Rate of Ligand Exchange of Tris(acetylacetonato)iron(III) with 2-Thenoyltrifluoroacetone in Organic Solvents

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The rate of exchange of acetylacetonate ions ($acac^-$) in tris(acetylacetonato)iron(III) with 2-thenoyltrifluoroacetonate ions (tta^-) has been measured in several organic solvents. The rate was independent of the concentration of Hacac and Htta and nearly the same in carbon tetrachloride, benzene, acetone, and 4-methyl-2-pentanone. However, the rate was much greater in ethanol. The rate of exchange in carbon tetrachloride, benzene, and acetone was found to be enhanced by water, ethanol, and several acids. The enhancement was smaller in acetone than in nonpolar solvents and the stronger the acid, the greater the catalytic effect. The rate controlling step of the exchange reaction was the rupture of an acetylacetonate ion from iron(III) in the complex. These observations have been discussed and possible mechanisms proposed.

In the course of studies of the chemical equilibria of metal complexes in organic solvents, it was found that exchanging the ligand of tris(acetylacetonato)iron(III) in organic solvents with other chelating ligands proceeded rather slowly. In the present paper, the rate of exchange with 2-thenoyltrifluoroacetonate ions has been studied photometrically.

Experimental

Reagents. All reagents were of reagent grade. The tris(acetylacetonato)iron(III) ($Fe(acac)_3$), acetylacetone (Hacac), 2-thenoyltrifluoroacetone (Htta), and trioctylphosphine oxide (TOPO) were supplied by Dojindo Co., Kumamoto. The organic solvents were also of analytical grade and subsequently passed through a dehydrating column containing an ion-exchanger resin supplied by Mitsubishi Kasei Co., Tokyo, and distilled.

Procedure. The experiments were conducted in a thermostatted room or in a thermostatted bath. A portion of the solvent containing a $Fe(acac)_3$ was added to another portion of the same solvent containing Htta. In several experiments, certain amounts of other materials such as an acid, TOPO, acetone, an alcohol, and/or water were added to the $Fe(acac)_3$ solution. The solution was agitated and transfferred to a glass cell (1 cm path). The change in the optical density of the solution at 550 nm was measured with a spectrophotometer (Hitachi double wavelength double beam spectrophotometer type-556 or Hitachi UV-VIS spectrophotometer type-101 or type-139) as a function of time and the increase in the $Fe(acac)_3$ concentration obtained. The water content was checked by the Karl Fischer titration.

Results

The temperature of the experiments in this study was 25 ± 0.3 °C except when the effect of the temperature was examined. All the data were found to indicate that the reaction was first order with respect to $Fe(acac)_3$ in the initial stage.

Dependence on Hacac Concentration. The rate of exchange of $acac^-$ in $Fe(acac)_3$ with tta^- was measured at several concentrations of Hacac. It was found that the rate was always independent of the co-existing Hacac concentration, at least below 0.1 mol dm^{-3}. When the Htta solution was added to the $Fe(acac)_3$ solution in the absence of Hacac the results were reproducible, at least within 5 min of the dissolution of the $Fe(acac)_3$ crystals. $Fe(acac)_3$ solutions containing no Hacac however were not stable on standing for a long time, especially under light. The addition of, for example, 10^{-3} mol dm^{-3} of Hacac to a solution of 10^{-4} mol dm^{-3} of $Fe(acac)_3$ stabilized the solution. Thus in the present study, ten to hundred times of Hacac to $Fe(acac)_3$ by molar ratio was added to the initial solution.

Dependence on Htta Concentration. The rate was measured in the concentration range of Htta from 10^{-4} to 2×10^{-1} mol dm^{-3} where it was found that the rate was independent of the Htta concentration unless it was below 10^{-3} mol dm^{-3}. This was however found to be an apparent effect; under such conditions the exchange was thermodynamically incomplete and this has been discussed later.

Effect of Solvent. The rate of exchange was measured in carbon tetrachloride and in four other solvents. The rate in ethanol was too high to be measured by the method employed but that in benzene as well as in acetone and 4-methyl-2-pentanone (MIBK) was measurable. No determination was made in water because of low solubilities of the complexes and ligands but the rate in water would be expected to be too high for the measurement as will be seen from the description on the effect of water.

From the experimental results, the rate may be written as

$$v_0 = -d[Fe(acac)_3]/dt = k_0[Fe(acac)_3]. \qquad (1)$$

The rate constants in these solvents obtained from the slope of the plot of log $[Fe(acac)_3]$ *vs.* time are listed in Table 1(a).

Effect of Water. The effect of water in the solvent was examined in carbon tetrachloride, benzene, and acetone and Fig. 1 gives the results. The rates in dehydrated carbon tetrachloride and benzene were identical with each other and increased with increase in the water content and became 2.0 and 3.7 times greater in water-saturated carbon tetrachloride and benzene, respectively. The explanation for this is in terms of the amount of water in the water-saturated solvents. The increase in the rate by water was smaller in acetone than in the two nonpolar solvents. Determination of the water content in the "dehydrated" solvents (experimental section) was not possible but the content was presumed to be lower than 10^{-4} mol dm^{-3}.

Table 1. Summary of constants

$v = [Fe(acac)_3](k_0 + k_c[C])$. k_c represents k_w, $k_{alc.}$, and k_{acid}, respectively (*cf.* Eqs. 2, 4, and 5).

(a) Rate constant

Solvent	$\log (k_0/s^{-1})$
Carbon tetrachloride	−3.2
Benzene	−3.2
Acetone	−3.5
4-Methyl-2-pentanone	−3.2
Ethanol	too high to be measured
Water	too high to be measured

(b) Catalytic constant

Catalyzer	$\log (k_c/s^{-1}\ mol^{-1}\ dm^3)$ Solvent		
	CCl_4	C_6H_6	$(CH_3)_2CO$
Water	−1.2	−1.2	−2.4
Ethanol	−0.8	−0.8	−2.0
Methanol	−0.8	—	—

(c) Catalytic constant in carbon tetrachloride

Acid	pK_a[a)]	$\log (k_c/s^{-1}\ mol^{-1}\ dm^3)$
Trichloroacetic acid	0.64	1.5
Dichloroacetic acid	1.26	1.2
Chloroacetic acid	2.87	0.6
Bromoacetic acid	2.90	0.6
1-Naphthoic acid	3.70	0.4

a) Taken from L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society Spec. Pud., **17** (1964).

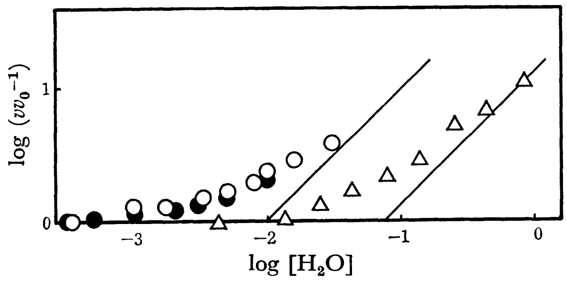


Fig. 1. Effect of water on the rate of exchange with tta^-. v is the rate in the presence of water and v_0 is that in the dehydrated solvent otherwise identical conditions. ●: CCl_4, ○: C_6H_6, △: $(CH_3)_2CO$.

The rate of reaction enhanced by water may be written as

$$v_w = -d[Fe(acac)_3]/dt = k_w[Fe(acac)_3][H_2O]^a. \quad (2)$$

The overall rate is then;

$$v = v_0 + v_w = [Fe(acac)_3](k_0 + k_w[H_2O]^a). \quad (3)$$

The plot of $\log v$ *vs.* $\log [H_2O]$ reached an asymptote and thus $\log v = \log k_W + \log [H_2O]$; "$a$" was concluded to be unity. The values of k_W are listed in Table 1(b).

Effect of Alcohol. The effect of ethanol was examined in carbon tetrachloride, benzene, and acetone. Some experiments were conducted on the effect of methanol in carbon tetrachloride. The rate of exchange was enhanced by the alcohols and may be written as

$$v_{alc.} = -d[Fe(acac)_3]/dt = k_{alc.}[Fe(acac)_3][alcohol]^a. \quad (4)$$

The results were analyzed and from the analysis, "a" was concluded to be unity. The values for the constant $k_{alc.}$ were determined in a similar manner to that for water and the values are listed in Table 1(b).

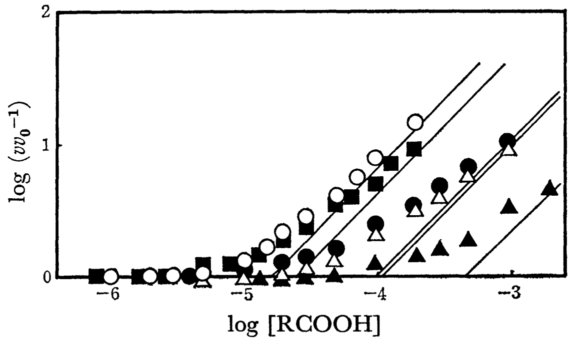


Fig. 2. Enhancement of the rate by acids in CCl_4. v is the rate in the presence of the acid and v_0 is that in the absence otherwise identical conditions. ○: CCl_3COOH, ■: $CHCl_2COOH$, ●: $CH_2ClCOOH$, △: $CH_2BrCOOH$, and ▲: 1-naphthoic acid. The straight lines of slope +1 give the calculated asymptotes, $\log (vv_0^{-1}) = \log k_{acid}k_0^{-1}[RCOOH]$ (*cf.* Eq. 6).

Effect of Acids. The rate was enhanced by various carboxylic acids. Figure 2 gives the results in carbon tetrachloride. The rate of reaction catalyzed by acids may be written as

$$v_{acid} = -d[Fe(acac)_3]/dt = k_{acid}[Fe(acac)_3][RCOOH]^a. \quad (5)$$

From an analysis of the results, "a" was concluded to be unity in all cases and the rate may be thus written

$$v = v_0 + v_{acid} = [Fe(acac)_3](k_0 + k_{acid}[RCOOH]). \quad (6)$$

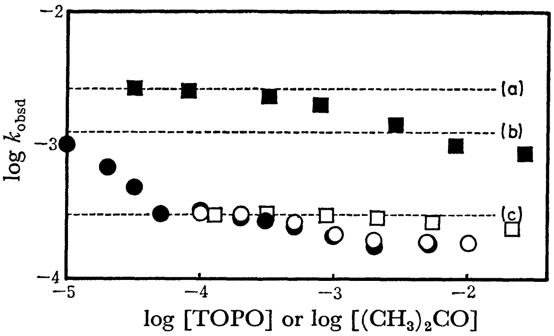


Fig. 3. Effect of TOPO and acetone on the rate. k_{obsd} is $v[Fe(acac)_3]^{-1} = (k_0 + k_{acid}[RCOOH])$ (*cf.* Eq. 6). Open symbols give the effect of TOPO (circles) and acetone (squares) on the rate in the absence of any acid in CCl_4. Closed squares give the effect of acetone on the rate in the presence of 2.0×10^{-4} mol dm^{-3} of dichloroacetic acid in CCl_4. Closed circles give the effect of TOPO on the rate in the presence of 4.2×10^{-5} mol dm^{-3} of trichloroacetic acid in CCl_4. Dotted lines show the values of k_{obsd} when the concentration of dichloroacetic acid was 2.0×10^{-4} mol dm^{-3} in the absence of acetone (a), the concentration of trichloroacetic acid was 4.2×10^{-5} mol dm^{-3} in the absence of TOPO (b), and when the solvent contained none of these materials (c). When the molar ratio of TOPO and trichloroacetic acid is 1: 1, the catalysis disappeared.

The values for the constant k_{acid} are given in Table 1(c).

Effect of Temperature. The rate of exchange was also determined at 15 and 35 °C. From these data and that at 25 °C, the activation energies were determined and the values of activation enthalpy ($\Delta H^{\ast}$) and entropy ($\Delta S^{\ast}$) for k_0 and k_c calculated the values of which given in Table 2.

TABLE 2. SUMMARY OF ACTIVATION PARAMETERS FOR k_c IN CARBON TETRACHLORIDE AT 25 °C[a)]

Catalyzer	$\Delta H^{\ast}$ (kJ mol^{-1})	$\Delta S^{\ast}$ (J K^{-1} mol^{-1})
Water	18 ± 3	-223 ± 20
Methanol	23 ± 3	-182 ± 15
Ethanol	23 ± 3	-176 ± 16
Trichloroacetic acid	22 ± 2	-160 ± 14

a) The values of $\Delta H^{\ast}$ and $\Delta S^{\ast}$ for k_0 in carbon tetrachloride at 25 °C were found to be 24 ± 3 (kJ mol^{-1}) and -226 ± 20 (J K^{-1} mol^{-1}), respectively.

Effect of TOPO, Acetone, and Water on Acid Catlaysis. The rate in carbon tetrachloride was determined as a function of the concentration of TOPO or acetone, the other concentrations being kept constant. The hydrogen-bond acceptors had little effect on the rate in the absence of acid catalyzers as seen from Fig. 3. However, in the presence of an acid catalyzer, the added TOPO lowered the rate and when the molar concentration of TOPO reached that of the acid catalyzer, the catalytic effect disappeared. Acetone also exhibited such an effect on the acid catalysis although the effect was much smaller than that with TOPO. Figure 3 illustrates the effect of acetone on the acid catalysis. Similar experiments were made on the catalysis by water but the effects of TOPO and acetone were, however, not large even in the water-saturated solvent.

Discussion

As described in a previous paper,[1)] the equilibrium constants for the ligand exchange in a given water-saturated solvent,

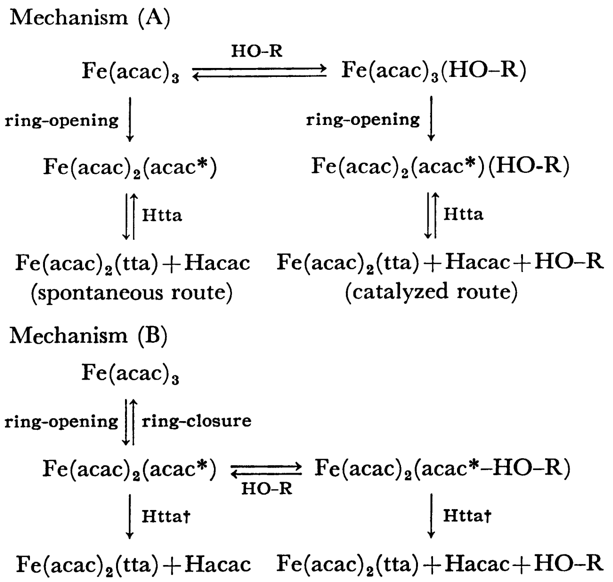
$$K_n = ([\mathrm{Fe(acac)_{3-\mathit{n}}(tta)_{\mathit{n}}}]/[\mathrm{Fe(acac)_3}]) \times ([\mathrm{Hacac}]/[\mathrm{Htta}])^n \tag{7}$$

can be calculated from the solvent extraction constants of iron(III) with Hacac and Htta in the same solvent. From separate experiments and previous data[2)] the value for K_3 in carbon tetrachloride was calculated as $10^{4.1}$. From this value it was statistically calculated that more than 99% of iron(III) at equilibrium was in the form of Fe(tta)$_3$ whenever the ratio [Htta]/[Hacac] was higher than 10. No such values for the equilibrium constants are available in the other solvents. However, since the extraction constants are little affected by the solvent if there are no special interactions between the complex and the solvent molecules, similar assumptions may also be possible in the other solvents. The spectra at equilibrium also indicated the complete change of the complex into Fe(tta)$_3$ when the ratio [Htta]/[Hacac] was higher than 10. Furthermore, all the spectra observed during the exchange reactions were found to be expainable in terms of two species, Fe(acac)$_3$ and Fe(tta)$_3$. Thus the correction for mixed complexes should be unnecessary in the data analysis.

Since the rate is independent of the concentrations of both ligands, Hacac and Htta, it is assumed that the rate-determining step is the isolation of the first acetylacetonate ion. The catalytic effect by the acids, alcohols, and water can be explained by both the following two mechanisms, (A) and (B). Since the catalyzers are assumed to be hydrogen-bond donors, they will be denoted as HO–R.

(A) The hydroxyl group of thc catalyzer works as a hydrogen-bond donor to one of the oxygens of acetylacetonate ions which are coordinating with the central metal ion and form a hydrogen-bond complex Fe(acac)$_3$(HO–R). This hydrogen-bond formation between the catalyzer and the oxygen of the chelating acetylacetonate ion weakens the coordination bond and thus accelerate ring-opening.

(B) Among the tris(acetylacetonato)iron(III) molecules, a certain fraction is in a five-coordinated state and an equilibrium is established between the six- and five-coordinated complexes (the unidentate acetylacetonate ion will be denoted by an asterisk as Fe(acac)$_2$(acac*)). The hydroxyl group works as a hydrogen-bond donor to the oxygen being octahedral at the free end of the unidentate ligand. The formation of the hydrogen-bond complex in such a way, Fe(acac)$_2$(acac*–HO–R), prevents the recombination of the oxygen at the free end with the central metal ion. Thus the relative concentration of the five-coordinated complex is increased and/or accelerates the isolation of the



† Addition of tta$^-$ ligand occures after the isolation of the unidentate acac$^-$ ligand which controls the reaction.

Fig. 4. Plausible reaction mechanisms. (acac* denotes unidentate acetylacetonato ligand, HO–R denotes a hydrogen-bond donating catalyzer such as water, alcohol, and carboxylic acid.)

acetylacetonate ion from the complex. The two mechanisms are summarized in Fig. 4.

In both of the mechanisms, the catalytic effect is caused by hydrogen-bond formation and the stronger the acid, the greater the catalytic effect, *i.e.* the greater tendency of a strong acid to form a hydrogen-bond complex than a weak one. A similar tendency was reported in a solvent extraction study where the oxygen in TOPO formed a more stable hydrogen-bond complex in a nonpolar solvent with a strong carboxylic acid as opposed to a weak one.3) However, the difference in catalysis due to the difference in the acid strength became smaller among the weaker acids; water and alcohols, which are very weak acids catalyze the reaction. This supports the fact that TOPO and various oxygen-containing solvent molecules form hydrogen-bond complexes with water in nonpolar organic solvents. The two β-diketones, Hacac and Htta, have also a hydroxyl group in the enol form and are weak acids (pK_a 9.0 and 6.3 approximately, respectively) but they did not catalyze the exchange reaction as is seen that the rate was not dependent on the concentrations of these materials. This is probably due to the fact that the enolic proton of these materials in nonpolar solvents is hydrogen-bonded with the other oxygen in the same molecule and forms an intramolecular chelate.

In mechanism (A), the rate-determining step is the first ring-opening and in mechanism (B) it is the isolation of the first acetylacetonate ion by breaking the second bond in the chelate. When mechanism (A) operates, the $\Delta H^{\ddagger}$ for k_c should be different from that for k_0 and dependent on the catalyzers. When mechanism (B) operates, the $\Delta H^{\ddagger}$ for k_c should not be dependent on the catalyzers. However, the experimental errors in the values of $\Delta H^{\ddagger}$ are too large to conclude whether mechanism (A) or (B) is operating in the reactions.

The formation of adducts of the Fe(acac)$_3$ chelate with TOPO and various other oxygen-coordinating reagents such as ketones is concluded to be only slight since "synergism" in solvent extraction of tris(β-diketonato)iron(III) is negligible.4) This is reasonable since TOPO and ketones did not catalyze the reaction by mechanism (A). These reagents could occupy the vacant site of the five-coordinated complex and could accelerate the reaction by preventing the recombination of oxygen at the free end of the unidentate ligand in mechanism (B). However, since no catalytic effect was observed, such an effect would be very slight.

TOPO greatly inhibited the catalysis attributed to the formation of a stable hydrogen-bond complex between TOPO and the catalyzer in the solvent. The catalysis completely disappeared by the addition of TOPO at a 1:1 molar ratio agrees with the previous result that TOPO formed a very stable 1:1 hydrogen-bond complex with carboxylic acids in a nonpolar solvent.4) Acetone inhibited the catalysis to a much smaller extent than TOPO attributable to the fact that the oxygen of acetone is a much weaker hydrogen-bond acceptor. The limited extent of the catalysis of water and ethanol in acetone may be due to the same reason.

According to the literature,3,5) the dimerization of the acids is only slight in the solvents when the concentration is lower than 10^{-3} mol dm^{-3}. Such a dimerization effect of the acids on catalysis should be negligible under the conditions of the present study. The intramolecular association of water or alcohol in these solvents is also slight3,5) and its effect on the catalysis should also be negligible.

When both water and an acid catalyzer co-exist in a solvent, each work as a hydrogen-bond donating catalyzer and, at the same time, as a hydrogen-bond accepting inhibitor for the catalysis. However, as already described, this was not clear in the present study, probably a consequence of the low concentrations.

The isotopic ligand exchange of metal chelates has been studied in several polar solvents and in some nonpolar solvents.6–16) In the present study, the ligand exchange was not isotopic and no direct comparison with previous results may be possible. However, the following observations in these previous studies may reasonably be compared with the present results.

In nonpolar solvents, especially in the dehydrated ones, the presence of isolated ions should be negligible. Thus the role of protons or hydronium ions in the reaction mechanism should also be negligible and the tendency observed among the catalyzers in the present study that the stronger the acid, the greater the catalytic effect, can be explained only in terms of the higher stabilities of the hydrogen-bond complex by the stronger acids, as already described. Based on this assumption, it can be concluded that water and alcohols are the same type of catalyzers as acids such as trichloroacetic acid although the hydrogen-bonds are weaker. Water was assumed not to assist the acid catalysis. This is quite different from the mechanism proposed for the reactions in polar solvents.9,10,16)

Solvation of the vacant site of the five-coordinated complex produced by the ring-opening of a chelate ligand was reported to accelerate the reaction by preventing ring closure10,16) which corresponds to mechanism (B).

In the isotopic exchange reaction of tetrakis(acetylacetonato) or tetrakis(trifluoroacetylacetonato)zirconium(IV) or hafnium(IV) in nonpolar solvents, the rate was dependent on both the metal complex and the free ligand concentration and the presence of an intermediate complex which was coordinated by both the leaving and incoming ligands as unidentate ligands and a transfer of the proton between the two unidentate ligands was assumed.6) The dependence of the rate on the ligand concentration was also reported in other papers and mechanisms explaining this observation were proposed.9,13,15)

A kinetic study on the ligand exchange of tris(*N*-benzoyl-*N*-phenylhydroxylaminato)oxovanadium(V) in chloroform or 1,2-dichloroethane with tropolonate ion added as the acid form tropolone was reported.17) This appears to be the only report of the systematic kinetic study of an exchange reaction of a metal chelate with a different ligand in nonpolar solvents. However, the reaction mechanism was not definitively proposed and a comparative discussion of the results with the present study seems to be difficult.

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