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Kinetics and Mechanisms of Ligand Exchange Reactions of Tris(acetylacetonato)-chromium(III), -cobalt(III), -ruthenium(III), and -rhodium(III) in Acetylacetone

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(Received May 15, 1979)

Tris(acetylacetonato[2-^{14}C])-cobalt(III), -chromium(III), -ruthenium(III), and -rhodium(III) undergo ligand exchange in acetylacetone(Hacac) at 85—190 °C without decomposition of the complexes. The exchange rate is proportional to the complex concentration, and the first-order rate constant k_0 decreases in the sequence Co(III)>Cr(III)>Ru(III)>Rh(III), $k_0/10^{-5}$ s^{-1} being 2.4 (93 °C), 5.6 (117 °C), 9.5 (158 °C), and 2.4 (185 °C), respectively. The activation enthalpies and entropies and deuterium isotope effect on k_0 are significantly different between the Co(III) and the Cr(III), Ru(III) and Rh(III) complexes. An intermediate involving an one-ended acetylacetonate and a solvent molecule(Hacac) is concluded to be formed in the rate-determining step. The S_N1 and the S_N2 mechanism are assigned to the exchange reactions of the Co(III) complex and the others, respectively, for the rate-determining steps.

The exchange reaction of solvo ligands with solvent molecules has been scarecely studied with bidentate ligands, although the reaction is profitable for the assignment of the substitution mechanisms. Pearson and Lanier[1] observed, as a unique example, the rate and the rate limits for the exchange of ethylene glycol coordinated to bivalent transition metal ions in ethylene glycol. In this work, the ligand exchange reactions of tris(acetylacetonato) complexes of tervalent transition metal ions(M(acac)$_3$; M(III)=Cr(III), Co(III), Ru(III), and Rh(III)) have been investigated in a reaction system consisting of only two components, the labelled complex as solute and acetylacetone (Hacac) as solvent.

In the previous papers, we have proposed the mechanisms of the ligand exchange reactions of Cr(acac)$_3$ and Co(acac)$_3$ in acetonitrile.[2,3] However, there remains an ambiguity in the mechanisms concerning participation of solvent molecule. In the present work, we have simplified the reaction system, confirmed the mechanisms of the reactions and suggested relative rates of individual steps in the substitution processes of the bidentate.

The ligand substitution kinetics of Co(III), Ru(III), and Rh(III) complexes containing O_6 core have been hardly studied,[3—5] although those of the N_5O type complexes represented by $[M^{III}(NH_3)_5H_2O]^{3+}$ containing the present metal ions have been systematically studied.[6,7] Therefore, we have also a unique opportunity of comparing the substitution mechanisms of the present exchange of the O_6 type complexes with those of the water exchange of the N_5O type complexes.[8—11]

Experimental

Materials. The labelled species, Hacac[2-^{14}C],[12] Hacac[*methylene*-$^2H_2$],[2] Co(acac[2-^{14}C])$_3$[3] and Cr(acac[2-^{14}C])$_3$[2] have been prepared and purified by the reported methods. The labelled complex, Ru(acac[2-^{14}C])$_3$, was prepared from ruthenium(III) chloride and Hacac[2-^{14}C] by the method of Wilkinson[13] and sublimed *in vacuo* (140 °C, 1 mmHg; 1 mmHg≒133 Pa). Both radioactive and non-active Rh(acac)$_3$ were prepared as follows; Hacac[2-^{14}C] or the ordinary Hacac (3 ml), and a few drops of water added to a mixture of rhodium(III) chloride trihydrate (0.5 g) and potassium hydroxide (0.3 g), and refluxed for 10 h at 110 °C and then for 2 h at 120 °C, with stirring. The Hacac and water were evaporated off from the resulting mixture, under a reduced pressure at room temperature. Light yellow crystals (0.3 g) were sublimed from the residue at 170 °C under 1 mmHg. Anal. (for the non-active Rh(acac)$_3$) Found; C, 44.71; H, 5.38%. Calcd for $RhC_{15}H_{21}O_6$; C, 45.01; H, 5.29%. Mp 262 °C for both the complexes (lit[14] 260 °C).

The deuterium content of Hacac[*methylene*-$^2H_2$] in the methylene moiety was determined to be 80% by PMR spectroscopy. Specific activities of Hacac[2-^{14}C] and the labelled complexes were *ca.* 10^4 and 10^3 dpm mg^{-1}, respectively. The solvent Hacac was dried over anhydrous sodium sulfate and distilled.

Kinetic Procedure. Aliquots of the solution of the labelled complex (0.003—0.009 M; 1 M=1 mol dm^{-3}) in Hacac or Hacac[*methylene*-$^2H_2$] containing 0.01—0.1 M water were sealed in 5 to 10 Pyrex glass tubes (10 mm in diameter, 50 mm in length) after degassing, and heated in a thermostated oil bath at 85—190 °C. The tubes were withdrawn one by one at appropriate time intervals and put into a cold water bath. From a given amount of the solution in each tube, the solvent was evaporated *in vacuo* at room temperature to recover the complex quantitatively in the original tube. The total amount of the recovered complex was dissolved in a given volume of acetonitrile and a given part of the solution was dissolved in toluene containing 0.1% *p*-terphenyl and 0.04% *p*-bis(5-phenyl-2-oxazolyl)benzene (POPOP) for scintillation pulse counting with a Nuclear Chicago Unilux IIA Liquid Scintillation Counter. The water content was determined for each portion of the solution by Karl Fischer titration.

Calculation of the Exchange Rate. The rates were calculated by the McKay equation

$$\text{Rate} = \frac{3[\text{M}][\text{Hacac}]}{3[\text{M}]+[\text{Hacac}]}\,\frac{\ln[(x_0-x_\infty)/(x_t-x_\infty)]}{t}$$

$$\fallingdotseq 3[\text{M}]\ln(x_0/x_t)/t \quad ([\text{Hacac}]\gg[\text{M}],\ x_\infty\fallingdotseq 0) \qquad (1)$$

where [M] and [Hacac] stand for the concentration of the complex and acetylacetone, respectively. The x's are the specific counting rates of the complex for the time indicated by the subscripts.

Hacac is in tautomeric equilibrium between enol and keto forms, but the interconversion rate in neat Hacac is significantly greater[15] than the present exchange rates in the given temperature ranges; the tautomers are not kinetically distinguishable. Therefore, the overall concentration of

Hacac was used in the kinetic treatment.

Results

Verification of the Exchange Reactions. In the case of the Cr(III) and Co(III) complexes, the McKay plots gave straight lines up to at least 50—60% of the completion of exchange (Fig. 1) and the visible absorption spectra and the water content of the reaction mixture did not vary throughout the reaction. Hence, no other reaction than the exchange takes place.

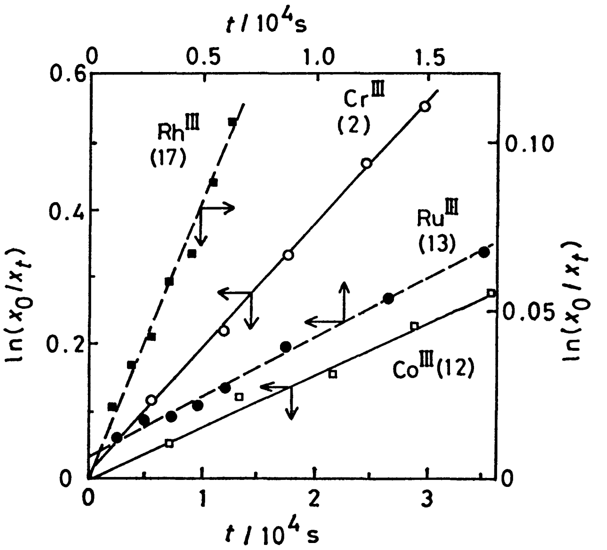


Fig. 1. Typical McKay plots for the ligand exchange of $M^{III}(acac)_3$ in acetylacetone. Numbers in parentheses stand for the experimental numbers in Table 1.

When the reaction mixture of the Ru(III) complex was heated at the given temperature, yellow substances were formed in the solution and water content increased gradually with time (Table 1). However, the visible absorption spectra of the solution did not change throughout the reaction. The linear McKay plots were obtained up to at least 50% of the completion of exchange. When the solvent was evaporated from 1 ml of the solution which had been heated for 3×10^4 s, a small amount of yellow oil (*ca.* a few mg at most) and the complex were left in the original tube. The oil was separated from the complex by vacuum distillation at 100 °C. The counting rate (^{14}C) of the oil was nearly zero. These facts show that the yellow substances should be formed not from the complex but from the solvent (probably, condensation polymerization of acetylacetone to give water as a by-product).

In the case of the Rh(III) complex, the similar changes in the color (the formation of the oil) and in the water content of the reaction mixture were observed as in the case of the Ru(III) complex. The counting rate of the oil recovered from the solution (heated for 10^4 s) was also nearly zero. The fact shows that the complex did not decompose. The McKay plots gave straight lines up to 10% of the completion of exchange and then the slopes of the plots increased steeply. The exchange rates were determined from the plots at the initial stage.

These facts show that the decrease of the specific counting rate of the complexes shown in Fig. 1 corresponds to the exchange of acetylacetonate between the complex and the solvent,

$$M^{III}(\overset{*}{acac})_3 + Hacac \rightleftharpoons M^{III}(acac)_3 + H\overset{*}{acac} \qquad (2)$$

where asterisks denote ^{14}C labelling.

Kinetic Data. The exchange rate was proportional to the concentration of the complex, [M], (Table 1) and expressed by

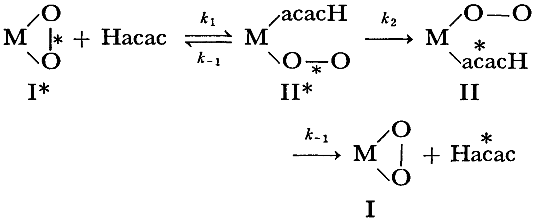
$$\text{Rate} = k_0[M] \qquad (3)$$

where k_0 is the observed first-order rate constant.[16] The k_0 values were independent of $[H_2O]$ for the Cr(III) and Co(III) systems (Table 1). For the Ru(III) and Rh(III) systems, the McKay plots gave straight lines, regardless of the increase in water concentration with the progress of the exchange (Fig. 1 and Table 1). Hence, the k_0 values can be reckoned to be independent of $[H_2O]$.

When Hacac[*methylene*-$^2H_2$] was used as the solvent in place of the ordinary Hacac, the k_0 values for the Cr(III) and Rh(III) systems decreased but those for the Co(III) system did not (Table 1). Ratio of the rate constants $k_0(H)/k_0(D)$ are calculated and given in Table 2, together with the activation parameters.

Discussion

Reaction Route of the Exchange. Since k_0 was independent of $[H_2O]$, the chemical species participating in the rate-determining step should be only M-(acac)$_3$ and Hacac. Consequently probable reaction routes are very much restricted. Equation 4 can be assumed almost exclusively as a common route for these exchange reactions,



$$\underset{\text{I*}}{M\begin{smallmatrix}/O\\ \mid *\\ \backslash O\end{smallmatrix}} + Hacac \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{II*}}{M\begin{smallmatrix}/acacH\\ \\ \backslash O\overset{}{\underset{*}{-}}O\end{smallmatrix}} \xrightarrow{k_2} \underset{\text{II}}{M\begin{smallmatrix}/O-O\\ *\\ \backslash acacH\end{smallmatrix}} \xrightarrow{k_{-1}} \underset{\text{I}}{M\begin{smallmatrix}/O\\ \mid\\ \backslash O\end{smallmatrix}} + H\overset{*}{acac} \qquad (4)$$

where O–O and I* denote $acac^-$ and $M(\overset{*}{acac})_3$, respectively. (Two $acac^-$ chelates are omitted in these species.) The original complex I* and a solvent molecule(Hacac) produce an intermediate II*, which is converted into II through the proton transfer, and then II changes into I and $H\overset{*}{acac}$. The intermediate II* involves an one-ended bidentate and a solvent molecule as unidentates. Such a type of the intermediate is generally accepted as an intermediate for dissociation and formation reactions of chelates in octahedral complexes in coordinating solvents.[17–19] Acetylacetone, with a donor number *ca.* 17,[20] can be regarded as coordinating solvent. Therefore, the formation of II* is considered to be reasonable.

The k_1 step in Eq. 4 should be the rate-determining step. If k_2 were smaller than k_1, the proton transfer process would be the rate-determining step. However, such a mechanism does not interpret the different

Table 1. Rates and first-order observed rate constants for the ligand exchange of $M^{III}(acac)_3$ in Hacac

Exp. No.	M(III)	T / °C	[M] / 10^{-3} M	$[H_2O]$ / M	Rate / 10^{-7} M s^{-1}	k_o / 10^{-5} s^{-1}
1	Cr(III)	108.9	3.04	0.035		2.4 ±0.3
2		117.1	2.98	0.025	1.6	5.4 ±0.3
3			5.67	0.025	3.4	6.0 ±0.3
4			3.00	0.086		5.6 ±0.5
5			2.95	0.013		4.0 ±0.4[b)]
6		124.9	2.87	0.043		11.2 ±0.3
7	Co(III)	85.0	4.28	0.048		0.73±0.08
8		93.0	4.32	0.048	1.0	2.4 ±0.3
9			8.01	0.030	2.4	2.3 ±0.3
10			4.33	0.077		2.3 ±0.2
11			4.40	0.028		2.3 ±0.1[b)]
12		101.1	4.28	0.048		6.8 ±0.6
13	Ru(III)	150.0	3.11	0.01—0.03[a)]		5.2 ±0.2
14		157.5	3.11	*ca.* 0.03		9.5 ±0.3
15		165.1	3.11	*ca.* 0.04		16.3 ±0.5
16	Rh(III)	179.7	4.35	0.04—0.07[a)]		1.60±0.09
17		185.2	4.35	0.02—0.07[a)]	1.0	2.37±0.17
18			8.55	*ca.* 0.05		2.39±0.12
19			4.33	*ca.* 0.05		2.23±0.13[c)]
20			4.27	*ca.* 0.03		1.85±0.13[b)]
21		190.2	4.35	0.03—0.05[a)]		3.33±0.30

a) Increased with time. b) In Hacac[*methylene*-$^2H_2$] (deuterium content: 80%). c) In Hacac[*methylene*-$^2H_2$] (deuterium content: 37%).

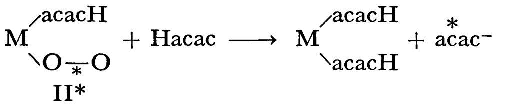
Table 2. Activation parameters and deuterium isotope effect on rate for the ligand exchange of $M^{III}(acac)_3$ in Hacac

M(III)	ΔH^* / kcal mol^{-1}	ΔS^* / cal K^{-1} mol^{-1}	$k_o(H)$[a)] / $k_o(D)$
Cr(III)	28.8±0.7	−5.0±2.2	1.5
Co(III)	36.4±2.2	+19.2±6.1	1.0
Ru(III)	27.4±1.8	−14.6±4.5	—
Rh(III)	28.3±0.5	−19.0±1.4	1.4

a) The ratio of the rate constants of the exchange in normal and deuterated acetylacetone(Hacac[*methylene*-$^2H_2$]).

values of the kinetic parameters shown in Tables 1 and 2 among the complexes(*vide infra*).

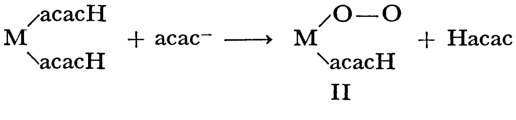
Besides the k_2 process, an alternative route (Eqs. 5—7) containing the complete dissociation of the coordinated $\overset{*}{\mathrm{acac}}^-$ might be considered between II* and II in Eq. 4. (Notations are identical with those for Eq. 4.)



$$\mathrm{M}\begin{array}{l}\diagup \mathrm{acacH}\\ \diagdown \mathrm{O}\underset{*}{-}\mathrm{O}\end{array} + \mathrm{Hacac} \longrightarrow \mathrm{M}\begin{array}{l}\diagup \mathrm{acacH}\\ \diagdown \mathrm{acacH}\end{array} + \overset{*}{\mathrm{acac}}^- \qquad (5)$$

II*

$$\overset{*}{\mathrm{acac}}^- + \mathrm{Hacac} \longrightarrow \mathrm{H}\overset{*}{\mathrm{acac}} + \mathrm{acac}^- \qquad (6)$$



$$\mathrm{M}\begin{array}{l}\diagup \mathrm{acacH}\\ \diagdown \mathrm{acacH}\end{array} + \mathrm{acac}^- \longrightarrow \mathrm{M}\begin{array}{l}\diagup \mathrm{O}-\mathrm{O}\\ \diagdown \mathrm{acacH}\end{array} + \mathrm{Hacac} \qquad (7)$$

II

However, the route is not consistent with the observed $k_o(H)/k_o(D)$ values for the Cr(III) and Rh(III) systems (Table 2), since it is unlikely that the k_o values are governed by the proton transfer process (Eq. 6) which is considered to be much faster than the dissociation process (Eq. 5). For the Co(III) complex, the complete dissociation of $acac^-$ (Eq. 5) has been suggested to be much slower than the exchange in acetonitrile.[3)] Therefore, the k_2 process in Eq. 4 must be indispensable for the exchange to take place.

So far as k_1 is very small as compared with k_{-1} and k_2 and the stationary-state condition is assumed for II* in Eq. 4, k_o is expressed by Eq. 8,

$$k_o = k_1\frac{k_2}{k_{-1}+k_2} \qquad (8)$$

where k_1 is taken to be first-order ([M]≪[Hacac]). The k_1 process represents the rate-determining step, and the term $k_2/(k_{-1}+k_2)$ indicates a branching ratio for the accomplishment of the exchange from II*.

Substitution Mechanisms of the Rate-determining Step. Table 2 shows that the Co(III) complex gives different activation parameters and $k_o(H)/k_o(D)$ values from those of the other complexes. The ΔH^* value for the Co(III) complex is distinctly higher than those for the others. The ΔH^* values for substitution processes of complexes containing the present tervalent metal ions are reported to be in similar ranges to one another.[6)] The Co(III) complex has positive ΔS^*, whereas others have negative values. The difference reaches 24—38 cal K^{-1} mol^{-1}. These facts suggest the different mechanisms between the Co(III) and the other complexes. Since the rate-determining step is reckoned to be the k_1 process, the acitivation parameters should reflect mostly those for this step. It is most likely that the intermediate II* in Eq. 4 is formed by the S_N1 and the S_N2 mechanism for the Co(III) and the other complexes, respectively.[21]

The difference in $k_o(H)/k_o(D)$ values in Table 2 is also interpreted on the basis of the same assignment of the mechanism. The Co(III) complex gives no isotope effect, whereas the Cr(III) and Rh(III) complexes have the ratio more than unity. If $k_{-1} \ll k_2$ in Eq. 8,

$$k_o = k_1 \tag{9}$$

If $k_{-1} \gg k_2$

$$k_o = k_1 k_2 / k_{-1} \tag{10}$$

Since the deuterium isotope effect on k_o must be attributable to that on k_2, Eqs. 9 and 10 should be applicable to the Co(III) and the other complexes with their inequalities, respectively. The rate constant k_{-1} can be assumed to be much more susceptible to the nature of M^{III} than k_2 is, since the k_{-1} process contains the dissociation and formation processes of M^{III}–O bonds, whereas the k_2 process does not. So far as k_2 for these metal complexes remains without big difference, the rate constant for the ring closure, k_{-1}, should be responsible for the difference in the inequalities [k_{-1}(for Co(III)) $\ll k_2 \ll k_{-1}$(for Cr(III) and Rh(III))]. The relatively high k_{-1} values assumed for the Cr(III) and Rh(III) complexes might be related to the labilization of cis position by the S_N2 action of unbound atom of a ligand (cis anchimeric effect).[22] Some fast substitution of Cr(III) complexes was interpreted by this effect. Therefore, an intermediate of S_N2 type (IV in Fig. 2) with a structure similar to that proposed for the effect[23] is suggested to be formed on going from I* to II*. On the contrary, such an effect is not expected for the S_N1 substitution. The relatively small k_{-1} assumed for the Co(III) complex is thus accounted for. An intermediate such as III in Fig. 2 may be present in the Co(III) system.

On the other hand, on the assumption that the proton transfer (k_2) in Eq. 4 is the rate-determining step, the following kinetic results are not interpreted; i) the different values of the activation parameters and $k_o(H)/k_o(D)$ for the Co(III) complex with those for the others and ii) a common sequence of the $M(acac)_3$ for the rates of the present exchange and the racemization in chlorobenzene (*vide infra*, the racemization cannot contain such a proton transfer process.)

The two unidentates in II* and II should be cis to each other, at least when the proton is transferred. The presence of trans isomer cannot be excluded, but it does not seem to play important role in the exchange reactions. It may be a dead end species, even if it is formed.

Therefore, the mechanisms illustrated in Fig. 2 can be proposed. The relatively slow and fast ring-closure processes (the k_{-1} step) compared with the proton transfer process (the k_2 step) are suggested for the Co(III) and the other complexes, respectively.

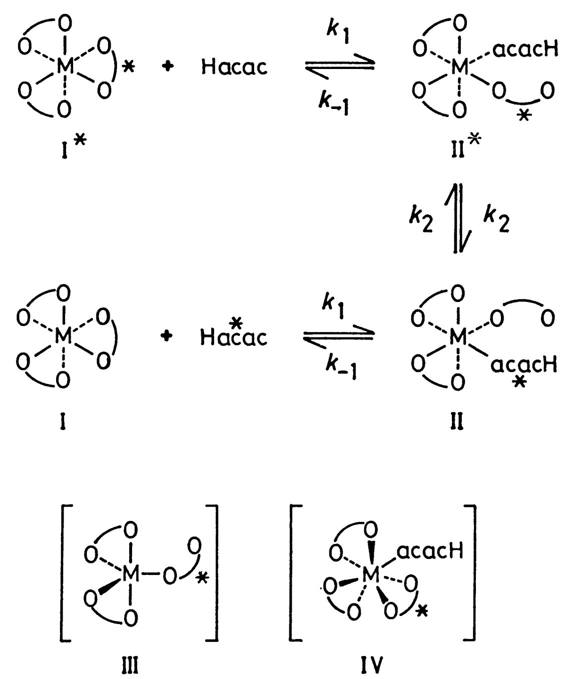


Fig. 2. Mechanisms of the ligand exchange of $M^{III}(acac)_3$ (I) in acetylacetone. The routes I*→III→II* (S_N1) and I*→IV→II*(S_N2) are proposed for the Co(III) and the Cr(III), Ru(III), and Rh(III) complexes, respectively. (The structures of III and IV are only provisional.)

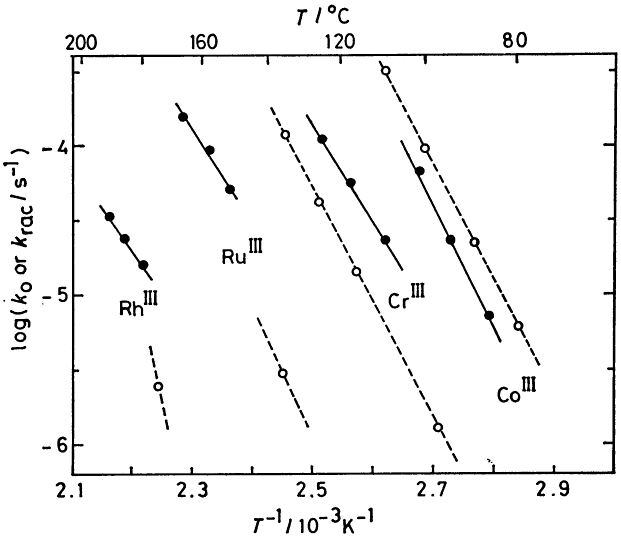


Fig. 3. Arrhenius plots for the reactions of $M^{III}(acac)_3$. Full circles with a solid line: the ligand exchange in acetylacetone (k_o). Open circles with a broken line: the racemization in chlorobenzene(k_{rac}, appoximate values for Ru(III) and Rh(III)[24]).

Comparison of Rates with Racemization. The Arrhenius plots for the exchange (k_o) and the racemization(k_{rac}, in chlorobenzene)[24] of the complexes are given in Fig. 3. The rates of both the reactions decrease in the sequence under the given conditions.

Co(III) > Cr(III) > Ru(III) > Rh(III)

The common sequence suggests that each $M(acac)_3$ has similar reactivities for both the inter- and intramolecular processes.

However, the correlation of the Arrhenius plots of both the reactions for the Co(III) complex is different from that for the other complexes; $k_o > k_{rac}$ and the less steep slopes for k_o in the Cr(III), Ru(III), and Rh(III) complexes, whereas $k_o \doteqdot k_{rac}$(k_{rac} is rather slightly bigger than k_o) and similar gradient of the slopes for the Co(III) complex. A common S_N1 mechanism for both the exchange in acetonitrile and the racemization in chlorobenzene has been concluded for the Co(III) complex, despite of the difference of the solvent.[3] These facts and the conclusion support the difference in the proposed mechanisms for the exchange reactions, so far as the one-ended bond-rupture mechanism(S_N1)[25] opperates commonly in the racemization of these complexes.

Comparisons of the Mechanisms with Related Reactions. The substitution mechanisms for the present exchange reactions can be compared with those of the substitution reactions of unidentates in the tervalent metal complexes, since the rate-determining step of the former reactions is concluded to be the replacement of one of coordinated oxygen atoms in a chelate ring by an Hacac molecule and is comparably simple with that of the latter ones.

Comparison of Mechanisms with Those for Complexes Containing N_5O Core: The water exchange and the anation of various ligands to pentaammineaqua complexes of Co(III),[7,9] Cr(III),[7,10,26–28] Ru(III)[29,30] and Rh(III)[31–36] have been systematically studied in aqueous solutions. The S_N1 and the S_N2 mechanisms were predominantly assigned to the reactions of the Co(III) and the other complexes, respectively. Especially, the mechanisms assigned to the water exchange on the basis of ΔV^* values are generally accepted to be most convincing.[8–11] The Co(III) complexes have a rather exceptional mechanism[37] commonly in both the present and the reported exchange systems, despite of the difference in the charge of the complexes, the assortment of the coordinating atoms, the dentate number of the leaving and entering ligands and the property of the solvents. The ionic radius of M^{III}[11,38] (Co^{III}:52.5, Cr^{III}:61.5, Ru^{III}:68, Rh^{III}:66.5 pm)[41] seems to be commonly an important factor in determining the mechanisms of the exchange reactions of these complexes containing O_6 and N_5O cores.

Comparison of Mechanism among Complexes Containing O_6 Core: The S_N2 mechanism for the present exchange of $Cr(acac)_3$ is consistent with that for the solvent exchange of $Cr(H_2O)_6^{3+}$[37], $Cr(dmf)_6^{3+}$[38] and $Cr(dmso)_6^{3+}$[39] (dmf=*N*,*N*-dimethyformamide, dmso=dimethyl sulfoxide) and for the anation of various ligands to hexaaqua complex ion.[40] The S_N2 mechanism is considered to commonly operate in these reactions of the $Cr^{III}O_6$ complex.

Little information is available concerning the substitution mechanism of the $M^{III}O_6$ type complexes of Co(III), Ru(III), and Rh(III). An S_N2 mechanism is concluded in the exchange of $Rh(acac)_3$, but an S_N1 mechanism was proposed for the water exchange and the bromide anation of $Rh(H_2O)_6^{3+}$.[4,5] The proposed mechanisms for the present Co(III) and Ru(III) complexes may be the first examples for O_6 type complexes of Co(III) and Ru(III), and should be compared with other examples in future.

The author wishes to thank Professor Kazuo Saito for helpful discussions. This work was supported by the Grant-in-Aid from the Ministry of Education.

References

1) R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

2) H. Kido and K. Saito, *Inorg. Chem.*, **16**, 397 (1977).

3) H. Kido and K. Saito, *Bull. Chem. Soc. Jpn.*, **52**, 3544 (1979).

4) W. Plumb and G. M. Harris, *Inorg. Chem.*, **3**, 542 (1964).

5) R. J. Buchacek and G. M. Harris, *Inorg. Chem.*, **15**, 926 (1976).

6) J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 47 (1974).

7) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).

8) F. Monacelli and E. Veil, *Inorg. Chim. Acta*, **1**, 467 (1967).

9) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

10) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).

11) S. B. Tong and T. W. Swaddle, *Inorg. Chem.*, **13**, 1538 (1974).

12) K. Saito and K. Masuda, *Bull. Chem. Soc. Jpn.*, **41**, 384 (1968).

13) G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6146 (1952).

14) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

15) M. Kato, private communication.

16) The equation is estimated for the Ru(III) complex.

17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, J. Wiley and Sons Inc., New York (1967), p. 223.

18) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).

19) U. Nickel, H. Hoffmann and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, **72**, 526 (1968).

20) M. Nishizawa, private communication.

21) For the S_N2 exchange reactions, the equation $k_o = k_o'[\text{Hacac}]$ ($[\text{Hacac}] = 9.7$ M) is suggested. The ΔS^* values calculated for k_o' are -7.3, -17.4 and -23.8 cal K^{-1} mol^{-1} for the Cr(III), Ru(III), and Rh(III) complexes, respectively, being slightly more negative than those for k_o.

22) H. Ogino, T. Watanabe and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975) and references cited therein.

23) S. N. Choi and D. W. Carlyle, *Inorg. Chem.*, **13**, 1818 (1974).

24) R. C. Fay, A. Y. Girgis and U. Klabunde, *J. Am. Chem. Soc.*, **92**, 7056 (1970).

25) A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970).

26) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **51**, 821 (1973).

27) T. Ramasami and A. G. Sykes, *Inorg. Chem.*, **15**, 2885 (1976) and references cited therein.

28) L. Mønsted, *Acta Chem. Scand.*, **A**, **32**, 377 (1978).

29) J. A. Broomhead, L. Kane-Maguire and D. Wilson, *Inorg. Chem.*, **14**, 2575 (1975) and references cited therein.

30) H. Sakamoto, K. Yoshikuni, S. Ohno, K. Ohkubo, and A. Ohyoshi, *Chem. Lett.*, **1974**, 1309 and references cited therein.

31) F. Monacelli, *Inorg. Chim. Acta*, **2**, 263 (1968).

32) H. L. Bott, A. J. Poë and K. Shaw, *J. Chem. Soc.*,

Sect. A, **1970**, 1745.

33) C. Chatterjee and P. Chaudhuri, *Indian J. Chem.*, **11**, 777 (1973).

34) E. Borghi and F. Monacelli, *Inorg. Chim. Acta*, **23**, 53 (1977).

35) S. C. Chan, *Aust. J. Chem.*, **20**, 61 (1967).

36) R. van Eldik, *Z. Anorg. Allg. Chem.*, **416**, 88 (1975).

37) D. R. Stranks and T. W. Swaddle, *J. Am. Chem. Soc.*, **93**, 2783 (1971).

38) S. T. D. Lo and T. W. Swaddle, *Inorg. Chem.*, **14**, 1878 (1975).

39) D. L. Carle and T. W. Swaddle, *Can. J. Chem.*, **51**, 3795 (1973).

40) D. Thusius, *Inorg. Chem.*, **10**, 1106 (1971) and references cited therein.

41) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969), **26**, 1046 (1970).