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Rate and Mechanism of Ligand Exchange of Several Tris(β-diketonato)-iron(III) Complexes with 4-Isopropyltropolone in Carbon Tetrachloride

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The rate of ligand exchange of seven tris(β-diketonato)iron(III) in carbon tetrachloride with 4-isopropyltropolone was measured by a spectrometric method in order to determine the effect of the chemical properties of the leaving ligand on the reaction mechanism. It was found from the dependence of the rate on the leaving and entering ligands and also from the values of $\Delta H^{\ne}$ and $\Delta S^{\ne}$ that the exchange reaction of iron(III) complexes with acetylacetone and its two phenyl-substituted derivatives proceeds by a dissociative mechanism. It was also found that reactions with trifluoroacetylacetone and its phenyl- and 2-thienyl-substituted derivatives proceeds by an associative mechanism. An hexafluoroacetylacetonato complex formed an intermediate with the entering ligand in the first stage of the reaction and then a ligand exchange occured. It was concluded from these results that the ligand exchanges of more stable complexes were controlled by the break of a leaving ligand. Less stable ones were controlled by bond formation with the entering ligand.

In previous studies,[1–3] it was found that the ligand-exchange reaction producing a less stable complex of tris(β-diketonato)iron(III) in carbon tetrachloride proceeded by a dissociative mechanism while the one producing a more-stable complex proceeded by an interchange mechanism. In the present paper, the ligand exchange is further studied with seven tris(β-diketonato)iron(III) using only one entering ligand, 4-isopropyltropolone, which forms a complex more stable than any of these starting compounds. The effect of the nature of the leaving ligand on the reaction mechanism is also considered.

Experimental

All procedures were similar to ones described previously.[1] Iron(III) complexes with acetylacetone (2,4-pentanedione; Hacac), benzoylacetone (1-phenyl-1,3-butanedione; Hbza), dibenzoylmethane (1,3-diphenyl-1,3-propanedione; Hdbm), trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione; Htfa), benzoyltrifluoroacetone (1-phenyl-4,4,4-trifluoro-1,3-butanedione; Hbfa), and 2-thenoyltrifluoroacetone (1-(2-thienyl-)-4,4,4-trifluoro-1,3-butanedione; Htta) were synthesized by a conventional method.[4] The iron(III) complex with hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hhfa) was supplied by Tokyo Kasei Co., Tokyo. The 4-isopropyltropolone (Hipt) was supplied by Takasago Perfumery Co., Tokyo. It was dissolved in an aqueous dilute sodium hydroxide solution and then precipitated by a small excess of acetic acid. The precipitates were filtered off and further purified by recrystallization from benzene–petroleum ether. Carbon tetrachloride was purified and dehydrated in the same manner as described previously.[1] A carbon tetrachloride solution containing one of the iron(III) complexes (FeA_3) and β-diketone (HA) in concentration ratios of two to ten FeA_3 to HA was mixed with a portion of the same solvent containing a certain amount of Hipt. The concentration of the complex in the resultant solution was 1×10^{-5} to 2×10^{-4} mol dm^{-3} and that of Hipt was 1×10^{-4} to 1×10^{-1} mol dm^{-3}. In each run, the optical absorption at a certain wavelength of the sample was measured as a function of time.

Data Treatment. When the ligand exchange of FeA_3 with Hipt is controlled by the first exchange reaction and the whole iron(III) species may be exchanged to $[Fe(ipt)_3]$ as under the conditions of the present study, the rate of the ligand-exchange reaction may be expressed from the decrease in the FeA_3 concentration as:

$$V = -\mathrm{d}[\mathrm{FeA_3}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{FeA_3}]. \tag{1}$$

The concentration of the unexchanged species may be given by:

$$[\mathrm{FeA_3}] = [E-\varepsilon_3\times[\mathrm{Fe(III)}]](\varepsilon_0-\varepsilon_3)^{-1} \tag{2}$$

where ε_0 and ε_3 give the molar absorption coefficients of the FeA_3 and $[Fe(ipt)_3]$ species and [Fe(III)] gives the total concentration of the iron(III) complex in the solutions.

Results

Under the conditions employed, it was found that the spectrum of the sample solution containing one of the starting complexes and Hipt always completely changed to that of $[Fe(ipt)_3]$ when an equilibrium was established. For this reason, the data analysis was achieved using Eq. 2. The molar absorption coefficient used for the data analysis was as follows: 160 for $[Fe(acac)_3]$ at 550 nm; 530 for $[Fe(bza)_3]$ at 550 nm; 220 for $[Fe(dbm)_3]$ at 590 nm; 270 for $[Fe(tfa)_3]$ at 550 nm; 130 for $[Fe(bfa)_3]$ at 590 nm; 360 for $[Fe(tta)_3]$ at 590 nm; 140 for $[Fe(hfa)_3]$ at 590 nm; and 3180 and 2130 for $[Fe(ipt)_3]$ at 550 and 590 nm.

Rate of Ligand Exchange of $[Fe(acac)_3]$, $[Fe(bza)_3]$, and $[Fe(dbm)_3]$. The rate of ligand exchange of $[Fe(acac)_3]$, $[Fe(bza)_3]$, and $[Fe(dbm)_3]$ with Hipt was first order with respect to the starting complex. The rate was independent of the leaving ligand but in all cases first order in Hipt in the higher and lower concentration regions. However, it was also found that the rate was independent of the entering ligand in the intermediate concentration region. Figure 1 gives the results as a function of the Hipt concentration at 298 K. The kinetic data in Fig. 1 may generally be represented by the following equation:

$$k_{\mathrm{obsd}} = \frac{k_{\mathrm{A}}(1+k_{\mathrm{C}}[\mathrm{Hipt}])[\mathrm{Hipt}]}{k_{\mathrm{B}}+[\mathrm{Hipt}]}. \tag{3}$$

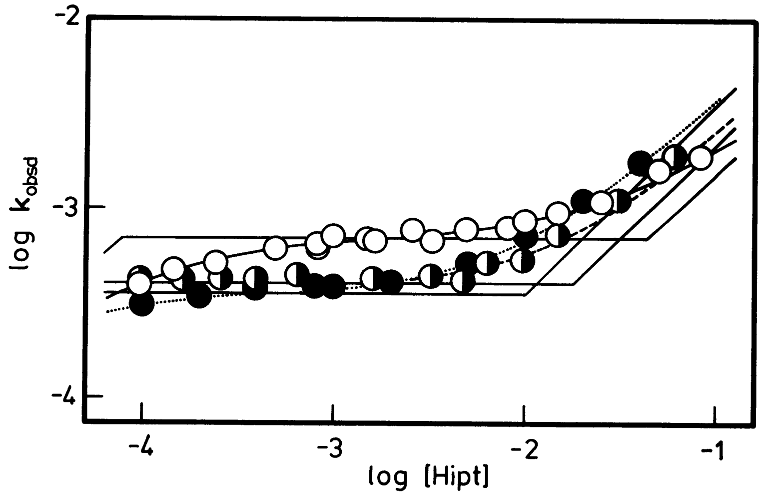

Fig. 1. Rate of $[Fe(acac)_3]$ (-○-), $[Fe(bza)_3]$ (--◑--), and $[Fe(dbm)_3]$ (···●···) reaction with Hipt as a function of the entering ligand concentration at 298 K. The curves are calculated by introducing the constants in Table 1 into Eq. 3. The straight lines are the asymptotes for the curves.

TABLE 1. SUMMARY OF RATE CONSTANTS AND ACTIVATION PARAMETERS

	$[Fe(acac)_3]$	$[Fe(bza)_3]$	$[Fe(dbm)_3]$	$[Fe(tfa)_3]$	$[Fe(bfa)_3]$	$[Fe(tta)_3]$
$\log (k_A/s^{-1})$	-3.16 ± 0.06	-3.41 ± 0.10	-3.45 ± 0.05	—	—	—
$\log (k_B/mol\,dm^{-3})$	*ca.* -4.5	<-5.0	*ca.* -4.9	—	—	—
$\log (k_C/mol^{-1}\,dm^3\,s^{-1})$	1.36 ± 0.27	1.75 ± 0.40	1.99 ± 0.12	—	—	—
$\log (k_D/mol^{-1}\,dm^3\,s^{-1})$	—	—	—	0.16 ± 0.09	-0.46 ± 0.06	-0.53 ± 0.05
$\Delta H^{\neq}/kJ\,mol^{-1}$	82 ± 2	88 ± 2	85 ± 2	47 ± 1	52 ± 1	52 ± 1
$\Delta S^{\neq}/J\,K^{-1}\,mol^{-1}$	-29 ± 5	-12 ± 5	-25 ± 5	-84 ± 2	-81 ± 2	-81 ± 2

The constants k_A, k_B, and k_C obtained from these data by a least-squares program are listed in Table 1.

Rate of Ligand Exchange of [Fe(tfa)₃], [Fe(bfa)₃], and [Fe(tta)₃]. The rate of ligand exchange between these complexes with Hipt was first order with respect to the starting complex and independent of the leaving ligand. However, in all cases, it was first order with respect to the entering ligand. Figure 2 gives the results as a function of the Hipt concentration at 298 K. These results may be represented by the following equation:

$$k_{obsd} = k_D[\text{Hipt}]. \tag{4}$$

The values of the constant k_D obtained from these data are listed in Table 1.

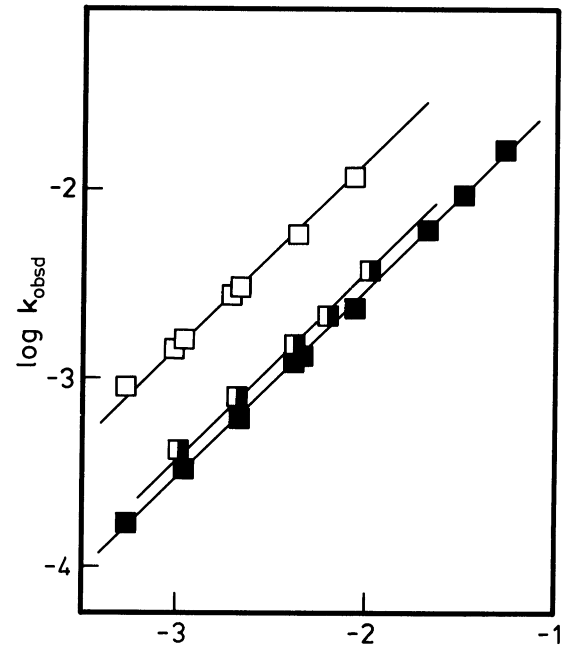

Fig. 2. Rate of $[Fe(tfa)_3]$ (□), $[Fe(bfa)_3]$ (◨), and $[Fe(tta)_3]$ (■) reaction with Hipt as a function of the entering ligand concentration at 298 K. The straight lines are calculated by introducing the constants in Table 1 into Eq. 4.

Rate of Ligand Exchange of [Fe(hfa)₃]. In the course of the study of the ligand exchange of $[Fe(hfa)_3]$ with Hipt, it was found that the color of a sample solution changed rather rapidly from orange to green after mixing the complex and ligand solutions. The color then gradually changed due to the ligand exchange until the solution became completely that of $[Fe(ipt)_3]$. It was concluded from the absorption of the mixed solutions at equilibrium, that this change was not due to the formation of mixed complexes, $[Fe(hfa)_2(ipt)]$ and $[Fe(hfa)(ipt)_2]$, but due to an association between the $[Fe(hfa)_3]$ and Hipt. However, the data in these experiments were not accurate enough to allow a further data analysis of such an association reaction and no final conclusions regarding the mechanism of the ligand exchange reaction of $[Fe(hfa)_3]$

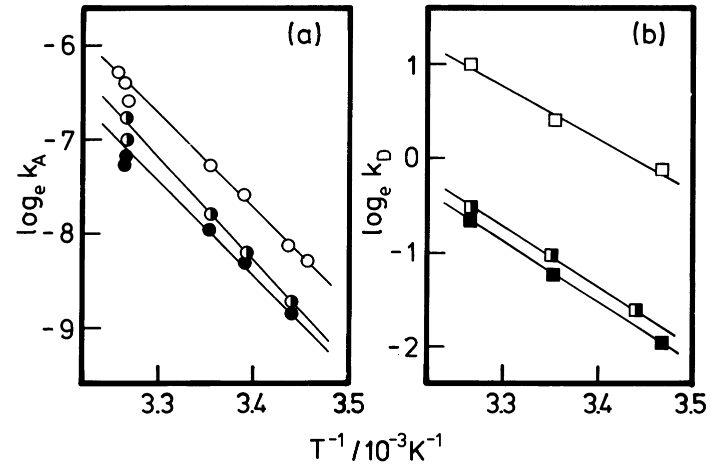

Fig. 3. Arrhenius plot of the ligand exchange reactions.
(a) Dependence of k_A for [Fe(acac)$_3$] (○), [Fe(bza)$_3$] (◑), and [Fe(dbm)$_3$] (●) reaction as a function of temperature.
(b) Dependence of k_D for [Fe(tfa)$_3$] (□), [Fe(bfa)$_3$] (◧), and [Fe(tta)$_3$] (■) reaction as a function of temperature.

could be drawn.

Effect of Temperature. The ligand-exchange rate was also determined at various temperatures. Figures 3(a) and (b) give the $\log_e k_A$ or k_D *vs.* $1/T$ plot. As seen from Fig. 3(a), the results with [Fe(acac)$_3$], [Fe(bza)$_3$], and [Fe(dbm)$_3$] seems to be somewhat erroneous at high temperatures for some unknown reasons. This kind of inaccuracy was also observed in a previous study.[1] However, it can also be seen from the figure that the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained from the slope of the lines are reasonable. The values of the activation enthalpy and entropy obtained from these data are listed in Table 1.

Discussion

Since the ligand-exchange data for [Fe(acac)$_3$], [Fe(bza)$_3$], and [Fe(dbm)$_3$] with Hipt could be represented by Eq. 3, the reaction should proceed through a dissociative or an interchange mechanism. The values of the activation parameters of the ligand exchange of [Fe(acac)$_3$] with Hipt are similar to those when the entering ligand was Htfa or Htta in the previous paper.[1] For this reason, the mechanism of this reaction was concluded to be dissociative. The values of the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) of the reactions of [Fe(bza)$_3$] and [Fe(dbm)$_3$] with Hipt also indicate a dissociative nature of the mechanism and this seems to be reasonable because the leaving ligand from the complexes are chemically similar to that of [Fe(acac)$_3$]. Thus, it was assumed that the reaction mechanism for these three complexes should be similar to that found in the previous paper:[1]

$$\mathrm{FeA_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FeA_3^*} \xrightarrow[+\mathrm{Hipt}]{k_2} [\mathrm{FeA_2(ipt)}] + \mathrm{HA}. \tag{5}$$

Here FeA$_3$* gives a complex one of whose chelate ring is open. When the chemical species FeA$_3$* is assumed to be in a steady-state, the rate may be written as:

$$V = \frac{k_1[\mathrm{Hipt}]}{k_{-1}/k_2 + [\mathrm{Hipt}]}[\mathrm{FeA_3}]. \tag{6}$$

As seen from Eq. 3, k_1 in Eq. 6 corresponds with k_A and k_{-1}/k_2 with k_B. The k_C value was calculated from data obtained in a higher Hipt concentration region where the rate is dependent on the entering ligand. This dependence should be due to a catalytic reaction by Hipt.[1]

The first-order dependence on the entering ligand found with the three complexes of the β-diketones having one trifluoromethyl group, indicates that the reaction proceeds by an associative mechanism:

$$\begin{aligned} \mathrm{FeA_3} + \mathrm{Hipt} &\xrightarrow{k} [\mathrm{FeA_3(Hipt)}] \\ &\xrightarrow{\text{fast}} [\mathrm{FeA_2(ipt)}] + \mathrm{HA}. \end{aligned} \tag{7}$$

Thus the rate should be represented by:

$$V = k[\mathrm{Hipt}][\mathrm{FeA_3}]. \tag{8}$$

The value of k in Eq. 8 is naturally identical to the value of k_D in Table 1, which was obtained on the basis of Eq. 4. As seen from Table 1, the value k_D of [Fe(tfa)$_3$] is somewhat different from those of [Fe(tta)$_3$] and [Fe(bfa)$_3$]. This could be caused by various factors such as the difference in the ability of the complexes to accept an entering ligand and as the difference in the steric hindrance by these ligands.

Among complexes of a certain metal ion with homologous ligands such as β-diketones, the order of the ability as an acceptor of several neutral ligands to form adducts in nonpolar organic solvents is usually opposit to that of their stability. In other words, less stable complexes tend to form more stable adducts. This has been observed in the "synergistic" solvent extraction of metal β-diketonates.[5] The replacement of a methyl group of a β-diketone with a trifluoromethyl group increases the acid-dissociation constant. This, consequently, causes a decrease in the ability to form complexes with metal ions. For example, the values of $\mathrm{p}K_a$ is about $10^{9.0}$, $10^{6.1}$, and $10^{4.3}$, respectively, for Hacac, Htfa, and Hhfa in a 1 $\mathrm{mol\,dm^{-3}}$ sodium perchlorate solution.[6] The values of β_3 are about 10^{27}, 10^{20}, and 10^{10}, respectively, for [Fe(acac)$_3$],[7] [Fe(tfa)$_3$],[8] and [Fe(hfa)$_3$].[9] From these data, it can reasonablly be assumed that [Fe(hfa)$_3$] should be the strongest acceptor for neutral ligand to form adducts and [Fe(acac)$_3$] should be the weakest among these three.

In separate experiments, the absorption spectra of [Fe(acac)$_3$], [Fe(tfa)$_3$], and [Fe(hfa)$_3$] in carbon tetrachloride and in 4-methyl-2-pentanone (MIBK) were measured. It was observed that each spectrum of [Fe(acac)$_3$] and [Fe(tfa)$_3$] was not affected by the solvents. However, that of [Fe(hfa)$_3$] in the visible region was much lower in MIBK than in carbon tetrachloride. This change in the spectrum seems to be caused by stronger interactions between the MIBK molecules and the complex. The fact that this occured only with [Fe(hfa)$_3$] also illustrates the higher ability of [Fe(hfa)$_3$] to act as an acceptor of a neutral ligand than the other two complexes.

In previous studies[10,11] it was suggested that a reaction in aqueous solutions could be represented as $\mathrm{Fe^{3+}+HX \rightarrow FeX^{2+}+H^+}$ where HX was an acid to form a chelate complex proceeded by an associative interchange mechanism. When this assumption is also valid with β-diketones, the order of complex formation ($V=k_{\mathrm{CF}}[\mathrm{Fe^{3+}}][\mathrm{HA}]_{\mathrm{enol}}$: log k_{CF} for Hipt is 1.3,[10] for Hacac is 0.7,[12] for Htfa is 0.8,[13] and for Htta is 0.1[14]) should indicates the order of nucleophilic tendency of these ligands. Furthermore, if the order of nucleophilic tendency would be similar to the order of the nucleophilic tendency of the ligands in nonpolar solvents, Hipt should be a stronger donor than any of the β-diketones studied in the previous paper, Hacac, Htfa, and Htta.[1]

The mechanism of the ligand-exchange reactions treated in this study may be written as follows. (1) The nature of the mechanism of the ligand-exchange reactions of [Fe(acac)$_3$], [Fe(bza)$_3$], and [Fe(dbm)$_3$] whose ability to accept a donor was smaller than the other tris(β-diketonato)iron(III), was dissociative. (2) The ligand-exchange reaction of [Fe(hfa)$_3$], whose ability to accept a donor was the greatest among the complexes studied here, proceeded after an association of the complex with the entering ligand. (3) The ligand-exchange reactions of [Fe(tfa)$_3$], [Fe(bfa)$_3$], and [Fe(tta)$_3$] who had intermediate ability as an acceptor proceeded by an associative mechanism. In the previous paper,[1] it was assumed from the activation parameters that the exchange reactions of [Fe(tfa)$_3$] with Hacac and Htta which are weaker donors than Hipt proceeded by an interchange mechanism. Those of [Fe(tta)$_3$] with Hacac and Htfa also proceeded by a mechanism of the same type. These reactions indicate that the mechanism is very much affected by the nature of the bonds between the metal ion and leaving ligands.

Gutmann[15] pointed out that the rate of dissociation of a ligand from a complex is higher if the donecity of the other ligands is greater. A tendency of this type has been suggested by the present study though the complexes treated here contained only one kind of ligand. The mechanism of the ligand exchange of the three iron(III) chelates with the β-diketones having no trifluoromethyl group were always dissociative. On the other hand, those of the other complexes were in all cases not dissociative. This may be explained in terms of the fact that the donecity of the ligands in the latter complexes is lower than of the ligands in the former. At the same time, the latter complexes are better acceptors of the entering ligand to form associates.

Ishihara, Funahashi, and Tanaka[16] measured the activation volume of the complex formation of iron(III) with Hipt in water, *N,N*-dimethylformamide, and dimethyl sulfoxide. They interpreted the data of activation volume in terms of the bulkiness of both the entering ligand and the coordinated solvent molecules. The present results indicate that the ability of the complex as an acceptor and the ability of the entering ligand as a donor are also important factors which affect the type of the reaction mechanism.

The rate of ligand exchange of [Fe(bza)$_3$] in hexane with Hacac and the effect of butanol as a catalyst for this reaction was studied using a spectrometric method.[17]

Kido and Saito[4] concluded that the ligand-exchange reaction of [Fe(acac)$_3$] with Hacac in undiluted acetylacetone proceeds by an associative mechanism. Since the medium and the entering ligand in our study are different, no direct comparison of the results from the two studies is possible.

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