Yanagido, Gifu 501-11, Japan

Volume Profile for Aquations of the (Carboxylato)pentaamminecobalt(III) Complex

Yoichi Kitamura,*[1a] Kouzou Yoshitani,[1b] and Tetsuroh Itoh[1a]

Received October 8, 1987

The activation volume (ΔV^*) and reaction volume (ΔV) have been experimentally obtained for nine reactions of the title complex. ΔV ranges from −14 to −18 $\mathrm{cm^3\,mol^{-1}}$ for the carboxylato leaving ligand and from −3 to −6 $\mathrm{cm^3\,mol^{-1}}$ for the carboxylic acid leaving ligand. ΔV^* is approximately half of the corresponding ΔV. This feature supports an interchange mechanism for these reactions.

Introduction

Volume profiles for aquations of anionopentaamminecobalt(III)

$$\mathrm{Co(NH_3)_5X^{n+} + H_2O = Co(NH_3)_5H_2O^{3+} + X} \qquad (1)$$

were investigated previously for X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{Me_2SO}$, $\mathrm{H_2O}$, $\mathrm{OHCH_3}$, $\mathrm{OHCH_2CH_3}$, $\mathrm{OHCH(CH_3)_2}$, $\mathrm{OC(NH_2)_2}$, $\mathrm{OC(NH_2)(NHCH_3)}$, $\mathrm{OC(NHCH_3)_2}$, $\mathrm{OCH(NH_2)}$, $\mathrm{OCH(NHCH_3)}$, and $\mathrm{OCH(N(CH_3)_2)}$.[2-5] It was suggested that the correlation

$$\Delta V^* = (0.51 \pm 0.02)\Delta V + (1.2 \pm 0.2) \qquad (2)$$

exists between their ΔV^* and ΔV values.[6] Equation 2 means that the partial molal volume ($\bar{V}$) of the transition state is close to the corresponding mean $\bar{V}$ of the initial and the final state. It was interpreted that the entering $\mathrm{H_2O}$ and the leaving X participate almost equally in the transition state, and an interchange mechanism was supported. In the present work, we intend to check the applicability of eq 2 to the extended series of reaction 1 with carboxylato and carboxylic acid leaving ligands.

In previous work at normal pressure, it was shown that the aquation velocity of $\mathrm{Co(NH_3)_5(RCOO)^{2+}}$ (R = H, $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{CHCl_2}$, $\mathrm{CH_2Cl}$, and $\mathrm{CCl_3}$) depends more or less on the acidity of the solution.[7,8] This dependence was remarkable when the corresponding RCOOH was weak acid. In the case of R = H and $\mathrm{C_2H_5}$, the aquation rate constant k_{obsd} depends linearly on $[\mathrm{H^+}]$:[8]

$$k_{\mathrm{obsd}} = k_0 + k_1[\mathrm{H^+}] \qquad (3)$$

Thus, it was considered that the reaction proceeds through two paths:[8]

k_0 path

$$\mathrm{Co(NH_3)_5(RCOO)^{2+} + H_2O \xrightarrow{k_0} Co(NH_3)_5H_2O^{3+} + RCOO^-} \qquad (4)$$

k_1 path

$$\mathrm{Co(NH_3)_5(RCOO)^{2+} + H^+ \overset{K}{\rightleftharpoons} Co(NH_3)_5(RCOOH)^{3+}} \qquad (5)$$

$$\mathrm{Co(NH_3)_5(RCOOH)^{3+} + H_2O \xrightarrow{k_H} Co(NH_3)_5H_2O^{3+} + RCOOH} \qquad (6)$$

$$\mathrm{RCOOH \overset{K_a}{\rightleftharpoons} RCOO^- + H^+} \qquad (7)$$

$$k_1 = Kk_{\mathrm{H}}$$

---

(1) (a) Ehime University. (b) Gifu University.

(2) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739–2746.

(3) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642–2646.

(4) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139–3143.

(5) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687–3691.

(6) Kitamura, Y. *Inorg. Chem.* **1985**, *24*, 2–3.

(7) Kuroda, K. *Nippon Kagaku Zasshi* **1961**, *82*, 572–577.

(8) Kuroda, K. *Nippon Kagaku Zasshi* **1961**, *82*, 1481–1484.

0020-1669/88/1327-0996$01.50/0