solvent molecule of crystallization that is also hydrogen-bonded to the diolate oxygen (O_5 or O_5') through its hydroxy proton (H_S or H_S').

It is believed that **1** is only the first member of a family of nonionic polynuclear molybdenum(VI) peroxo complexes stabilized by chelating organic ligands. An analogous peroxo complex has been synthesized with homochiral (*S*)-1,2-propanediol. Its crystal structure and peroxo group reactivity are currently under investigation.

Acknowledgment. I am thankful to Professor V. W. Day for helpful discussions on hydrogen bonding.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal structure data, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles, close contacts involving hydrogen atoms, and nonbonding interactions (15 pages); a listing of structure factors (8 pages). Ordering information is given on any current masthead page.

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Ligand Isotopic Exchange Kinetics of Tris(acetylacetonato)aluminum(III) in Acetylacetone under Atmospheric and Elevated Pressures

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The rate of ligand isotopic exchange of ^{14}C-labeled tris(acetylacetonato)aluminum(III), Al(acac)$_3$, in acetylacetone (Hacac) was expressed by $R = (k_1 + k_2[H_2O])[Al(acac)_3]$, where $[Al(acac)_3] = 0.0012$–0.0057 mol dm^{-3} and $[H_2O] = 0.022$–0.162 mol dm^{-3} at 15–40 °C under atmospheric pressure and at 25 °C under pressures up to 237 MPa. The rate constants k_1 and k_2 decreased with an increase in pressure, on deuteriation of protolytic hydrogens of water and acetylacetone, and on addition of acetonitrile. The activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$, were 85 ± 5 and 79 ± 4 kJ mol^{-1}, −38 ± 18 and −34 ± 14 J K^{-1} mol^{-1}, and +10 ± 2 and +5 ± 1 cm^3 mol^{-1}, for k_1 and k_2, respectively. An interchange mechanism to form an intermediate containing both a one-ended acac$^-$ and a Hacac or a water molecule are concluded for the rate-determining steps of the k_1 and k_2 paths, respectively.

Introduction

The ligand isotopic exchange of tris(acetylacetonato)aluminum(III), [Al(acac)$_3$], with ^{14}C-labeled acetylacetone (Hacac-[^{14}*C*]) in toluene, tetrahydrofuran (THF), and ethyl acetate at 0–35 °C gave moderate $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values and was subject to the catalytic effect of water and acids.[2-4] The activation mode of the substitution process, however, has not been disclosed. The acetylacetonate (acac$^-$) exchange of tris(acetylacetonato)metal complexes in neat acetylacetone (Hacac) is a kind of solvent exchange reaction. We have discussed, taking advantage of the simplicity of the system, the mechanism of the substitution process of neutral complexes of various tervalent metal ions such as vanadium, chromium, iron, cobalt, ruthenium, and rhodium, on the basis of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, and the deuterium isotope effect on the rates.[5-9]

On the other hand, many workers have studied the solvent exchange of hexakis(unidentate)aluminum(III) cations, e.g. $[Al(H_2O)_6]^{3+}$, $[Al(dmf)_6]^{3+}$ (dmf = *N,N*-dimethylformamide), $[Al(Me_2SO)_6]^{3+}$ (Me_2SO = dimethyl sulfoxide), etc., and postulated a dissociative-interchange mechanism.[10-23] Considerably large positive activation volumes, $\Delta V^{\ddagger}$, as well as positive $\Delta S^{\ddagger}$, were understood to be useful in elucidating the mechanism.[10,17,19,20]

We have extended kinetic studies of the ligand isotopic exchange of [Al(acac)$_3$] to that in neat Hacac and applied the pressure technique for clarifying the substitution mechanism.

Experimental Section

Materials. [Al(acac)$_3$] was prepared by the known method,[24] recrystallized, and sublimed at ca. 160 °C at 1 torr (1 torr = 133.3 Pa).[4] The labeled complex was prepared by the ligand exchange method and dried in vacuo (250 mg, ca. 8.1 pCi mg^{-1}).

Hacac was dried with anhydrous calcium sulfate and distilled at 132–138 °C. The water content was determined by Karl Fischer titration to be 0.012 M (M = mol dm^{-3}). Hacac[^{2}*H*$_2$] (74% deuteriated at the methylene moiety) was prepared by the reported method.[9]

Kinetic Procedure. Reactions under Atmospheric Pressure. Kinetic runs were carried out similarly to the procedure previously described.[7] The labeled complex (ca. 7 mg) was dissolved in the solvent (ca. 7 cm^3 of Hacac or Hacac[^{2}*H*$_2$], with additional water or deuterium oxide, respectively, whenever necessary) and kept thermostated. Six or seven portions (0.50 cm^3 each) were pipetted out at appropriate time intervals and chilled at −60 °C. The solvent was evaporated off in vacuo at ca. 0 °C to recover the complex quantitatively, which was submitted to the liquid scintillation counting. The water content of the reaction mixture remained constant during the kinetic runs within the error of Karl Fischer titration (±2 × 10^{-3} M).

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Table I. Dependence of Complex Concentration and Solvent Composition on the McKay Rate R and the Observed Rate Constant k_o at 25 °C

$[Al(acac)_3]/10^{-3}$ M	[Hacac]/M	$[H_2O]/10^{-2}$ M	pressure/MPa	$R/10^{-7}$ M s^{-1}	$k_o/10^{-4}$ s^{-1}
1.18	9.7	16.2	0.10	3.54	3.00
3.15	9.7	14.2	0.10	9.31	2.95
5.73	9.7	15.3	0.10	19.7	3.26
1.54	9.7	8.6	91.9	2.31	1.50
3.5	9.7	9.1	91.9	5.10	1.62
2.12	4.85[a]	5.5	0.10	1.90	0.896
2.03	4.85[a]	9.6	0.10	2.56	1.26
1.67	4.85[a]	15.3	0.10	2.82	1.69
1.09	1.9[a]	4.2	0.10	0.505	0.463
1.56	1.9[a]	14.7	0.10	1.75	1.12

[a] Diluted with acetonitrile.

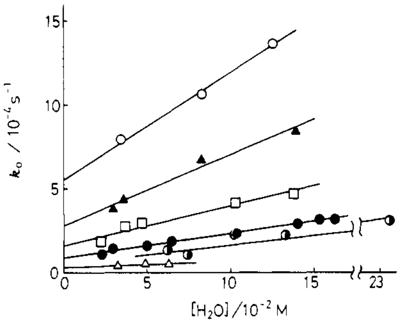

Figure 1. Influence of the water concentration on the exchange rate constant (k_o) of $[Al(acac)_3]$ ($(1.7-3.4) \times 10^{-3}$ M) in acetylacetone under atmospheric pressure: (△) 15 °C; (●) 25 °C; (◑) 25 °C in 74% methylene-deuteriated Hacac containing 74% D_2O; (□) 30 °C; (▲) 35 °C; (○) 40 °C.

Reactions under Elevated Pressures. The labeled complex (ca. 10 mg) was dissolved in 10 cm^3 of the solvent and dispensed at 0 °C into five vessels (1.7 cm^3 each) consisting of a Teflon pipe (1.4-cm diameter and 4.0-cm length) and two Teflon pistons with silicone rubber O-rings. The vessel was dipped into silicone oil (Shin-Etsu KF-96 10 cs) in a hole (1.5-cm diameter and 5.0-cm depth) of a stainless steel block (7 cm × 7.5 cm × 10 cm), which was thermostated at 25.0 ± 0.1 °C. The container was stoppered and locked with a stainless steel screw cap and the pressure applied through the silicone oil with a hand pump. After a given time lapse the vessel was taken out of the container and cooled to 0 °C. The solution was submitted to the kinetic analysis mentioned above. The concentration of water in the solution remained unchanged within the fluctuation $\pm 3 \times 10^{-3}$ M. A Bourdon tube calibrated with Heise's standard gauge was used for the pressure measurements (17.6, 42.1, 91.9, 140, 188, and 237 MPa (±0.5 MPa)).

Calculation of the Reaction Rate. The exchange rate R was calculated by the simplified McKay equation (eq 1), where x_0 and x_t are the specific counting rates of the complex at time zero and t, respectively. x_∞ was

$$R = 3[\text{complex}] \ln (x_0/x_t)/t \qquad (1)$$

practically zero under the present experimental conditions, since [Hacac] ≫ [complex]. The time zero ($t = 0$) was set at 1 min after mixing the complex with Hacac for runs under normal pressure and at 5 min after plunging for runs at higher pressures.

Results

Verification of the Exchange. The recovered complex from the reaction mixture gave a UV absorption identical with that of pure $[Al(acac)_3]$. The McKay plots $\ln (x_0/x_t)$ vs. t gave straight lines at least until the specific activity of the recovered complex decreased to ca. 40% of the original complex. These facts indicate that the ligand isotopic exchange took place exclusively under the given experimental conditions.

Rate under Atmospheric Pressure. The exchange rate R was proportional to the concentration of the complex as shown in Table I. k_o was dependent on the water concentration (Figure 1) and is expressed by eq 2. The k_1 and k_2 values at 15, 25, 30, 35, and

$$\begin{aligned} R &= k_o[\text{complex}] \\ &= (k_1 + k_2[H_2O])[\text{complex}] \qquad (2) \end{aligned}$$

40 °C gave activation enthalpies and entropies as shown in Table II. Both k_1 and k_2 decreased on deuteriation of the acidic hydrogens of Hacac and added water (Figure 1), and the ratios k_1^H/k_1^D and k_2^H/k_2^D were 1.6 and 1.5 at 25 °C, respectively (Table II). When Hacac was diluted with CH_3CN to make [Hacac] = 4.85 and 1.94 M, the rate decreased linearly (Table I).

Pressure Effect. The exchange rate R was also proportional to the complex concentration at 91.9 MPa (Table I). The dependence of k_o upon the water concentration under various

Table II. Rate Constants and Activation Parameters for the Ligand Isotopic Exchange between $[Al(acac[^{14}C])_3]$ and the Solvent Hacac[a]

temp/°C	pressure/MPa	$k_1{}^b/10^{-5}$ s^{-1}	$k_2{}^b/10^{-3}$ M^{-1} s^{-1}
15.0	0.10	2.9 (±1.8)	0.43 (±0.35)
25.0		9.1 (±0.9)	1.48 (±0.11)
30.0		14.6 (±2.5)	2.70 (±0.28)
35.0		28.3 (±5.6)	4.20 (±0.67)
40.0		56.6 (±8.1)	6.32 (±0.91)
25.0[c]	0.10	8.06 (±1.31)	1.46 (±0.12)
	17.6	5.53 (±0.56)	1.46 (±0.06)
	42.1	5.06 (±0.29)	1.38 (±0.03)
	91.9	4.14 (±2.89)	1.29 (±0.30)
	140	4.41 (±2.13)	1.07 (±0.22)
	188	3.00 (±0.30)	1.04 (±0.03)
	237	2.49	0.93

param	k_1	k_2
$\Delta H^\ddagger$/kJ mol^{-1}	84.8 (±5.4)	79.2 (±4.2)
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	-37.6 (±17.9)	-33.9 (±13.9)
$\Delta V^\ddagger/cm^3$ mol^{-1}	+10.2 (±1.8)	+5.0 (±0.4)
k^H/k^D [d]	1.6	1.5

[a] $R = (k_1 + k_2[H_2O])[\text{complex}]$, where $[\text{complex}] = (1.54-5.73) \times 10^{-3}$ M and $[H_2O] = (2.2-16.1) \times 10^{-2}$ M. [b] Errors are calculated at the 70% confidence level. [c] Runs were carried out in a high-pressure vessel. [d] Deuterium isotope effect. The k^D's were obtained from the experiments using Hacac[methylene-$^2H_2$] and D_2O.

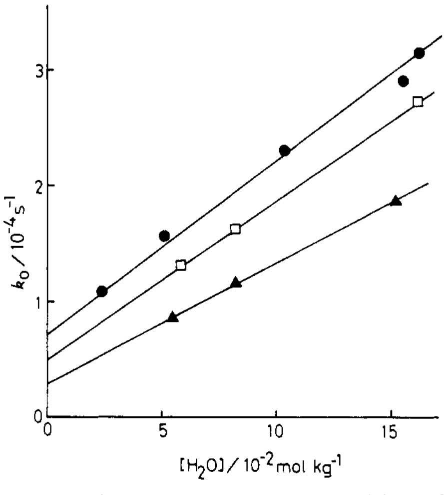

Figure 2. Observed exchange rate constant (k_o) of $[Al(acac)_3]$ ($(1.54-3.23) \times 10^{-3}$ M) in acetylacetone at 25 °C under elevated pressures: (●) 0.10 MPa; (□) 42.1 MPa; (▲) 188 MPa.

Table III. Kinetic Data for the Ligand Exchange and Related Reactions of Aluminum(III) Complexes[a]

complex	process[b]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$\Delta V^{\ddagger}/V_S^{\circ}$[c]	solvent	ϵ[d]	DN[e]	ref
$[Al(acac)_3]$	k_1	85	−38	+10	+0.10	Hacac	26	~18[f]	this work
	k_2	79	−34	+5	+0.05	Hacac	26	~18[f]	this work
	k_2	80	−16			toluene	2.4		3
	k_1	90	−51			EtOAc	6.1	17	2
	k_o	90	−33			thf	7.4	20	3
	k_{rac}	133	+227			$C_2H_5OH-C_5H_{12}$	25[g]	~30[g,f]	30
$[Al(H_2O)_6]^{3+}$	k_o	85	+42	+6	+0.32	H_2O	78	18	13
$[Al(dmf)_6]^{3+}$	k_o	88	+28	+14	+0.18	dmf−CH_3NO_2	37[h]	26[h]	17
$[Al(Me_2SO)_6]^{3+}$	k_o	83	+22	+16	+0.22	Me_2SO	47	28	19
$[Al(tmp)_6]^{3+}$	k_o	85	+38	+23	+0.20	tmpa−CH_3NO_2	21[i]	23[i]	20
$[Al(CH_3CN)_6]^{3+}$	k_o	79–80	+35–+41			CH_3CN	36	14	22

[a] Legend: Hacac = acetylacetone; EtOAc = ethyl acetate; thf = tetrahydrofuran; dmf = *N*,*N*-dimethylformamide; Me_2SO = dimethyl sulfoxide; tmpa = trimethyl phosphate. [b] k_o = observed rate constant of ligand exchange ($k_o = k_1 + k_2[H_2O]$ for $[Al(acac)_3]$); k_{rac} = racemization rate constant. [c] V_S° = partial molar volume of the ligand. [d] Relative permittivity (dielectric constant). [e] Donor number.[28] [f] Estimated from the association constant with $[V^{IV}(O)(acac)_2]$ in CH_2Cl_2. [g] For ethanol. [h] For DMF. [i] For TMPA.

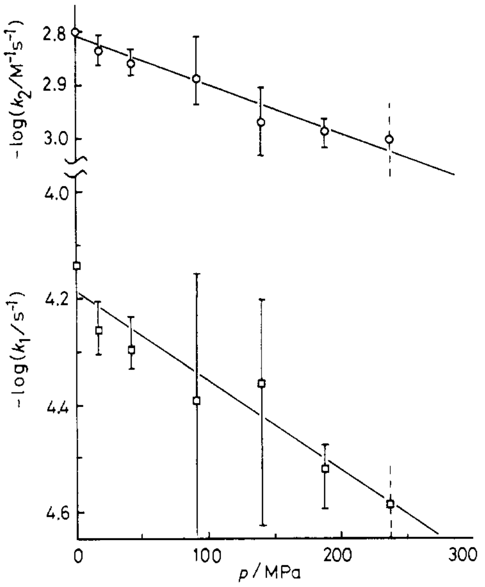

Figure 3. Pressure dependence of k_1 and k_2 for the ligand isotopic exchange of $[Al(acac)_3]$ in Hacac at 25 °C: (□) k_1; and (○) k_2.

pressures is shown in Figure 2. Both k_1 and k_2 decreased linearly with an increase in pressure (Figure 3). Volumes of activation are given in Table II. The compressibility of activation, $\Delta\beta^{\ddagger}$, was zero in the given pressure region.

Discussion

Exchange Mechanism. Since the reaction system is simple, the possible mechanisms are limited to those previously suggested (Figure 4).[5-9] The k_1 path proceeds in three steps consisting of two elementary processes: (1) a substitution process, replacement of one end of the chelated acac$^-$ by the solvent Hacac, and (2) an intramolecular proton-transfer process, transfer of a proton between the two unidentate ligands in intermediate III. The third step is the reversed process of the first, i.e. replacement of the unidentate Hacac by the free end of unidentate acac$^-$ to give the original complex.

The concentration of III is very low as compared with that of I, since no significant signals other than those for Hacac and $[Al(acac)_3]$ were observed in the aromatic proton resonance region of the NMR spectrum in CD_3CN ([complex] = 0.3 M, [Hacac] = 1.9 M). Additivity of the absorbance at 305 nm, the shoulder due to $[Al(acac)_3]$ in Hacac, also supports this conclusion. Hence, $k_a \ll k_{-a}$.

When III is reckoned as a steady-state intermediate, eq 3 holds.

$$k_1 = k_a k_b/(k_{-a} + k_b) \qquad (3)$$

The probability to give the product out of intermediate III is related to the branching ratio, $k_b/(k_{-a} + k_b)$. The relative magnitude of k_{-a} to k_b can be estimated from the deuterium isotope effect. The primary kinetic isotope effect on the proton-transfer process is generally large ($k^H/k^D > 2$).[25] Deuterium may change the nucleophilic basicity of Hacac, but to a much smaller extent than does the proton-transfer rate. Provided that only k_b is subject to the deuterium isotope effect and that the k_b^H/k_b^D value falls in the range 2–10,[26] the k_b/k_{-a} ratio is calculated from the observed k_1^H/k_1^D ratio (=1.6) to be more than unity (1–10), and consequently the branching ratio is calculated to be more than 0.5 (0.5–0.9). We can thus conclude that $k_a \ll k_{-a} < k_b$ and that the first substitution step is substantially rate-determining.

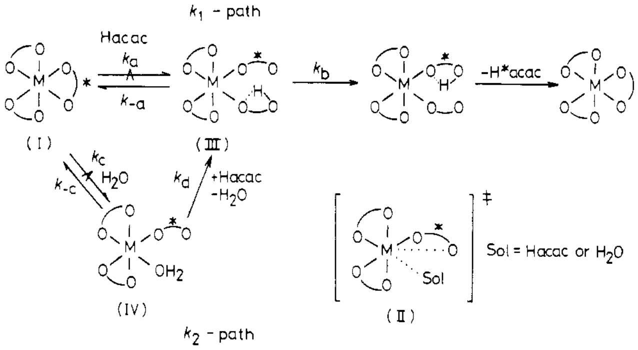

Figure 4. Plausible mechanism of the ligand exchange of $[Al(acac)_3]$ (I) in Hacac. Asterisks denote the presence of ^{14}C labeling, and arrows with circumflexes show the rate-determining step.

Similar values of activation parameters and deuterium isotope effects for k_1 and k_2 support our previous discussion that both paths would have a similar rate-determining step. A water molecule can give IV more easily than Hacac does III, and IV is converted into III quickly (Figure 4).

Mechanism of Ligand Substitution Process. The mechanism of the substitution process may be discussed with reference to the kinetic data for related reactions of Al^{III} complexes (Table III).

The usefulness of the activation volume $\Delta V^{\ddagger}$ for elucidating the activation mode (associative or dissociative) of ligand substitution reactions has been demonstrated particularly for solvent-exchange reactions.[10] A dissociative mechanism has been proposed for the exchange reactions involving unidentate solvent molecules, Me_2SO, DMF, CH_3CN, H_2O, etc., on the basis of $\Delta V^{\ddagger}$ values 5.7–23 cm^3 mol^{-1} and positive activation entropies $\Delta S^{\ddagger}$. Our moderately positive $\Delta V^{\ddagger}$ suggests an I_d mechanism, while the modest negative $\Delta S^{\ddagger}$ indicates an I_a mechanism. Such a confusion may be solved as follows.

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Table IV. Kinetic Data for the Ligand Exchange of $[M^{III}(acac)_3]$ in Hacac[a]

M^{III}	r/pm[b]	$\Delta H^{\ddagger}$[c]/kJ mol^{-1}	$\Delta S^{\ddagger}$[c]/J K^{-1} mol^{-1}	effect of [Hacac][d]	k_1^H/k_1^D	effect of $[H_2O]$[e]	mechanism	ref
Co	52.5	152	+80	0	1.0	0	I_d or D	5, 9
Cr	61.5	120	−21	1	1.5	0	I (see text)	5, 8
Al	53.0	85	−38	1	1.6	1	I (see text)	this work
Ru	68	115	−61			0	I_a	5
Rh	66.5	118	−79		1.4	0	I_a	5
V	64.0	73	−73	1	1.0	1	I_a	7
Fe	64.5	60	−92	1	1.0	1	I_a	6

[a] Rate equation is $k_o = k_1 + k_2[H_2O]$. [b] Ionic radius.[31] [c] For k_1. [d] $k_o = (k'_1 + k'_2[H_2O])[Hacac]^{0 \text{ or } 1}$ in Hacac–CH_3CN mixed solvent ([Hacac] = 2–9.7 M). [e] Presence (1) or absence (0) of k_2 term.

Swaddle[27] and Merbach[10] pointed out the usefulness of the ratio of $\Delta V^{\ddagger}$ to the partial molar volume $V_S°$ of the solvent molecule as a criterion for distinguishing the interchange mechanisms I_a or I_d in the absence of particular solvent–solvent interaction such as hydrogen bonding in the bulk. The greater the absolute value of the ratio $\Delta V^{\ddagger}/V_S°$, the nearer the mechanism is to the limiting A or D mechanism. The ratio is less than 0.1 for the present system and ca. 0.2 for those systems involving unidentate solvent molecules. Therefore, a mechanism of less dissociative mode is suggested for the present system; i.e., a more enhanced participation of the incoming ligand in the transition state is expected.

Both electrostatic and steric effects could be encountered. However, the electrostatic effect does not seem to be governing. The unidentate molecules in Table III have greater donor numbers[28] than Hacac and their aluminum complexes have a +3 overall charge. If the electrostatic factor were predominant, they would exhibit more extensive participation of I_a character than our complex does. A high positive charge could enhance the ligation of the polar solvent molecules around the first coordination sphere in the ground state, but this would be less so in the transition state, where the coordination bonds are elongated. Therefore, the $\Delta V^{\ddagger}$ value could be greater for +3 complex cations than for our chargeless complex. The extent of such second-sphere ligation may be related to the dielectric constant (ϵ) of the solvent. The difference of $\Delta V^{\ddagger}$ values among the +3 complexes is not related to the ϵ values. Such a contribution may not be ignored but does not seem to be ruling factor.

It seems as if steric factors play an important role in determining the $\Delta V^{\ddagger}$ values. A significant effect of the bulkiness of the ligand was seen on the observed $\Delta V^{\ddagger}$ value in a couple of instances.[29] Bulky solvent molecules repulse each other at the coordination sphere to decrease the contribution of the incoming ligand in the transition state. Coordinated $acac^-$ has two methyl groups as do Me_2SO and DMF but seems to provide a less crowded coordination sphere than Me_2SO and DMF do, because of the flat enolate ring. The stacking of Hacac on the coordinated $acac^-$ may be possible in both the transition and the ground states. This may be the reason why the present exchange has less dissociative character.

Comparison with Related Reactions. $[Al(acac)_3]$ was resolved and the racemization rate determined.[30] The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are largely positive in mixtures of isopentane–ethanol (1:1 v/v) and isopentane–diethyl ether (4:1) (Table IV), and a mechanism via a pentacoordinated state involving a unidentate $acac^-$ was suggested. This result supports our view that the participation of Hacac in the transition state is particularly significant in our exchange reaction and forms a striking contrast to the fact that the racemization of $[Co(acac)_3]$ gave almost the same $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values as those of ligand isotopic exchange in Hacac, which proceeds via an I_d or D mechanism.[9]

We have shown that the ligand isotopic exchanges of $[M(acac)_3]$ (M = V, Cr, Fe, Ru, Co, and Rh) in neat Hacac[5-7] have a common rate-determining step at k_a in the k_1 path and that the substitution mechanism has been discussed on the basis of kinetic data in Table IV.[5-9] This view is also true for the present exchange. The moderately negative $\Delta S^{\ddagger}$ value for Al, together with Cr, suggests in-between character in the substitution mechanism. The Cr complex is claimed to undergo ligand exchange dissociatively in CH_3CN and associatively in neat Hacac.[5,8] The substitution of Al complexes is concluded to proceed through an interchange mechanism largely affected by the nature of the ligand as mentioned above.

The difference between $[Co(acac)_3]$ and $[Al(acac)_3]$ could be pointed out. Tervalent ions of Co and Al have similar small ionic radii (0.53 and 0.525 Å),[31] and their complexes have been understood to exhibit similar ligand substitution mechanisms of I_d or limiting D character because of the small size of the metal center. We have found, however, a rather significant difference in activation parameters, especially in $\Delta S^{\ddagger}$, indicating that Al has less dissociative character in substitution than Co does. The reason may be related to the difference in the electron configurations of both ions with and without d electrons, which can repulse an incoming electron pair in the transition state to make an interchange mechanism dissociative, but we have to wait for the $\Delta V^{\ddagger}$ values for $[Co(acac)_3]$.

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Registry No. Hacac, 123-54-6; $Al(acac)_3$, 13963-57-0; D_2, 7782-39-0; H_2O, 7732-18-5; acetonitrile, 75-05-8.

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