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Kinetics of Ligand Exchange between Tris(acetylacetonato[2-^{14}C])cobalt(III) and Acetylacetone in Acetonitrile. Evidence for S_N1 Mechanism

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Tris(acetylacetonato[2-^{14}C])cobalt(III) undergoes ligand isotopic exchange with acetylacetone(Hacac) in acetonitrile at 85—100 °C without decomposition and solvolysis. The exchange rate is proportional to the complex concentration (0.002—0.007 M, 1 M = 1 mol dm^{-3}), the first-order rate constant k_0 being independent of [Hacac] (0.001—0.97 M). $k_0 = 1.6 \times 10^{-5}$ s^{-1} at 93.2 °C. The activation enthalpy and entropy are 38 ± 4 kcal mol^{-1} (1 cal = 4.18 J) and 23 ± 8 cal K^{-1} mol^{-1}, respectively. Trichloroacetic acid (<0.02 M) gives acid catalysis. The rate-determining step should be the S_N1 Co–O cleavage in a chelate ring to give a five coordinate intermediate.

The complexes of Co(III) along with those of Cr(III) and Ni(II) have played an essential role for enabling us to understand the mechanism of octahedral substitution.[1,2] A number of kinetic studies were carried out on Co(III)N$_5$O type complexes represented by $[Co(NH_3)_5(H_2O)]^{3+}$.[3] However, little information is available concerning kinetics and mechanisms of ligand substitution processes of spin-paired Co(III) complexes containing Co(III)O$_6$ core. Kinetics of aquation of $[Co(ox)_3]^{3-}$ [4] and $[Co(mal)_3]^{3-}$ [5] (ox = oxalate, mal = malonate) are complicated for discussing the substitution mechanism around the metal ion. Water exchange[6] and the anation of chloride[7] for $[Co(H_2O)_6]^{3+}$ were kinetically studied only in the presence of $[Co(H_2O)_6]^{2+}$.

In a previous paper, we discussed the mechanism of the ligand exchange between Cr(acac[2-^{14}C])$_3$ and acetylacetone (Hacac) in acetonitrile.[8] The rates of the ligand exchange of the present complex in toluene, anisole, and chlorobenzene under conditions involving partial decomposition of the complex were observed.[9] We have found that the decomposition of Co(acac)$_3$ in acetonitrile subsides on elimination of dissolved oxygen, and have reinvestigated the ligand exchange kinetics to disclose the substitution mechanism at the low-spin Co(III)O$_6$ core.

Experimental

Materials. Acetylacetone[2-^{14}C] was prepared and purified as reported.[10] Acetylacetone was dehydrated with calcium sulfate and distilled. Co(acac[2-^{14}C])$_3$ and Co(acac)$_3$ were synthesized from the labelled and the commercial ligand, respectively, by the usual method,[11] and sublimed *in vacuo* at *ca.* 130 °C. Deuterium oxide (spectroscopic grade, E. Merck, 99.75%) was used without further purification. Trichloroacetic acid was sublimed *in vacuo*. Acetonitrile was distilled twice in the presence of phosphorus pentaoxide.

Kinetic Procedure. Two ml portions of acetonitrile solution containing Co(acac[2-^{14}C])$_3$ (0.0017 to 0.0070 M, 1 M = 1 mol dm^{-3}), Hacac (0.001 to 0.97 M), and water (0.02 to 0.12 M), were degassed and sealed in 3—5 Pyrex glass tubes (diam. 10 mm, length 80 mm) *in vacuo* (10^{-3} mmHg). The tubes were simultaneously heated in a silicone oil bath at 85—101 °C, withdrawn one by one at appropriate time intervals and put into a cold water bath. Hacac, water and acetonitrile were collected individually from the 1 ml portions by distilling into small tubes in a liquid nitrogen bath *in vacuo* at room temperature to leave Co(acac)$_3$ in the original tubes. (Trichloroacetic acid, whenever present in the reaction mixture also remained in the original tubes.) Both Hacac and Co(acac)$_3$, quantitatively recovered and found to be spectroscopically pure, were separately dissolved in anisole containing 0.1% *p*-terphenyl and 0.04% *p*-bis(5-phenyl-2-oxazolyl)benzene(POPOP), the counting rate being measured with a Nuclear Chicago Unilux IIA Liquid Scintillation Counter. The specific counting rate was calculated from the counting rate and the original weight of the compounds. The water content of the reaction mixture was determined by the Karl Fischer titration before and after the kinetic run; it remained unchanged within experimental error.

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

$$\text{Rate} = \frac{-3[\text{Co}][\text{Hacac}]}{3[\text{Co}]+[\text{Hacac}]} \frac{\ln(1-F)}{t},$$

where [Co] and [Hacac] stand for the concentrations of the complex and the free ligand, respectively, t is the lapse of time in seconds, and F the fraction of reaction which is expressed by $(x_0-x_t)/(x_0-x_\infty)$, x being the specific counting rate of the complex or the free ligand at the time indicated by subscript.

Hacac is in tautomeric equilibrium between enol and keto form, but the intercoversion rate is *ca.* 10—100 times as great as the exchange rate in the given temperature range. The total concentration of Hacac, therefore, was taken to be [Hacac].

Results

The absorption spectra of the reaction mixtures remained unchanged throughout the reaction. The McKay plots gave straight lines up to at least 75% completion of the exchange. The F values individually calculated from the measured specific counting rates of Hacac and Co(acac)$_3$ coincide with each other within experimental error. Thus no reactions other than the isotopic exchange

$$\text{Co}(\overset{*}{\text{acac}})_3 + \text{Hacac} \rightleftharpoons \text{Co(acac)}_3 + \text{H}\overset{*}{\text{acac}} \qquad (1)$$

took place during the course of heating. No significant zero time exchange was observed. The rate is proportional to the complex concentration (0.0017—0.0070 M) as shown in Table 1, and expressed by

$$\text{Rate} = k_0[\text{Co}], \qquad (2)$$

where k_0 is the observed first-order rate constant. The k_0 value is independent of the water (0.017—0.119 M, Table 1) and the free ligand concentrations (0.001—1 M, Fig. 1). Thus we have

Table 1. Rates and observed first-order rate constants for the isotopic exchange between $Co(acac)_3$ and Hacac in acetonitrile at 101.1 °C ([Hacac]$=9.75\times10^{-3}$ M)

[Co] / 10^{-3} M	[H_2O] / 10^{-3} M	R / 10^{-8} M s^{-1}	k_o / 10^{-5} s^{-1}
1.74	69	8.9±0.4	5.1±0.2
3.48	66	18 ±1	5.1±0.2
6.59	72	38 ±2	5.4±0.3
3.48	17	17 ±1	4.9±0.3
3.48	119	18 ±1	5.3±0.3

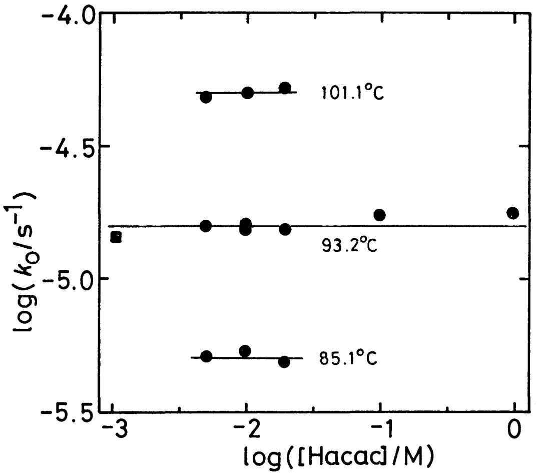


Fig. 1. Log-log plots of the observed rate constant k_o *vs.* the concentration of the free ligand, [Hacac], for the ligand exchange of Co(acac[2-^{14}*C*])$_3$ in acetonitrile. ([Co]$=3.5\times10^{-3}$ M (circles), 9.9×10^{-3} M (square). [H_2O]$=7\times10^{-2}$ M.)

$$k_o = k_i[\text{Hacac}]^0[\text{H}_2\text{O}]^0. \qquad (3)$$

When D_2O was added to the reaction mixtures in place of H_2O, no change occured in k_o.

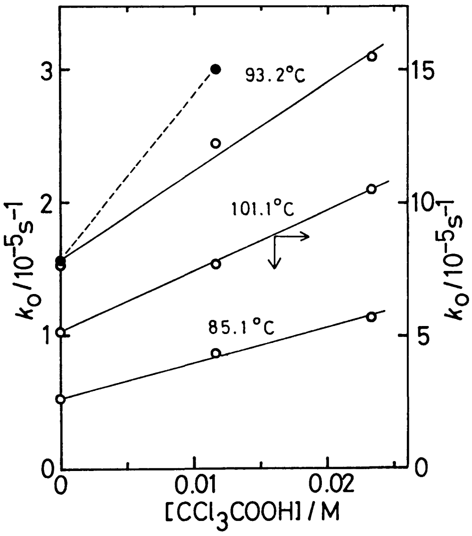


Fig. 2. Influence of trichloroacetic acid and deuterium oxide on the exchange rate. ([Co]$=3.5\times10^{-3}$ M, [Hacac]$=9.7\times10^{-3}$ M and [H_2O]$=7\times10^{-2}$ M for open circles. D_2O(5×10^{-2} M)+H_2O(2×10^{-2} M) as the original ingredients for full circles.)

In the presence of trichloroacetic acid, the exchange proceeded apparently by 20—30% at zero time, which would be separation induced exchange. The k_o value depends on the acid concentration at given concentrations of the complex (0.0035 M), the free ligand (0.0097 M) and water (0.07 M) (Fig. 2). The solid lines have intercepts, which coincide with k_i values obtained in the absence of the acid. Thus we have

$$k_o = k_i + k_a[\text{CCl}_3\text{COOH}]. \qquad (4)$$

When D_2O was added to the reaction mixture in place of H_2O, k_o increased significantly in the presence of the acid (Fig. 2). Ratio of the rate constants (k(H)/k(D)) was calculated on the assumption that equilibrium was attained for all the dissociable protons and deuterons in the reaction system.

The rate constants are summarized in Table 2 together with the activation parameters and k(H)/k(D) values.

Discussion

Equation 4 indicates that the exchange (Eq. 1) proceeds by the two paths, k_i and k_a.

Rate-determining Steps of the k_i Path. Equations 2 and 3 indicate the participation of only the complex in the rate-determining step of the k_i path.

The k_i value is similar to that of the first-order rate constant k_{rac} of the racemization of $Co(acac)_3$ in chlorobenzene in a similar temperature region.[12] Their activation enthalpies and entropies are also very

Table 2. Kinetic data for ligand exchange, racemization and isomerization of tris (β-diketonato)cobalt(III) in organic solvents

Reactions	Rate constants: Parameters	85.1 °C	93.2 °C	101.1 °C	k(H)/k(D)	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}
			$Co(acac)_3$				
Exchange$^{a,e)}$	k_i/10^{-5} s^{-1}	0.51±0.02	1.56±0.02	5.14±0.21	1.0	38 ±4	23 ±8
	k_a/10^{-4} M^{-1} s^{-1}	2.9 ±0.2	7.2 ±0.5	22.9±0.4	0.4	34 ±3	18 ±7
Racemizn.$^{b,f)}$	k_{rac}/10^{-5} s^{-1}	1.4$^{c)}$	4.0$^{c)}$	13$^{c)}$	...	34.1±0.6	14 ±2
			fac-Co(bzac)$_3$$^{d)}$				
Isomerizn.$^{g)}$	k_{iso}/10^{-4} s^{-1}	1.83±0.12$^{b)}$	(96.1 °C)		...	32.0±0.5	11.0±1.3
		1.89±0.09$^{a)}$	(95.8 °C)		...	...	...

a) In acetonitrile. b) In chlorobenzene. c) Interpolated value. d) bzac$^-$=benzoylacetonate. e) This work. f) Ref. 12. g) Ref. 13.

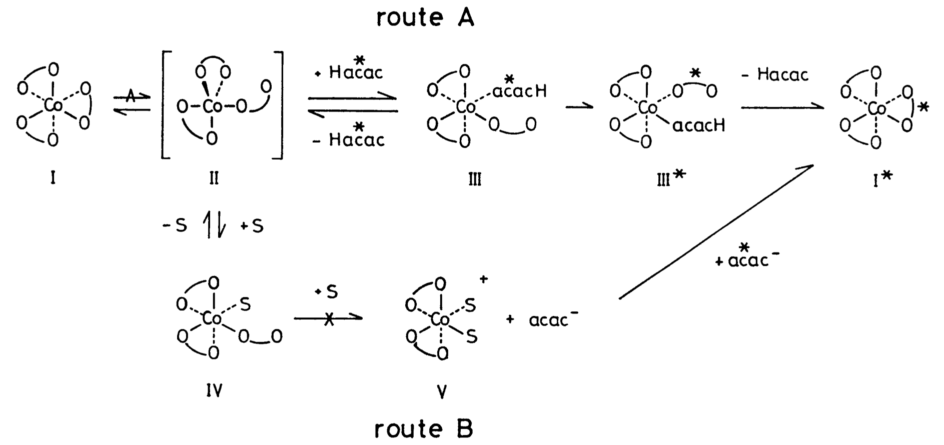


Fig. 3. Proposed mechanism for the ligand exchange of Co(acac[2-^{14}C])$_3$ in acetonitrile. (The structure of II is provisional. Asterisks denote ^{14}C labelling. Arcs and S represent acetylacetonate and acetonitrile or H_2O, respectively.)

similar (Table 2). This suggests a common rate-determining step for the reactions, despite the difference in solvent. The mechanism of the racemization has not been verified, but it is anticipated to be very similar to that of the racemization and the isomerization of *fac*- and *mer*-tris(benzoylacetonato)cobalt(III) (Co(bzac)$_3$) in chlorobenzene,[13] on the basis of similar values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Girgis and Fay verified that these reactions of Co(bzac)$_3$ proceed by an intramolecular mechanism and found that the rates are independent of solvents including chlorobenzene and acetonitrile. The racemization of Co(acac)$_3$ in these solvents might proceed similarly. The present k_i value was also insensitive to the variation of solvent, *e.g.* no change by use of acetylacetone as solvent.[14] Thus, there should be a common rate-determining step for these inter- and intra-molecular reactions. It should be the first cleavage of Co–O bond. The bond break would take place by the S_N1 mechanism, since the solvent-assisted S_N2-like path does not seem feasible in these reactions. Consequently, five-coordinate intermediate containing a unidentate acetylacetonate would be formed (I→II in Fig. 3).[15] The intermediate might have an achiral structure, *e.g.*, a trigonal bipyramid shown in Fig. 3.

Mechanism for k_i Path. After the rate-determining step, the k_i path can proceed *via* two possible routes A and B (Fig. 3). In route A, II interacts with free $\overset{*}{\text{Hacac}}$ to form III containing both unidentates, acac⁻ and $\overset{*}{\text{Hacac}}$, as ligands. III is converted into III* by a proton transfer process, and III* turns to I*. In route B, II loses one acac⁻ to give V. The solvent molecule or water may occupy the vacant site. V can pick up $\overset{*}{\text{acac}}^-$. However, route B is unlikely. If the dissociation of the unidentate acac⁻ proceeded fast, direct exchange of acac⁻ between the complex molecules could take place at a measurable rate even in the absence of free Hacac. Such an interchange for Co(bzac)$_3$ was much slower than the isomerization.[13] The intermediate IV, even if it is formed, might be in equilibrium only with II as a dead end species. Therefore, the k_i path must proceed *via* route A. The exchange of the k_i path is understood to consist of the substitution processes (I→III and III*→I*) connected with a proton transfer process (III→III*). The substitution processes should be identical with each other, since reaction routes of exchange reactions are symmetrical.

The substitution process can be reckoned to proceed by the S_N1 mechanism. The mechanism is also in line with the observed activation parameters, a large positive value of $\Delta S^{\neq}$ and a rather large value of $\Delta H^{\neq}$. It is thus demonstrated for the first time that a low-spin complex with Co(III)O$_6$ core undergoes ligand substitution by the S_N1 mechanism, as almost all other complexes with different ligating atoms.[1]

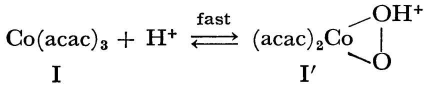
Structure of the Intermediate. The intermediate II seems stable towards the Co–O bond cleavage of the unidentate ligands. Even in the absence of free Hacac, II undergoes racemization but not dissociation. Such a stability may be attributed to the conjugated structure of the ligand. The Co–O bond may be stabilized by concentration of negative charge on the coordinated oxygen, which is partly neutralized with positive charge on the central metal ion. Hence, the structure Co–O–C(CH$_3$)=CH–C(CH$_3$)=O, is presumed for the unidentate in II, III, III*, and IV. This structure is found in *trans*-[Pt^{II}(C$_5$H$_7$O$_2$)$_2$(PEt$_3$)$_2$] in solution (CDCl$_3$) and crystals.[17]

The structure of the intermediates III and III* could not be determined exactly. The enol form of the incoming Hacac is more feasible than the keto form. Enol was found to be much more reactive over keto in the ligand exchange of Ti^{IV}(acac)$_3^+$ in acetonitrile.[18] The keto oxygen of enol Hacac could coordinate to Co(III). Coordination of enolic acetylacetone as a unidentate is found in crystals of Mn^{II}Br$_2$(Hacac)$_2$.[19,20]

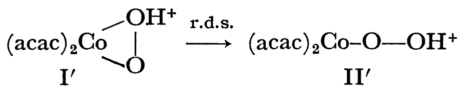
The two unidentates in III (and III*) should be cis to each other, at least when the proton is exchanged. The presence of a trans isomer cannot be excluded, but it does not seem to play an important role in the ligand exchange reaction. It may be a dead end species, even if it is formed.

k_a Path. The exchange reaction (Eq. 1) is catalyzed by trichloroacetic acid (Eq. 4). A remarkable

deuterium isotope effect ($k(\mathrm{H})/k(\mathrm{D})=0.4$) was found for the acid catalyzed $\mathrm{k_a}$ path (Table 2). A $k(\mathrm{H})/k(\mathrm{D})$ value less than unity indicates the participation of a proton in a pre-equilibrium step.[21] A plausible mechanism is proposed in the following.



$$\underset{\mathrm{I}}{\mathrm{Co(acac)_3}} + \mathrm{H^+} \overset{\text{fast}}{\rightleftharpoons} \underset{\mathrm{I'}}{(\mathrm{acac})_2\mathrm{Co}\begin{matrix}\diagup\mathrm{OH^+}\\ |\\ \diagdown\mathrm{O}\end{matrix}} \qquad (5)$$



$$\underset{\mathrm{I'}}{(\mathrm{acac})_2\mathrm{Co}\begin{matrix}\diagup\mathrm{OH^+}\\ |\\ \diagdown\mathrm{O}\end{matrix}} \xrightarrow{\text{r.d.s.}} \underset{\mathrm{II'}}{(\mathrm{acac})_2\mathrm{Co{-}O{-}OH^+}} \qquad (6)$$

where O–O$^-$ denotes acac$^-$, and II′ is a five-coordinated intermediate. The fate of II′ is considered to be similar to that of II in the $\mathrm{k_i}$ path (Fig. 3). The observed ΔH^{*} value for k_a slightly lower than that for k_i may be due to an easier cleavage of a Co–O bond with the aid of H$^+$.

Comparison with Cr(acac)$_3$. The ligand exchange of Cr(acac)$_3$ in acetonitrile in high [Hacac] (>0.1 M) region was considered to proceed *via* III type intermediate (Fig. 3) by the $S_\mathrm{N}2$ attack of the free ligand, in view of the first-order dependency of k_0 on [Hacac] and the values of the activation parameters.[8] However, the present k_i value did not change with the increase of [Hacac] up to 1 M (Fig. 1). This indicates that an $S_\mathrm{N}1$ operates in the $\mathrm{k_i}$ path even in the high [Hacac] region. The difference in mechanism is in line with that in the general understanding of substitution mechanisms of these two kinds of metal complexes containing $\mathrm{N_5O}$ core (Cr(III): $S_\mathrm{N}2$; Co(III): $S_\mathrm{N}1$).[1]

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