November, 1984] *Bull. Chem. Soc. Jpn.*, *57*, *3083—3087 (1984)*

Kinetics of Ligand Exchange of Tris(β-diketonato)iron(III) with Acetylacetone, Trifluoroacetylacetone, and 2-Thenoyltrifluoroacetone in Carbon Tetrachloride

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(Received February 17, 1984)

The ligand of tris(β-diketonato)iron(III) with acetylacetone (Hacac), trifluoroacetylacetone (Htfa), or 2-thenoyltrifluoroacetone (Htta) in carbon tetrachloride was exchanged with another ligand among these. The rate was measured in order to learn about the reaction mechanism in this medium; one in which no intermediates with the solvent molecules were expected. From the dependence of the rate on the particular leaving and entering ligand and from the values of ΔH^* and ΔS^*, it was concluded that in an exchange involving [Fe(acac)$_3$] there is always a proceeding dissociative mechanism and for [Fe(tta)$_3$] and [Fe(tfa)$_3$] with Hacac there is an interchange mechanism. Exchanges with a fluorinated β-diketone is thought to have a character intermediate to these two mechanisms.

Kinetic studies on the ligand exchange of metal complexes have been, in most cases, carried out in aqueous solutions and several explanations for models in which the solvent molecules also react as ligands to form intermediate species have been proposed from the experimental results. When nonpolar- and non-solvating-type solvents are employed instead of water, however, it is expected that more direct information about the effects of the chemical properties of the leaving and entering ligand on the reaction mechanism can be obtained.[1,2] For this reason, the rates of nonisotopic ligand exchanges for three tris(β-diketonato)iron(III) complexes in carbon tetrachloride were determined in the present study. Considerations are made on the reaction mechanism for situations where the effect of the solvent molecules is considered slight.

Experimental

Materials. All reagents were reagent grade. The β-diketones, 2,4-pentanedione (acetylacetone; Hacac), 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone; Htfa), and 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (2-thenoyltrifluoroacetone; Htta) were supplied by Dojindo Co., Kumamoto. The Htta was recrystallized from benzene–petroleum ether before use. Iron(III) complexes of these β-diketones were synthesized by the conventional method[3] and recrystallized from benzene–petroleum ether. The purity was checked by an elementary analysis as: [Fe(acac)$_3$] (Found: C 51.25, H 6.02%, Calcd: C 51.01, H 5.99%), [Fe(tfa)$_3$] (Found: C 34.95, H 2.34, F 33.10%, Calcd: C 34.98, H 2.35, F 33.20%), and [Fe(tta)$_3$] (Found: C 40.11, H 1.71, S 13.25, F 23.62%, Calcd: C 40.07, H 1.68, S 13.37, F 23.77%). The carbon tetrachloride was washed three times with water, treated with a dehydrating resin, (SK1B, Mitsubishi Kasei Co., Tokyo) and distilled.

Procedures. The experiments were carried out in a thermostated bath (±0.3 K) located in a thermostated room (±0.6 K). A carbon tetrachloride solution containing 1×10^{-5} to 4×10^{-4} mol dm^{-3} of one of the iron(III) complexes (FeA$_3$) and an excess amount of the ligand (HA) was mixed with a solution containing 1×10^{-4} to 1 mol dm^{-3} of another entering ligand (HB). In order to study ligand exchange equilibrium, the mixed solution was left standing and its optical absorption was measured at 375 nm (exchange of [Fe(acac)$_3$] with Htfa), or 550 nm (for all of the other reactions) after it had become a certain constant value. This was repeated for several molar ratios of the two ligands, HA and HB. While the rate of ligand exchange was being studied, the optical absorption of the solution was measured several times.

Data Treatment. The exchange equilibrium of the iron(III) complex with the entering ligand in the solution may be expressed as;

$$\mathrm{FeA_3} + n\mathrm{HB} \rightleftharpoons \mathrm{FeA_{3-\mathit{n}}B_{\mathit{n}}} + n\mathrm{HA}$$
$$K_n = [\mathrm{FeA}_{3-n}\mathrm{B}_n][\mathrm{HA}]^n[\mathrm{FeA_3}]^{-1}[\mathrm{HB}]^{-n}. \tag{1}$$

The optical absorption of the solution at equilibrium is given by;

$$E = [\mathrm{Fe(III)}](\varepsilon_0+\varepsilon_1K_1R+\varepsilon_2K_2R^2+\varepsilon_3K_3R^3) \times (1+K_1R+K_2R^2+K_3R^3)^{-1}, \tag{2}$$

where ε_n is the molar extinction coefficient of the FeA$_{3-n}$B$_n$ complex and R is the concentration ratio (R=[HB][HA]$^{-1}$). The values of K_n and ε_n were obtained by analyzing the data using a successive-approximation program.[4]

The kinetic data on ligand exchange can be treated as follows. When the whole exchange reaction is controlled by the exchange of the first ligand of FeA$_3$, the successively formed three species, FeA$_2$B, FeAB$_2$, and FeB$_3$, should be in equilibrium with each other. Under such conditions, the following conditional over-all extinction coefficient can be defined if R is kept constant, since the molar ratios of the three successive complexes should always be constant;[5]

$$\varepsilon_\mathrm{T} = (\varepsilon_1K_1R+\varepsilon_2K_2R^2+\varepsilon_3K_3R^3)(K_1R+K_2R^2+K_3R^3)^{-1}. \tag{3}$$

This conditional constant can be calculated on the basis of Eqs. 1 and 2 and, at the same time, can be determined from the absorption at equilibrium if the starting complex, FeA$_3$, is nearly completely changed into the ligand exchanged species. Thus, from information on absorption and the total concentration of iron(III) in the solution, the concentration of the FeA$_3$ species after a certain time interval can be written as;

$$[\mathrm{FeA_3}] = (E-\varepsilon_\mathrm{T}\times[\mathrm{Fe(III)}])(\varepsilon_0-\varepsilon_\mathrm{T})^{-1}. \tag{4}$$

From the decrease in the FeA$_3$ concentration, the rate of ligand exchange can be expressed as;

$$V = -\mathrm{d}[\mathrm{FeA_3}]/\mathrm{d}t = k_\mathrm{obsd}[\mathrm{FeA_3}], \tag{5}$$

where k_obsd is the observed rate constant of the exchange reaction.

Results

Ligand Exchange Equilibria. From the absorption data of the equilibrated solutions, the values of K_n and ε_n were obtained as listed in Table 1.

Rate of Ligand Exchange of [Fe(acac)₃]. The rate of ligand exchange of $[Fe(acac)_3]$ with Htfa or Htta was found to be first order with respect to $[Fe(acac)_3]$ and independent of the leaving ligand. Figure 1 gives the results as a function of the concentration of the entering ligand at 298 K. When the entering ligand was Htta, the value of k_{obsd} was independent of its concentration in the range of 10^{-3} to 10^{-2} mol dm^{-3}, though a first-order dependence appeared below and above this range. When the entering ligand was Htfa, on the other hand, no region was apparently found where the rate was independent of its concentration. However, both data could be explained well by assuming the same type of reaction if the effect of the entering ligand as an acid catalyzer, as will be described later, is corrected.

Rate of Ligand Exchange of [Fe(tfa)₃]. In the course of the study of the ligand exchange of $[Fe(tfa)_3]$ with Hacac, it was found that absorption at 375 nm rapidly increased just after the addition of a Hacac solution to the $[Fe(tfa)_3]$ solution. This enhancement in the absorption was concluded to be due to an association of $[Fe(tfa)_3]$ and Hacac which proceeded much more rapidly than the ligand exchange. Spectrometric data were analyzed after a correction for this intermediate was made. Figure 2 gives the results at 298 K as a function of the entering ligand. In the higher ligand concentration range, the value of the observed rate constant is independent of the entering ligand, but in the lower region it is proportional to its concentration.

Rate of Ligand Exchange of [Fe(tta)₃]. A similar type of increased absorption at 550 nm was also found upon the addition of Hacac to the $[Fe(tta)_3]$ solution. The rate of ligand exchange of $[Fe(tta)_3]$ with Hacac or Htfa was found to be first order with respect to the iron(III) complex and independent of the leaving ligand. The dependence on each entering ligand was first order when the concentration was lower than 0.2 mol dm^{-3} and independent above this value. Figure 3 gives the results.

The results in Figs. 1 to 3 can be represented by the following general equation;

$$k_{obsd} = \frac{k_A(1+k_C[HB])[HB]}{k_B+[HB]}. \tag{6}$$

Table 1. Summary of equilibrium constants

	$[Fe(acac)_3]$ + Htfa (375 nm)	$[Fe(acac)_3]$ + Htta (550 nm)	$[Fe(tfa)_3]$ + Htta (550 nm)
$\log K_1$	1.83	2.31	0.90
$\log K_2$	2.73	3.45	1.35
$\log K_3$	2.73	3.59	1.17
ε_0/mol^{-1} dm^3 cm^{-1}	2020	160	270
ε_1/mol^{-1} dm^3 cm^{-1}	2600	460	720
ε_2/mol^{-1} dm^3 cm^{-1}	3100	1010	1240
ε_3/mol^{-1} dm^3 cm^{-1}	3530	2150	2150

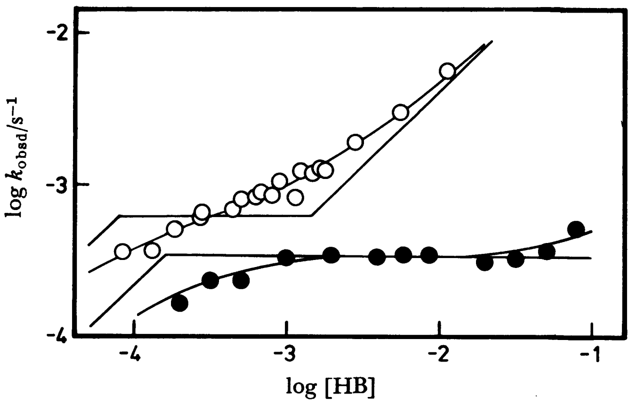

Fig. 1. Rate of $[Fe(acac)_3]$ reaction with Htfa (○) and Htta (●) as a function of the entering ligand concentration at 298 K. The curves are caluclated by introducing the constants in Table 2 into Eq. 6. The straight lines are the asymptotes for the curves.

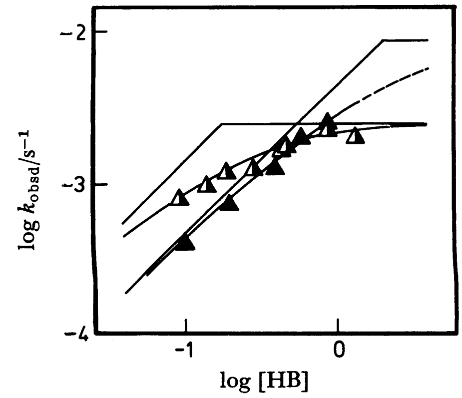

Fig. 2. Rate of $[Fe(tfa)_3]$ reaction with Hacac (△) and Htta (▲) as a function of the entering ligand concentration at 298 K. The curves are calculated by introducing the constants in Table 2 into Eq. 6. The straight lines are the asymptotes for the curves.

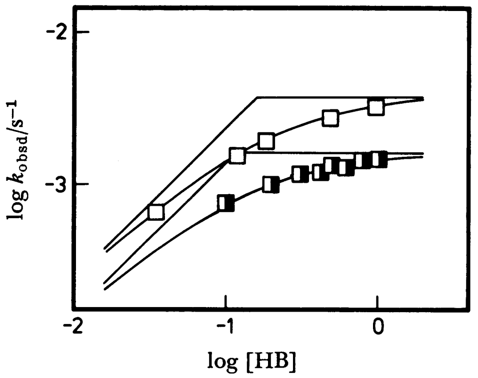

Fig. 3. Rate of $[Fe(tta)_3]$ reaction with Hacac (◨) and Htfa (□) as a function of the entering ligand concentration at 298 K. The curves are calculated by introducing the constants in Table 2 into Eq. 6. The straight lines are the asymptotes for the curves.

Table 2. Summary of constants and activation parameters

	[Fe(acac)$_3$]		[Fe(tfa)$_3$]		[Fe(tta)$_3$]	
	+Htfa	+Htta	+Hacac	+Htta	+Hacac	+Htfa
log (k_A/s^{-1})	−3.2	−3.5	−2.6	−2.1	−2.8	−2.4
log (k_B/mol dm^{-3})	*ca.* −4	*ca.* −4	−0.8	0.3	−0.9	−0.8
log (k_C/mol^{-1} dm^3 s^{-1})	2.8	0.7	—	—	—	—
ΔH^*/kJ mol^{-1} †	83	82	56	63	62	68
ΔS^*/J K^{-1} mol^{-1} †	−27	−38	−106	−74	−89	−64

† The estimated errors of ΔH^* and ΔS^* for the reactions of [Fe(tfa)$_3$] and [Fe(tta)$_3$] are around ±1 and ±5 while that for the reactions of [Fe(acac)$_3$] are ±5 to 10 and ±20 to 30, respectively.

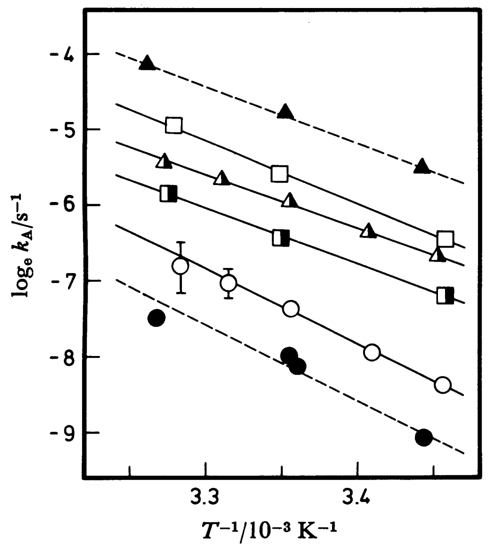

Fig. 4. Arrhenius plot of the rate constant k_A of the reaction of [Fe(acac)$_3$] with Htfa (○) and Htta (●), [Fe(tfa)$_3$] with Hacac (◭) and Htta (▲), and [Fe(tta)$_3$] with Hacac (◨) and Htfa (□).

From the information in Fig. 1, the value of the constant k_C was obtained. From the results expressed in Figs. 2 and 3, this term was concluded to be negligible. The values of the constants obtained are listed in Table 2.

Activation Parameters of Ligand Exchange Reactions. The rate of ligand exchange was also measured at 288 and 306 K (and 293 and 302 K for [Fe(acac)$_3$] and Htfa or [Fe(tfa)$_3$] and Hacac reaction). Figure 4 gives the $\log_e k_A$ *vs.* $1/T$ plot. The results regarding the reaction of [Fe(acac)$_3$] with Htfa and Htta were found to be somewhat more erroneous than those of other reactions, especially at higher temperatures. The activation parameters, ΔH^* and ΔS^*, obtained from these data are listed in Table 2.

Effect of Trichloroacetic Acid. In a previous study, it was found that the rate of ligand exchange of [Fe(acac)$_3$] with Htta in carbon tetrachloride was accelerated by the presence of several acids.[2] In the present study, the effect of trichloroacetic acid was measured. The reactions of [Fe(acac)$_3$] with both Htta and Htfa were accelerated by trichloroacetic acid already at a concentration of 10^{-5} mol dm^{-3} and that of [Fe(tta)$_3$] with Htfa was also accelerated by a presence of 10^{-3} mol dm^{-3}. The rates of other reactions were not affected by trichloroacetic acid in a concentration range of 10^{-5} to 10^{-3} mol dm^{-3}.

Discussion

It was concluded from the absorption data of the mixed sample solutions at equilibrium that more than 99% of the starting complex, FeA$_3$, had been changed to the ligand exchanged species under the conditions of the R employed for the kinetic experiments. Thus from the total concentration of iron(III) and the absorption at equilibrium, the value of ε_T in Eq. 3 should be obtained. This was confirmed since the values calculated by introducing the constants in Table 1 into Eq. 3 agreed well with this observed value. From this, the analysis of the kinetic data in the present study by using Eq. 4 and the values of ε_T should be reasonable.

Some experiments were made under conditions of R where the chemical species formed from FeA$_3$ were only of the FeA$_2$B type complex and FeAB$_2$ and FeB$_3$ were negligible. The rate was always similar to that obtained at values of R where exchange was complete. Thus, the rates of ligand exchange of the FeA$_2$B and of FeAB$_2$ species were much higher than that of the FeA$_3$ species. This should support the assumption already made that the rate was, in all the cases, not affected by the concentration of the leaving ligand and, consequently, the controlling step was the exchange of the first ligand of FeA$_3$. Thus, the discussion below is made on the basis of this assumption.

In the present study, it is assumed that (i) the solvation with carbon tetrachloride should be very weak and, thus, any intermediate species containing the solvent molecules is negligible, and (ii) the presence of any charged species is negligible in the solution. The results in Figs. 1 to 3 are generally represented by Eq. 6, but since the term k_C represents a catalytic effect with the entering ligand itself, as will be seen later, the results should be given by the following equation if this effect is statistically substracted;

$$k_{\text{obsd}} = \frac{k_A[\text{HB}]}{k_B + [\text{HB}]}. \qquad (7)$$

This equation suggests that the reaction may possibly proceed by two types of ligand-exchange mechanisms. One is the dissociative mechanism which is represented by;

$$\text{MA}_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{MA}_3{}^* \xrightarrow[+\text{HB}]{k_2} \text{MA}_2\text{B} + \text{HA},$$

where the superscript "*" denotes a complex one of whose chelate ring is open. When the rate constant for the ring opening is given by k_1, that for its backward reaction by k_{-1} and that for the entering of HB by k_2, the following equation is obtained;

$$V = \frac{k_1[\mathrm{HB}][\mathrm{FeA_3}]}{(k_{-1}/k_2)+[\mathrm{HB}]}. \tag{8}$$

The other is the interchange mechanism which is represented by;

$$\mathrm{MA_3} + \mathrm{HB} \overset{K}{\rightleftharpoons} \mathrm{MA_3{*}HB} \xrightarrow{k} \mathrm{MA_2B} + \mathrm{HA},$$

$$V = \frac{k[\mathrm{HB}][\mathrm{FeA_3}]}{K^{-1}+[\mathrm{HB}]}. \tag{9}$$

Here, $\mathrm{MA_3}$ is in equilibrium with its associate with HB and the reaction is controlled by the formation of the first chelate ring with the anion of the entering ligand $\mathrm{B^-}$ involving a proton-transfer from the entering HB to the leaving $\mathrm{A^-}$.

It is known that if a reaction proceeds by a dissociative mechanism, the value of ΔH^* is large and ΔS^* is positive or nearly zero while if it proceeds by an interchange mechanism, the ΔH^* is smaller than that by a dissociative mechanism and the ΔS^* is negative. After observing this general tendency and the values in Table 2, it may be concluded that the ligand exchange of the $[\mathrm{Fe(acac)_3}]$ complex proceeds by a dissociative mechanism while that of $[\mathrm{Fe(tfa)_3}]$ and $[\mathrm{Fe(tta)_3}]$ proceeds by an interchange mechanism, although the ligand exchange of $[\mathrm{Fe(tta)_3}]$ with Htfa may have an intermediate character of these two becasue of the intermediate magnitude of the values of ΔH^* and ΔS^*. Although the reactions of $[\mathrm{Fe(acac)_3}]$ with Htta and Htfa are assumed to proceed by a dissociative mechanism, the values of k_1 are not similar. One explanation for this may be that the amount and/or the effect on the rate of the minor contents in the systems such as water, impurities in the reagents *etc.*, are not identical. However, further experiments seem to be necessary in order to solve this problem.

It seems to be reasonable that a catalytic effect of the acids, including that with the entering β-diketone to the complex which is also a weak acid, appears only in the exchange reaction of $[\mathrm{Fe(acac)_3}]$ with the fluorinated β-diketones and not in the exchange of $[\mathrm{Fe(tta)_3}]$ or $[\mathrm{Fe(tfa)_3}]$ with acetylacetone or with the other fluorinated β-diketone if the former reaction proceeds by a dissociative mechanism and the latter by an interchange mechanism. When the reaction proceeds by a dissociative mechanism, the leaving ligand, $\mathrm{acac^-}$, easily accepts a proton from a stronger acid. This should help in the dissociation of the ligand from the complex, but acetylacetone in an acid form, Hacac, may not give up a proton so easily to the leaving ligand. On the other hand, when the reaction proceeds by an interchange mechanism and when the dissociation of the proton from the entering ligand which is accompanied by the closure of the chelate ring controls the whole reaction, another acid whether it is stronger or weaker can not assist the leaving of the proton and, thus, can not catalyze the reaction.

The enhancement of the absorption properties of a solution of $[\mathrm{Fe(tfa)_3}]$ or $[\mathrm{Fe(tta)_3}]$ just after the addition of acetylacetone has been explained by a mechanism involving the interaction of the complex with the β-diketone from the statistical treatment of optical data. This may support the conclusion that the ligand exchange in these cases proceeds by an interchange mechanism, although such a change was not clearly observed with the addition of Htfa to the $[\mathrm{Fe(tta)_3}]$ solution or with the addition of Htta to the $[\mathrm{Fe(tfa)_3}]$ solution. A similar change in the absorption, but probably due to a somewhat different cause, was also found in the "inert" solvent, benzene, in the previous paper.[6]

Adduct formation of uncharged chelate complexes in nonpolar solvents with an uncharged ligand has been studied from the stand point of the "synergistic effect" of solvent extraction.[7] The tendency of metal chelates with acetylacetone to accept a neutral ligand is generally smaller than of those with fluorinated β-diketones. It is also known that the neucleophilic tendency of ligands to form such adducts is greater with those ligands to form more stable complexes and, thus, Hacac should be more neucleophilic than the other two. From these, the interactions of the complex and the entering ligand should be stronger with the chelates with the fluorinated β-diketones and, thus, it seems to be reasonable that they tend to exchange by an interchange mechanism while that with acetylacetone exchanges by a dissociative mechanism. The values k_B for the reaction of $[\mathrm{Fe(tfa)_3}]$ and $[\mathrm{Fe(tta)_3}]$ in Table 2 correspond to the inverse of the formation constant of the interacted species. The value is smaller for reactions with $[\mathrm{Fe(tfa)_3}]$ with Hacac than with Htta (the former forms a larger amount of interacted species), and is nearly the same in the reactions of $[\mathrm{Fe(tfa)_3}]$ and $[\mathrm{Fe(tta)_3}]$ with Hacac and, thus, the adducts are similarly stable.

In the previous work,[2] a set of values of ΔH^* and ΔS^* for the ligand exchange of $[\mathrm{Fe(acac)_3}]$ with Htta in carbon tetrachloride was reported. However, from recalculations made using data obtained in both the previous and present work, it was concluded that the values in Table 2 should be employed. In the present study, the results of experiments with Htta were found to be less reproducible than those with other β-diketones.

In aqueous solutions, the water molecules might also act as an entering ligand whose concentration is constant and much higher than any other entering ligands present. Thus, formation of intermediates with water molecules is expected prior to the entrance of the ligand to be studied. Since no such intermediates with solvent molecules could be formed in carbon tetrachloride, the effect of the chemical properties of the ligands on the reaction mechanism could be recognized more clearly than in aqueous solutions. The use of benzene in the kinetic study of the ligand exchange of iron(III) complexes was reported[6] but since the ligands are different, no direct comparison of this previous study with the present one seems to be possible.

Isotopic ligand exchange of tris(acetylacetonato)-iron(III) in an acetylacetone medium was studied and the reaction mechanism was reported to be associative.[3] However, since the nature of the solvent and the entering ligand is different, the present results may not be compared directly with the previous study.

In a previous kinetic study of the isotopic ligand exchange of aluminium(III), indium(III), gallium(III), and beryllium(II) complexes where the ligand was 2,4-pentanedione, 1-phenyl-1,3-butanedione, or 1,3-diphenyl-1,3-propanedione in tetrahydrofuran, the rate was always lower when the acidity of the ligand was weaker (pK_a is greater).[8]

There have been other reports on the isotopic and non-isotopic ligand exchange of complexes of other metal ions in organic solvents (for example Refs. 9—14). However, direct comparison of the present data with these previous results does not seem to be possible because of the difference of the medium.

We are grateful to Dr. Shigeru Suzuki of the Tokyo College of Pharmacy, for the elementary analysis of the complexes.

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