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RATE OF LIGAND EXCHANGE OF TRIS(ACETYLACETONATO)IRON(III) WITH TRIFLUOROACETYLACETONE AND TRIS(TRIFLUOROACETYLACETONATO)IRON(III) WITH ACETYLACETONE IN CARBON TETRACHLORIDE

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The rate of ligand exchange of tris(acetylacetonato)iron(III) with trifluoroacetylacetone and tris(trifluoroacetylacetonato)-iron(III) with acetylacetone in carbon tetrachloride has been measured spectrophotometrically and the reaction mechanism was discussed. Use of non-polar solvents as the medium was concluded to be favorable for kinetic studies of this type.

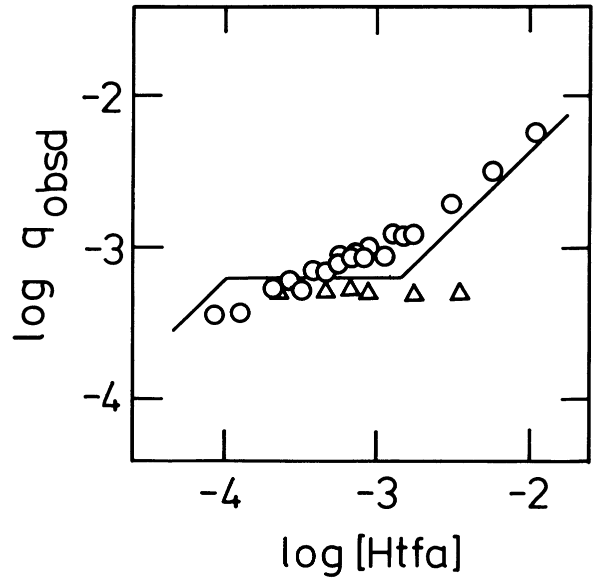
The rate of ligand exchange of iron(III) complex of acetylacetone(2,4-pentanedione, Hacac) with trifluoroacetylacetone(1,1,1-trifluoro-2,4-pentanedione, Htfa) and of trifluoroacetylacetone with acetylacetone has been measured in carbon tetrachloride. Experiments were made in a similar manner as in a previous study.[1)] The tris-complexes, $[Fe(acac)_3]$ and $[Fe(tfa)_3]$, were prepared by conventional methods.[2)] A solution of carbon tetrachloride containing each of these complexes and both of Hacac and Htfa was placed in a thermostated bath and the optical absorption at 375 nm was measured at a certain time interval. The absorption was also measured at equilibrium. The data were treated in a similar manner as in the previous paper.[1)]

The rate under such conditions may generally be given as;

$$V = -d[FeA_3]/dt = q_{obsd}[FeA_3] \tag{1}$$

where q_{obsd} is the observed first order rate constant and A^- is the ligand in the dissociated form.

The rate of ligand exchange of $[Fe(acac)_3]$ with Htfa was first order with respect to the total amount of iron(III) but independent of the leaving ligand. Figure 1 gives the rate of ligand exchange of $[Fe(acac)_3]$ as a function of the Htfa concentration. In the experiments with $[Fe(tfa)_3]$, an increase in the extinction coefficient of the sample solution was found just after the addition of Hacac to $[Fe(tfa)_3]$ solutions and since it was dependent on the Hacac concentration, this change was concluded to be due to an association of $[Fe(tfa)_3]$ with Hacac. Figure 2 gives the values of q_{obsd} as a function of the Hacac concentration obtained after a correction for this increase has been made. Experiments were also made at different temperatures in order to determine the values of activation parameters. It was found that the rate of ligand exchange of $[Fe(acac)_3]$ with Htfa was catalyzed by trichloroacetic acid above 2×10^{-5} mol dm^{-3} but that of $[Fe(tfa)_3]$ with Hacac was not affected.



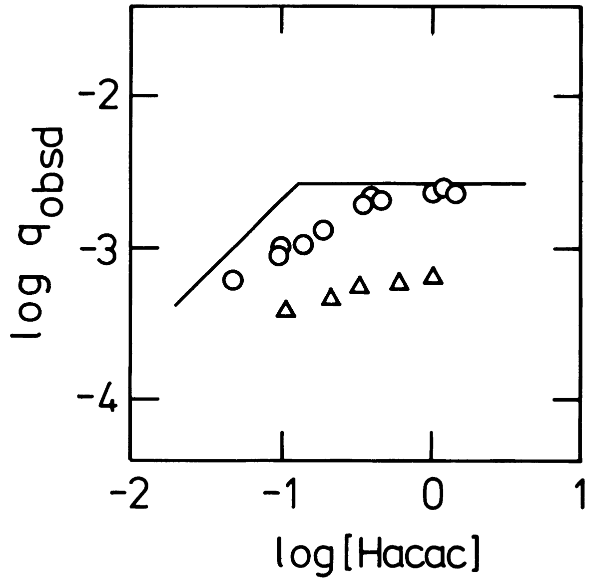


Fig. 1. (left) Rate of $[Fe(acac)_3]$ reaction with Htfa in carbon tetrachloride (○) and in 4-methyl-2-pentanone (△) as a function of Htfa concentration at 298 K. The straight lines are the asymptotes; (from right to left) $\log q_{obsd} = \log k_A \times k_C + \log [Htfa]$, $\log q_{obsd} = \log k_A$, and $\log q_{obsd} = \log k_A/k_B + \log [Htfa]$ where $\log k_A = -3.2$, $\log k_B = -4.0$, and $\log k_C = 2.8$ (cf. Eq. 2).

Fig. 2. (right) Rate of $[Fe(tfa)_3]$ reaction with Hacac in carbon tetrachloride (○) and in 4-methyl-2-pentanone (△) as a function of Hacac concentration at 298 K. The straight lines are the asymptotes, $\log q_{obsd} = \log k_A$ and $\log q_{obsd} = \log k_A/k_B + \log [Hacac]$ where $\log k_A = -2.6$ and $\log k_B = -0.8$ (cf. Eq. 3).

It was also found that the rate of ligand exchange of $[Fe(acac)_3]$ with Htfa in 4-methyl-2-pentanone was similar with that in carbon tetrachloride but that of $[Fe(tfa)_3]$ with Hacac was as low as about 1/4 of that in carbon tetrachloride as is seen from Figs. 1 and 2.

From the data in Figs. 1 and 2, it was concluded that q_{obsd} of Eq. 1 in the case of $[Fe(acac)_3]$ exchanged with Htfa is given by;

$$q_{obsd} = k_A[Htfa](1+k_C[Htfa])/(k_B+[Htfa]) \qquad (2)$$

while that in the case of $[Fe(tfa)_3]$ exchanged with Hacac is expressed by;

$$q_{obsd} = k_A[Hacac]/(k_B+[Hacac]) \qquad (3)$$

From these observations, the mechanism of the reaction of $[Fe(acac)_3]$ with Htfa is assumed to be a dissociative type and thus the following equation may be written;

$$MA_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MA_3^{*} \xrightarrow[+HB]{k_2} MA_2B + HA \quad (k_1 \ll k_2 + k_{-1}) \ : \ V = k_1[MA_3][HB]/((k_{-1}/k_2)+[HB]) \qquad (4)$$

where "*" denotes an activated complex in which one of the bonds in the chelate rings is detouched. As seen from Eq. 4, the rate of reactions in carbon tetrachloride should be independent of Htfa in its higher concentration range. However, the rate in Fig. 1 show a first order dependence with respect to this reagent. This may be explained in terms that Htfa reacts both as the entering ligand and as an acid catalyzer by giving a proton to the leaving acac$^-$. The values of rate constants obtained are given in Table 1. The rate constant catalyzed by Htfa, k_C , determined in Eq. 2 is also given in Table 1. The activation parameters (of k_1 for the reaction of $[Fe(acac)_3]$ and of k for the reaction of $[Fe(tfa)_3]$) are also given in Table 1.

Table 1. Summary of Constants and Activation Parameters at 298 K

$[Fe(acac)_3]$ + Htfa					$[Fe(tfa)_3]$ + Hacac			
log k_1	log k_2/k_{-1}	log k_C	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	log k	log K	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
-3.2	(ca 4)	2.8	88.9	-7.2	-2.6	0.8	60.6	-91.1

The unit is: $k_1(s^{-1})$, $k(s^{-1})$, $k_2/k_{-1}(mol^{-1}dm^3)$, $k_C(mol^{-1}dm^3s^{-1})$, $\Delta H^{\ddagger}(kJmol^{-1})$, $\Delta S^{\ddagger}(JK^{-1}mol^{-1})$, and $K(mol^{-1}dm^3)$.

The rate constant, k_1, agrees with the value of the reaction of $[Fe(acac)_3]$ with benzoyltrifluoroacetone(1-phenyl-4,4,4-trifluoro-1,3-butanedione, Hbfa) in carbon tetrachloride in an unpublished work by us. Kido and Saito$^{2)}$ estimated from the values of activation parameters ($\Delta H^{\ddagger}$ = 60.2 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -92.0 J K^{-1} mol^{-1}) that the isotopic exchange of the ligand of $[Fe(acac)_3]$ in acetylacetone proceeded by an associative mechanism. However, the findings that the value of k_1 of the ligand exchange of $[Fe(acac)_3]$ is similar when the entering ligand was Hbfa and when it was Htfa, that the value of $\Delta H^{\ddagger}$ is larger than the above literature value, and that the $\Delta S^{\ddagger}$ is close to zero support a dissociative mechanism for the reaction of $[Fe(acac)_3]$ in the present experiments.

When the exchange of $[Fe(tfa)_3]$ with Hacac proceeds by an interchange type mechanism, the association equilibrium of $[Fe(tfa)_3]$ and Hacac should be established in a short time, and consequently, the following equation may be written;

$$MA_3 + HB \underset{}{\overset{K}{\rightleftharpoons}} MA_3^{*}(HB) \xrightarrow{k} MA_2B + HA \ : \ V = k[MA_3][HB]/(K^{-1}+[HB]) \qquad (5)$$

The rate constant in Eq. 3 obtained from the results in Fig. 2 is given in Table 1 as well as the activation parameters obtained from the experiments at different temperatures. The findings that the $\Delta H^{\ddagger}$ was smaller than that of the reaction of $[Fe(acac)_3]$, that the $\Delta S^{\ddagger}$ was large with negative sign, and that a change in the optical absorption was observed due to formation of an associate of $[Fe(tfa)_3]$ with Hacac show that the reaction of $[Fe(tfa)_3]$ should be more associative in nature. Thus it should be reasonable to assume an interchange mechanism for this reaction. In the exchange of $[Fe(acac)_3]$ with Htfa, trichloroacetic acid (pK_a = 0.62)$^{3)}$ should assist the opening of the chelate ring. The acceleration by Htfa (pK_a = 6.10)$^{4)}$ in its higher concentration range in Fig. 1 should also be due to the same reason. In the exchange of $[Fe(tfa)_3]$ with Hacac (pK_a = 8.99),$^{4)}$ the three intermediates, six coordinated $[Fe(tfa)_3]$, five coordinated $[Fe(tfa)_3^{*}]$, and the associate, $[Fe(tfa)_3^{*}(Hacac)]$, should be in an equilibrium with each other and the reaction should be controlled by the step involving the formation of the chelate ring and the proton-transfer between the entering and leaving ligands. Trichloroacetic acid should not assist this proton-transfer as experimentally observed. The dependence of the rate on Hacac in Fig. 2 should be caused by changes in the amount of the associate formed. The fact that the ligand exchange rate of [Fe(tfa)$_3$] with Hacac was observed to be lower in 4-methyl-2-pentanone than in carbon tetrachloride while this was not found in the exchange of [Fe(acac)$_3$] with Htfa supports the above explanation; this nucleophilic solvent should associate with [Fe(tfa)$_3^*$] and then interfere with the formation of the associate. The finding that the dependence of the ligand exchange of [Fe(acac)$_3$] on Htfa disappeared when the solvent was 4-methyl-2-pentanone may be explained in terms that Htfa in carbon tetrachloride in this concentration range reacts as an acid catalyzer like as trichloroacetic acid does but the molecules are hydrogen-bonded in this solvent and its ability as the catalyzer disappears.

From the above results it is seen that in the exchange from [Fe(acac)$_3$] to [Fe(tfa)$_3$], the energy necessary for the break of the bond should be important in the activated state, and consequently, the reaction mechanism has a dissociative character but in the exchange from [Fe(tfa)$_3$] to [Fe(acac)$_3$], the energy for the bond formation should be more important and thus the mechanism has an interchange character.

Kinetics of ligand exchange of metal complexes with the same ligand in organic solvents (for example, ref. 2,5-7) and that with different ligands[8,9] have been reported.

In the present study, carbon tetrachloride was employed as the medium. This was very favorable in order to obtain the results which lead to the above conclusions. If it would be a polar solvent, several effects such as the presence of ionic species, strong interactions with the solvent molecules etc. should make the reaction mechanism more complicated and also statistical analysis of the data more difficult.

Details of the results will be reported elsewhere together with the results of experiments using other ligands.

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