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Kinetics and Mechanism of Ligand Exchange of Tris(acetylacetonato)-iron(III) in Acetylacetone

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Tris(acetylacetonato[2-^{14}C])iron(III) undergoes ligand exchange in acetylacetone at 4—16 °C without side reactions. The exchange rate is expressed by Rate$=(k_a+k_b[H_2O])$[complex]([complex]$\approx$0.01 M, $[H_2O]\approx 0.05$ M), and the rate constant (10.2 °C) and activation parameters are $k_a=(8.9\pm1.2)\times10^{-4}\ s^{-1}$, $\Delta H^{\neq}=14.4\pm0.9$ kcal mol^{-1}, $\Delta S^{\neq}=-22\pm3$ cal K^{-1} mol^{-1} and $k_b=(2.22\pm0.20)\times10^{-2}\ M^{-1}\ s^{-1}$, $\Delta H^{\neq}=16.9\pm0.4$ kcal mol^{-1}, $\Delta S^{\neq}=-6.1\pm1.3$ cal K^{-1} mol^{-1} (1 cal=4.18 J, 1 M=1 mol dm^{-3}). No deuterium isotope effect on the rate. The rate-determining steps seem to correspond to the formation of intermediates containing a one-ended acac$^-$ and an Hacac molecule (the k_a path), and the anion and a water molecule (the k_b path), by the S_N2 mechanism.

Although numerous studies of ligand substitution reactions of Fe^{III} complexes have been reported,1) almost all the studies are concerned with $[Fe(H_2O)_6]^{3+}$ and $[Fe(dmso)_6]^{3+}$ (dmso=dimethyl sulfoxide). These complexes undergo labile solvent exchange and anation reactions with various ligands, and both the S_N1 and the S_N2 mechanism have been proposed to these substitution processes. However, little information is available concerning the kinetics of Fe^{III} complexes containing bidentate ligands. Recently, the rate of the ligand substitution of tris(acetylacetonato)iron(III) with 2-thenoyltrifluoroacetone has been reported in organic solvents such as carbon tetrachloride and benzene, but the mechanism was not definitely proposed.2)

The reaction systems consisting of two components, tris(acetylacetonato)complexes of Cr^{III}, Co^{III}, Ru^{III}, or Rh^{III} as solute and acetylacetone (Hacac) as solvent, are suitable for understanding the mechanism of the ligand exchange between the two species.3) On extending of the kinetic studies of these systems, we have found a slow exchange of $Fe(acac)_3$ in Hacac at 10 °C. This paper deals with the kinetics and the mechanism of this exchange reaction examined by the isotopic labelling method.

Experimental

Materials. The labelled acetylacetone, Hacac[2-^{14}C]4) and Hacac[*methylene*-$^2H_2$] (the deuterium content in the methylene moiety: 80%)5) were prepared and purified by the reported methods. Tris(acetylacetonato)iron(III), $Fe(acac)_3$, was prepared from ammonium iron(III) sulfate dodecahydrate (1.9 g), acetylacetone (1.5 ml) and sodium hydrogencarbonate (1.3 g) in water (40 ml) at room temperature. The labelled complex, Fe(acac[2-^{14}C])$_3$, was prepared from Hacac[2-^{14}C] and $Fe(acac)_3$ by the ligand exchange method. The solution of $Fe(acac)_3$ (300 mg) in a mixed solvent of Hacac[2-^{14}C] (1 ml) and acetonitrile (0.5 ml) was heated at 80 °C for 1 h and evaporated to dryness under reduced pressure at room temperature to give orange crystals (*ca.* 300 mg of Fe(acac[2-^{14}C])$_3$), which were recrystalized from benzene–petroleum ether. Its UV and visible absorption spectra in acetonitrile coincided with the reported data.6) The specific activity of the complex was 0.005 μCi/mg.

The solvents, Hacac and acetonitrile, were purified by the reported method.5) Guaranteed grade of hexane was used without purification.

Kinetic Procedure. The free Hacac was separated from the complex in the reaction mixtures by the solvent extraction with hexane. The labelled complex (*ca.* 12 mg) and the solvent (6 ml of Hacac, Hacac[*methylene*-$^2H_2$] or Hacac diluted with acetonitrile) were placed separately in the two sections of a glass-stoppered flask with a branched bottom. The flask was kept in a thermostat (4.4±0.1, 10.2±0.1, or 16.2±0.1 °C) for *ca.* 30 min and rotated to unite the contents of the two sections. The complex dissolved within 10 s. Portions (0.5 ml) of the solution were taken out at appropriate time intervals and swiftly (<10 s) poured into a chilled (−30 °C) hexane layer (10 ml), which floated on a pure acetonitrile layer (1 ml) in a glass-stoppered thin test tube. The tube was shaken vigourously for 10 s and allowed to stand for *ca.* 1 min at −30 °C. A 1 ml portion of the acetonitrile layer was taken out and washed twice with hexane (10 ml) at −30 °C in a similar manner to be made free from Hacac. The complex is insoluble in hexane and present only in the acetonitrile layer. This acetonitrile solution contained sufficient amount of $Fe(acac)_3$ for kinetic analysis (*ca.* 70% of that in the original Hacac solution) and a negligible amount of Hacac. Spectrophotometry at 434 nm and the liquid scintillation counting of this acetonitrile solution gave the specific counting rate of the recovered complex. The exchange rate R was calculated by the McKay equation

$$R = \frac{3[\mathrm{Fe}][\mathrm{Hacac}]}{3[\mathrm{Fe}]+[\mathrm{Hacac}]}\,\frac{\ln[(x_0-x_\infty)/(x_t-x_\infty)]}{t}$$

$$\approx 3[\mathrm{Fe}]\ln(x_0/x_t)/t \quad ([\mathrm{Hacac}]\gg[\mathrm{Fe}],\ x_\infty\approx 0) \qquad (1)$$

where [Fe] and [Hacac] stand for the concentration of the complex and acetylacetone, respectively. The x's are the specific counting rates of the recovered complex at the times indicated by the subscripts.

The water contents (0.2—0.8 M; 1 M=1 mol dm^{-3}) of the reaction mixture were determined by the Karl Fischer titration.

Results

The visible absorption spectra of the reaction mixture containing the given amount of H_2O remained unchanged throughout the reaction, and were identical with those of the complex in anhydrous Hacac and in anhydrous acetonitrile ($[H_2O]<0.01$ M) within experimental errors at room temperature ($\lambda_{max}=434\pm0.5$ nm, $\log\varepsilon=3.55\pm0.02$). The water content also remained unchanged. The McKay plots gave straight lines up to at least 50% completion of the exchange (Fig. 1). No significant zero-time exchange was observed. Therefore, the decrease of the specific counting rate of the recovered complex corresponds exclusively to the exchange reaction (2).

$$\mathrm{Fe(\overset{*}{acac})_3 + Hacac \rightleftharpoons Fe(acac)_3 + H\overset{*}{acac}} \qquad (2)$$

The R in neat acetylacetone was proportional to the concentration of the complex (Table 1) and is given by

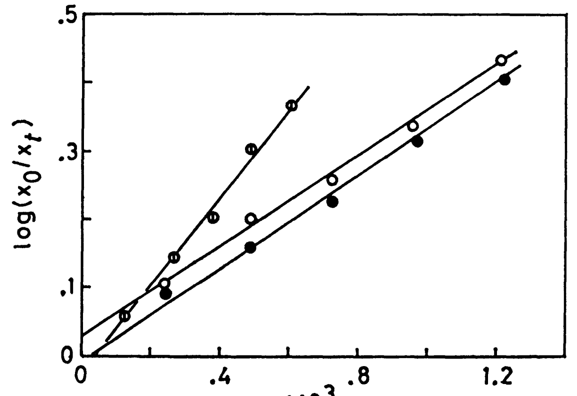


Fig. 1. Typical McKay plots for the ligand exchange of Fe(acac)$_3$ in acetylacetone (○, ⦶) and in acetylacetone[*methylene*-$^2H_2$](●) at 10.2(⦶) and 16.2(○,●) °C ([Fe]≈0.006 M).

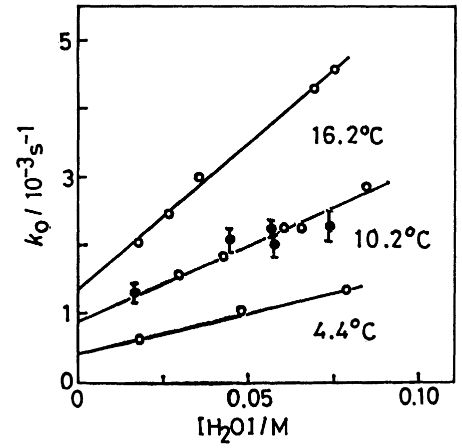


Fig. 2. Influence of the water concentration and the deuterium isotope effect on the exchange rate constant (k_0) of Fe(acac)$_3$ in acetylacetone(○) and in acetylacetone[*methylene*-$^2H_2$](●)([Fe]≃0.006 M).

TABLE 1. LIGAND EXCHANGE RATE OF Fe(acac-[2-$^{14}C_3$])$_3$ IN ACETYLACETONE AT 4.4 °C

[Fe] / 10^{-3} M	[H$_2$O] / M	R / 10^{-6} M s^{-1}	k_0 / 10^{-4} s^{-1}
5.78	0.018	3.7±0.1	6.4±0.2
9.75	0.021	6.5±0.2	6.7±0.2

$$R = k_0[\mathrm{Fe}] \qquad (3)$$

where k_0 is the observed first-order rate constant. The k_0 value was dependent on [H$_2$O] (Fig. 2), and expressed by Eq. 4 in the given concentration range,

$$k_0 = k_a + k_b[\mathrm{H_2O}]. \qquad (4)$$

The k_a and k_b values were obtained from the intercepts and the slopes of the lines in Fig. 2, respectively, and are shown in Table 2, together with the activation parameters.

When Hacac[*methylene*-$^2H_2$] was used as the solvent at 10.2 °C in place of the ordinary Hacac, the k_0 values coincided with those in Hacac within the experimental errors (Fig. 2).

The k_0 value increased linearly with the increase in concentration of Hacac in the mixed solvent with acetonitrile up to 9.7 M (in neat acetylacetone) under a given concentration of the complex and water (Fig. 3). The k_0 *vs.* [Hacac] plot has a very small intercept.

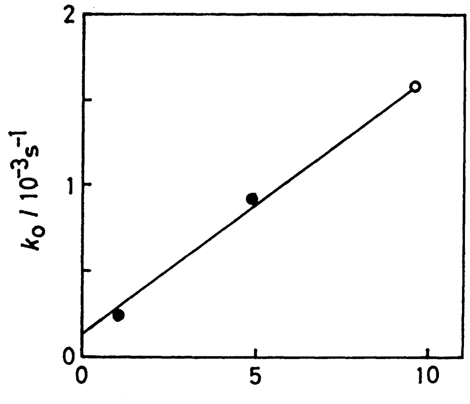


Fig. 3. Influence of the free ligand concentration on the exchange rate constant (k_0) of Fe(acac)$_3$ in acetylacetone(○) and in acetonitrile(●)([Fe]≃0.006 M, [H$_2$O]=0.03 M, 10.2 °C).

Discussion

Equation 4 indicates that the exchange in Hacac (Eq. 2) proceeds by two paths (the k$_a$ and k$_b$ path) in the presence of water. The linear plot of k_0 *vs.* [Hacac] (Fig. 3) suggests that the exchange reactions in Hacac and in the mixed solvent are essentially the same and expressed by Eq. 5 in the concentration region from 1 to 9.7 M of Hacac,

$$k_0 = k_0'[\mathrm{Hacac}]. \qquad (5)$$

If either k_a or k_b in Eq. 4 were independent of [Hacac], the k_0 *vs.* [Hacac] plot would not have such a small intercept shown in Fig. 3, because the k$_a$ and k$_b$ terms give comparable contributions to k_0 under the given

TABLE 2. KINETIC DATA FOR THE LIGAND EXCHANGE OF Fe(acac[2-^{14}C])$_3$ IN ACETYLACETONE

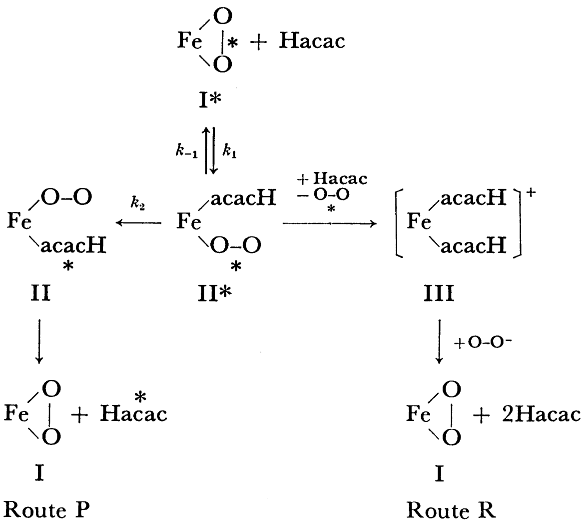
	Rate constants			$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Parameters	4.4 °C	10.2 °C	16.2 °C	kcal mol^{-1}	cal K^{-1} mol^{-1}
k_a/10^{-3} s^{-1}	0.44±0.04	0.89±0.12	1.35±0.10	14.4±0.9	−22±3
k_b/10^{-2} M^{-1} s^{-1}	1.16±0.08	2.22±0.20	4.24±0.19	16.9±0.4	−6.1±1.3

conditions (*cf.* Fig. 2, $[H_2O] \simeq 0.03$ M). Hence Eq. 6 holds at least in the vicinity of [Hacac]=9.7 M (in Hacac),

$$k_o \approx (k_a'+k_b'[H_2O])[\mathrm{Hacac}]. \qquad (6)$$

Equations 3 and 6 suggest that one $\mathrm{Fe(acac)_3}$ and one Hacac molecule participate in the k_a and k_b paths and one H_2O molecule also does in the k_b path.

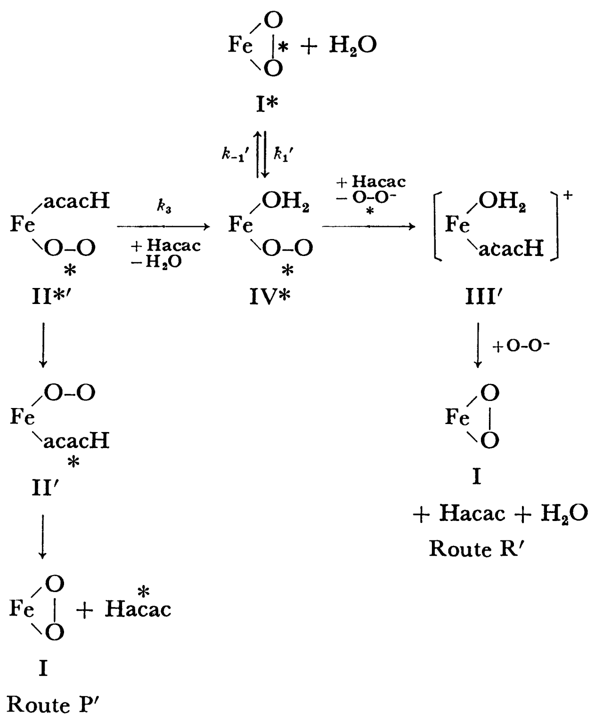
Possible Reaction Routes of the k_a and k_b Paths. Varieties of probable reaction routes for the k_a path are very much limited, since the reaction system is very simple and the chemical species participating in the rate-determining step should be only $\mathrm{Fe(acac)_3}$ and Hacac. Scheme 1 can be assumed almost exclusively as possible routes for the k_a path,[3]



Scheme 1.

where O–O and I* denote $\mathrm{acac^-}$ and $\mathrm{Fe(\overset{*}{acac})_3}$, respectively, and two $\mathrm{acac^-}$ chelates are omitted from each species. The intermediate II* is formed from I* and Hacac. (II* corresponds to an intermediate containing a one-ended bidentate and a solvent molecule; such a type of intermediate is generally accepted in substitution processes of bidentates.[3]) In the Route P, II* is converted into II through the proton transfer between the unidentate ligands, $\overset{*}{\mathrm{O{-}O}}{}^-$ and $\mathrm{H\overset{*}{acac}}$, and II turns to I and $\mathrm{H\overset{*}{acac}}$. In the Route R, II* changes into another cationic intermediate III by the replacement of unidentate $\overset{*}{\mathrm{O{-}O}}{}^-$ by free Hacac (III corresponds to a bis-chelate-type intermediate containing two solvent molecules, $[\mathrm{Fe(acac)_2(solvent)_2}]^+$), and III produces I by the ligation of $\mathrm{O{-}O^-}$ which is formed by the proton exchange between $\overset{*}{\mathrm{O{-}O}}{}^-$ and Hacac in the bulk or in the second coordination sphere of the complex.

Similar routes are possible for the k_b path shown in Scheme 2. I* and a water molecule produce an intermediate IV*. When H_2O or the unidentate $\overset{*}{\mathrm{O{-}O}}$ in IV* is replaced by the free Hacac, II*′ or III′ is formed, respectively. The intermediates II*′ and III′ undergo similar changes as in the P and R Routes in Scheme 1, to turn to I through the P′ and R′ Routes, respectively.



Scheme 2.

Reaction Mechanism. The activation enthalpies and entropies for k_a and k_b can be reckoned to have similar tendency to each other (Table 2). Hence both the paths are suggested to have similar reaction routes and rate-determining steps to each other. If the similar routes are P and P′ and the k_1 and the k_1' step are the slowest in each path, stationary-state conditions to II* and IV*, can be reasonably assumed to give Eqs. 7 and 8,

$$k_a = k_1[\mathrm{Hacac}]\frac{k_2}{k_{-1}+k_2} \qquad (7)$$

$$k_b[H_2O] = k_1'[H_2O]\frac{k_3[\mathrm{Hacac}]}{k_3[\mathrm{Hacac}]+k_{-1}'} \qquad (8)$$

Concentrations of the intermediates should be negligible as compared with those of I* and I, since the visible absorption spectra of the complex in the reaction mixture, in Hacac and in acetonitrile are almost identical to one another (*vide supra*). On the assumptions, $k_{-1} \ll k_2$ and $k_{-1}' \gg k_3[\mathrm{Hacac}]$, Eqs. 7 and 8 are further converted into Eqs. 9 and 10, respectively.

$$k_a = k_1[\mathrm{Hacac}] \simeq k_a'[\mathrm{Hacac}] \qquad (9)$$

$$k_b[H_2O] = k_1'[H_2O]\frac{k_3[\mathrm{Hacac}]}{k_{-1}'} \simeq k_b'[H_2O][\mathrm{Hacac}] \qquad (10)$$

These assumptions are not unreasonable. The proton transfer process(k_2) can be much faster than the ring-closure process(k_{-1}). On the contrary, if k_2 were much smaller than k_{-1}, k_a should be affected by k_2 (*cf.* Eq. 7) and deuterium isotope effect on the exchange rate should be observed as in the exchange of $\mathrm{Cr(acac)_3}$ in Hacac.[5] Moreover, replacement of H_2O in IV* by the free end of one-ended acetylacetonate ligand (k_{-1}', intramolecular) can be much faster than that by the free Hacac (k_3[Hacac], intermolecular).

Equations 9 and 10 are consistent with Eq. 6. The k_1 and k_1' steps correspond to the rate-determining steps and the term $k_3[\text{Hacac}]/k_{-1}'$ represents a branching ratio for the accomplishment of the exchange from IV*.

On the contrary, the combination of the R and R′ Routes does not seem adequate. When the first steps, I*→II* and I*→IV*, are considered to be the rate-determining steps, the first-order dependency of [Hacac] in the k_b term in Eq. 6 cannot be interpreted. On the other hand, when the second steps (II*→III, IV*→III′, *i.e.*, replacement of acetylacetonate unidentate by Hacac or H_2O) are assumed to be rate-determining or to be concerned in determining the rate as in the P′ Route mentioned above, the k_a term must have the second-order dependency with respect to [Hacac], which conflicts with the observation (Eq. 6). Such a type of one-ended acetylacetonate in II* and IV* has been claimed to be stablized towards replacement by free ligands such as Hacac, H_2O and acetonitrile in the exchange of $Co(acac)_3$ in acetonitrile. The stability has been attributed to the conjugated structure of the ligand, *i.e.*, concentration of negative charge on the coordinated oxygen ($Co{-}O{-}C(CH_3){=}CH{-}C(CH_3){=}O$).[7]

Alternative Routes. Besides the combination of the routes mentioned above, other sets of routes for the k_a and k_b paths can satisfy Eq. 6; a) the P Route for the k_a path and a water-assisted route, in which a water molecule assists the proton transfer in the P Route (II*→II in Scheme 1), for the k_b path, and b) catalytic action of Hacac or H_2O as a proton donor to the original complex or to some of the intermediates, *e.g.*, the formation of II* in the P Route without and with the aid of a proton of H_2O for the k_a and k_b paths, respectively. However, if these routes operated in the exchange, the deuterium isotope effect on k_a and k_b might be observed. In the exchange of $Cr(acac)_3$[5] and $Co(acac)_3$[7] in acetonitrile, the effect was significant in a water-assisted ($k_H/k_D=1.5$) and an acid-catalyzed ($k_H/k_D=0.4$) processes, respectively. Hence the routes shown in a) and b) are considered to be unlikely on the basis of the absence of the isotope effect in both k_a and k_b.

Therefore, the P and P′ Routes are concluded to be the most plausible mechanisms and illustrated again in Fig. 4.

Substitution Mechanism in the Rate-determining Steps. An S_N2 mechanism can be assigned to the rate-determining k_1 step on the basis of the negative value of $\Delta S^{\ddagger}$ (Table 2) and the first-order dependency of k_a on [Hacac] (Fig. 3). In the exchange of $Co(acac)_3$ in acetonitrile[7] and in Hacac,[3] $\Delta S^{\ddagger}$ has large positive values and the rate is independent of [Hacac]. An S_N1 mechanism has been clearly assigned to the exchange of the Co^{III} complex on the basis of these features and the almost identical rate of the exchange with that of the racemization.[8]

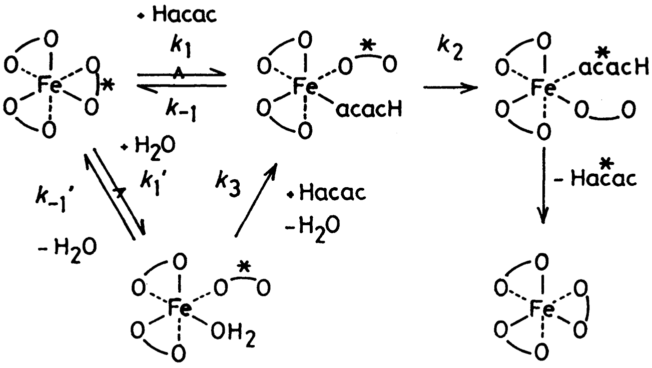


Fig. 4. Plausible mechanism of the ligand exchange of $Fe(acac)_3$ in acetylacetone.

The negative value of $\Delta S^{\ddagger}$ for k_b also suggests an S_N2 attack of H_2O in the k_1' step.

The $\Delta S^{\ddagger}$ value for k_b is less negative than that for k_a by *ca.* 16 cal K^{-1} mol^{-1}, while the $\Delta H^{\ddagger}$ value for k_b is slightly larger than that for k_b. On the other hand, the contributions of the k_a and the k_b term for the rate are comparable, while the concentration of H_2O (0.02—0.1 M) is much less than that of Hacac (9.7 M). The result suggests the prevailing nucleophilicity of H_2O over that of Hacac. Such a difference may be attributable to the steric factor of the nucleophiles.

Comparison with Related Reactions. Kinetic parameters of the present exchange and the solvent exchange reactions of $Fe^{III}O_6$ type complexes are collected in Table 3. The present k_0 is different from that of the other reactions involving unidentate ligands, the ratio amounting to 10^4. Such a marked inertness in substitution of bidentate ligands in iron(III) complexes has been also found in the aquation of $[Fe(C_2O_4)(H_2O)_4]^+$ ($k=3\times10^{-3}\,s^{-1}$ at 25 °C)[1d] and in the replacement of $acac^-$ in $Fe(acac)_3$ by 2-thenoyltrifluoroacetonate in CCl_4 ($k=6\times10^{-3}\,s^{-1}$ at 25 °C).[2]

On the other hand, the reactions in Table 3 exhibit a common tendency in the values of the activation parameters. There seems to be a common trend that these exchange reactions proceed *via* an S_N2 mechanism, regardless of the dentate number of the ligands. The assignment is consistent with the recent assignment

Table 3. First-order rate constants and activation parameters of the ligand exchange reactions of iron(III) complexes at 25 °C

Complex	Solvent	k_1/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	Reference
$Fe(acac)_3$	Hacac	0.0033(k_a)	14.4±0.9	−22±3	This work
$[Fe(H_2O)_6]^{3+}$	H_2O	150	—	—	a)
$[Fe(dmf)_6]^{3+}$	DMF	33	12.5±1.5	−10±5	b)
		61	10.1±1	−16.5±3.0	c)
$[Fe(dmso)_6]^{3+}$	DMSO	50	10±2	−11±4	d)

DMF=*N,N*-Dimethylformamide, DMSO=Dimethyl sulfoxide. a) Ref. 1e(*cf.* Ref. 1g). b) Ref. 1g. c) Ref. 1i. d) Ref. 1f.

of an S_N2 mechanism to the anation of NCS^- and Cl^- upon $[Fe(H_2O)_6]^{3+}$ on the basis of the values of the activation volume.[1p,q]

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