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REACTIVITY AND REACTION MECHANISM OF ACETYLACETONATO COMPLEXES OF TERVALENT METAL IONS IN SOLUTION

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate ion
DMF	dimethylformamide
DMSO	dimethyl sulphoxide
EtOAc	ethyl acetate

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Hacac	acetylacetone
THF	tetrahydrofuran
tmpa	trimethylphosphate

(Coordinated solvent molecules are in lower-case letters.)

A. INTRODUCTION

Structural studies of inorganic compounds have made remarkable progress in the first half of the 20th century since Werner's coordination theory was advocated, but the reactions of inorganic compounds have drawn rather limited attention from chemists. There were no planned synthetic paths for preparing coordination compounds. Virtually all inorganic reactions were thought to be rapid and unselective, the nature of the products being governed by thermodynamic and solubility factors. Before World War II only a limited number of studies dealt with stereochemistry [1]. Systematic studies of the ligand substitution reactions of metal complexes were initiated after World War II. A good review of these studies together with a list of papers is given in this issue by Basolo [2].

The advent of the use of radioisotopes enabled the isotopic exchange rate of ligands to be measured without the need to consider the thermodynamics of ligand substitution reactions. However, the application of this method was limited to very slow reactions because the experiment invoked a rather tedious procedure [3]. Taube [4] was the first to survey the qualitative and quantitative information on the rates of ligand substitution reactions of metal complexes consisting of various metal ions and ligands. He advocated the idea of substitution-labile and substitution-inert complexes, and considered that this distinction is the attribute of the central metal ion rather than that of the ligand. His classification is shown in Table 1.

The kinetics of ligand substitution reactions have been widely studied in the latter half of the 20th century. Remarkable progress in experimental apparatus has stimulated studies of both slow and rapid substitution reactions. The variety of coordination compounds was extended from octahedral transition metal complexes to their square-planar and tetrahedral complexes and also to the complexes of main group elements. The variety of ligands was also expanded from unidentate to bidentate and multidentate organic ligands and macrocyclic ligands. Several useful reviews and monographs have been published since the 1960s and a good deal of discussion has been set forth as to the mechanism of ligand substitution [5].

Examination of the available information related to substitution lability and the inert nature of various metal complexes tempted us to modify Taube's classification as shown in Table 1 [6]. The main group and transi-

TABLE 1

(a) Classification of octahedral metal complexes on the basis of ligand substitution rates

Almost always labile	Variable, depending on ligands etc.	Almost always inert
Central metal ions [6]		
Ions of 1A and 2A family, most rare earth ions, Cr(II), Mn(II), Co(II), Cu(II), Zn(II), Cd(II), Pb(II), Ti(III), V(III), Mn(III), Fe(III)	Some rare earth ions, V(II), Fe(II), Ni(II), Ru(II), Os(II), Ru(III), Al(III), Ga(III), In(III), Tl(III), Ti(IV), Mo(IV), Si(IV), Ge(IV), Sn(IV)	Cr(III), Mo(III), Co(III), Rh(III), Ir(III), Re(IV), Re(IV), Ir(IV), Pd(IV), Pt(IV)
Electron configuration		
Low valent d^0 and d^{10}, most high spin ions	High valent d^{10}, some high spin ions, some d^3, d^6 and d^8 ions	Some d^3 ions, most low spin ions

(b) Taube's classification according to electron configuration

	Labile	Inert
Electron configuration [4]	d^0, d^{10} and high spin complexes	d^3 and low spin complexes

tion metal ions of low and high electric charges might be better classified into three groups, almost always labile, almost always inert and variable depending on the ligand and reaction circumstances. At the same time we set out to study the kinetics and mechanism of ligand isotopic exchange reactions of tervalent metal complexes of tris(acetylacetonato) type [7] (eqn. (1)):

$$[\mathrm{M(acac)_3}] + \mathrm{Hacac}^* \rightleftharpoons [\mathrm{M(acac)_2(^*acac)}] + \mathrm{Hacac} \qquad (1)$$

Acetylacetonate(1 −) forms a variety of stable metal complexes without electric charge. The tris-bidentate type complexes with tervalent main group and transition metal ions have essentially the same octahedral structure. They are soluble in various organic solvents and thus provide a most useful counterpart to the aqua complexes of these metal ions, of which the ligand isotopic exchange kinetics have been extensively studied.

B. EXPERIMENTAL METHOD AND ANALYSIS

(i) The complexes

The complexes used in the present study are those of the tervalent ions of scandium [8], vanadium [9], chromium [10,11], molybdenum [12], manganese [12], technetium [13], iron [14], ruthenium [11], cobalt [11,15], rhodium [11], aluminium [16–18], gallium [12,19] and indium [12]. (Some other complexes with quadrivalent ions of titanium [20], silicon [21], germanium [22,23] and tin [24] were also studied.) The complexes were synthesized and purified by known methods. The manganese and iron complexes were of high spin configuration, and the technetium, cobalt, ruthenium and rhodium complexes of low spin configuration. Some complexes enabled us to obtain very precise kinetic information, e.g. those of aluminium and chromium, but some gave only limited information because of experimental difficulties.

(ii) Isotope labelling method

Acetylacetone [^{14}C] was synthesized from acetone-[1,3-^{14}C] or acetone-[2-^{14}C] and ethyl acetate, which was isotopically diluted with commercial acetylacetone (Hacac) and used throughout the experiment (ca. 0.01 μC). The acetylacetonato complexes were mostly isotope labelled.

The complexes were separated from Hacac and the ingredients in the reaction mixture by the following methods: (i) precipitation by addition of petroleum ether to the solutions in acetylacetone, ethyl acetate, tetrahydrofuran etc. [16]; (ii) extraction of free Hacac with hexane from the solution in acetonitrile [14]; (iii) vacuum evaporation of the solvent and free acetylacetone [10]. The difficulty of separation and the time required increase from methods (i) to (iii).

The recovered complex was weighed, dissolved in toluene containing *p*-terphenyl and *p*-bis(5-phenyl-2-oxazolylbenzene) (POPOP) and submitted to liquid scintillation counting. In method (ii) the concentration of the complex in acetonitrile was determined spectrophotometrically, and the specific counting rate was measured using the liquid scintillation method. Whenever the final specific counting rate (x_∞) could only be obtained experimentally with difficulty because of insufficient stability of the complex, the value was calculated from the initial counting rate and the amounts of complex and Hacac used for each kinetic run. Generally five or six measurements were made during one kinetic run.

(iii) Analysis of the result

The experimental results were analysed using McKay's formula [25]:

$$R = [3ab/(3a+b)] \ln[(x_0 - x_\infty)/(x_0 - x_t)]/t \qquad (2)$$

where a and b are the concentrations of the complex and free Hacac respectively, and the x terms are the specific counting rates at the times indicated by the subscripts. When Hacac is used as solvent, the formula simplifies to

$$R = 3a \ln(x_0/x_t)/t \qquad (3)$$

Approximately 50 kinetic runs were performed for each complex under varying conditions of concentration of Hacac, the complex, water and other ingredients, and of temperature and solvent. When the deuterium isotope effect was to be measured, the double-labelling technique was utilized by use of deuterated water and Hacac-^2H at the 3-position [10].

The exclusive participation of isotopic exchange in the reaction mixture was verified by spectrophotometry of the recovered complex and, whenever possible, by the coincidence between the absorption spectrum of the reaction mixture and the sum of the spectra of the components. The linearity of McKay's plot was also useful for verification.

(iv) Influence of various reaction conditions

The R vs. a plot was linear for all the kinetic runs, and the rate is discussed by use of k_0 in place of R (eqn. (4)).

It was virtually impossible to exclude water completely from the reaction mixture, regardless of the solvent used. Almost all the kinetic runs were performed in the presence of varying amounts of water. The first-order rate constant k_0 generally increases with increase in water concentration and an intercept is observed on the k_0 vs. water concentration plot:

$$R = k_0 a = a(k_1 + k_2[H_2O]) \qquad (4)$$

where k_1 indicates the rate of exchange without the aid of water catalysis. The estimated experimental error is generally $\pm 10\%$ for individual k values, but is sometimes larger, especially for k_1 values determined by extrapolation.

Protic acids often accelerate the exchange so that a third term is added to eqn. (4). This term consists of two sub-terms one of which is independent of and the other dependent on the water concentration [17]:

$$k_0 = k_1 + k_2[H_2O] + [\text{acid}](k_3 + k_4[H_2O]) \qquad (5)$$

In solvents other than neat Hacac, the influence of free Hacac concentration is often observed. Equation (6) represents the general formula for such a case:

$$k_0 = k_1' + k_2'[H_2O] + (k_3' + k_4'[H_2O])[\text{Hacac}] \qquad (6)$$

In some systems (cobalt and manganese) the k_3' and k_4' terms are missing, and in some systems (vanadium, scandium and indium), [Hacac] is represented by the concentration of the enol form of free Hacac (vide infra).

The enthalpy and entropy of activation were obtained from the usual Eyring plot over a temperature range of ca. 50 K. The activation volume was calculated on the basis of measurements made under 0.1–200 MPa, but only for limited systems because of experimental difficulties.

C. REACTION MECHANISM

The mechanism of exchange of the acetylacetonate of individual complexes has been discussed previously [8–19], and only a brief summary is given here with special reference to the exchange in neat Hacac.

(i) Reaction path

For the coordinated acetylacetonate to be replaced by another acac$^-$ in neat Hacac, the following three steps are essential: (1) the breakage of the coordination bond between the metal ion and acac$^-$; (2) the transfer of a proton from Hacac to acac$^-$; and (3) the formation of a metal–acac$^-$ bond. Through elaborate kinetic studies we have concluded that the reaction proceeds as shown in Fig. 1 [18].

An intermediate species **III** containing two bidentate acac$^-$ and one each of unidentate acac$^-$ and Hacac plays an important role. Proton transfer from incoming Hacac to leaving acac$^-$ should occur in this intermediate, and chelation of the incoming acac$^-$ follows. The last step is the reverse of

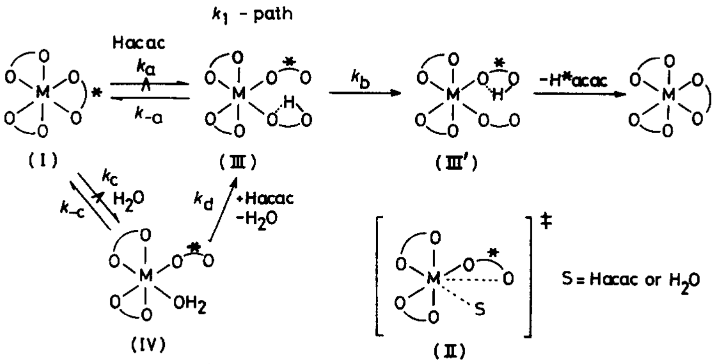

Fig. 1. A plausible mechanism for the ligand isotopic exchange of [M(III)(acac)$_3$] (**I**) in neat acetylacetone. Asterisks denote ^{14}C labelling, and arrows with circumflexes show the rate-determining step.

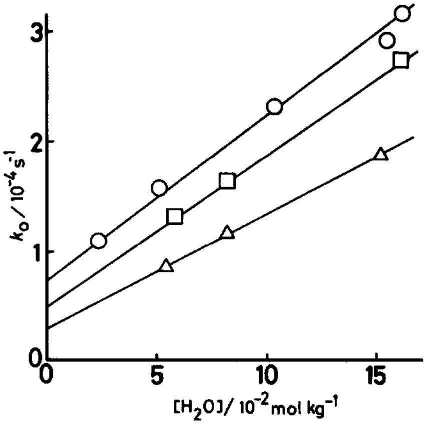

Fig. 2. Observed isotopic exchange rate constant k_0 of [Al(acac)$_3$] ((1.54–3.23)$\times 10^{-3}$ M) in acetylacetone at 25 ° C under elevated pressures: ○, 0.10 MPa; □, 42.1 MPa; △, 188 MPa.

the first, since the original complex is restored after isotopic exchange. The transition state from **I** to **III** may be illustrated with **II**. In the absence of catalysing species (k_1 term in eqn. (4)) the breakage of one metal–O bond (to form unidentate acac$^-$) can take place either spontaneously or through the association of a solvent molecule. These two mechanisms correspond to mechanisms Id and Ia, respectively. In the presence of water, an H_2O molecule can bind to the coordination site (**IV**) and is then replaced by Hacac to give the reaction intermediate **III**. This pathway corresponds to the k_2 term in eqn. (4).

(ii) Reaction mechanism of [Al(acac)$_3$]

This complex enabled a detailed discussion of the mechanism in various solvents to be given [16–18]. The results are summarized in Table 2.

The PMR spectrum of the reaction mixture gave only the signals of [Al(acac)$_3$] (0.3 M) and Hacac (1.9 M) in deuterated acetonitrile. Hence the concentration of the intermediate **III** is very low compared with that of **I**. The additivity of the absorbance at 305 nm and the shoulder due to **I** in Hacac also support this conclusion. Hence $k_a \ll k_{-a}$. If **III** is a steady state intermediate, eqn. (7) holds, and the ratio $k_b/(k_{-a}+k_b)$ indicates the probability of obtaining the product from **III**:

$$k_1 = k_a k_b/(k_{-a}+k_b) \qquad (7)$$

The magnitude of k_{-a} relative to k_b can be estimated from the deuterium isotope effect. The primary isotope effect on proton transfer is generally $k_H/k_D > 2$ [26]. Deuteration may change the nucleophilic basicity of Hacac,

TABLE 2

Kinetic data for ligand exchange and related reactions of aluminium(III) complexes

Complex	Solvent	Rate constant [a]	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})	$\frac{\Delta V^{\neq}}{V_s^0}$	Ref.
$[Al(acac)_3]$	Hacac	k_1	85	−38	+10	+0.10	18
	Hacac	k_2	79	−34	+5	+0.05	18
	Toluene	k_2 [b]	80	−16			17
	EtOAc	k_1	90	−51			17
	THF	k_0	90	−33			16
	$C_2H_5OH–C_5H_{12}$	k_{rac} [c]	133	+227			33
$[Al(H_2O)_6]^{3+}$	H_2O	k_0	85	+42	+6	+0.32	31
$[Al(dmf)_6]^{3+}$	DMP–CH_3NO_2	k_0	88	+28	+14	+0.18	29
$[Al(dmso)_6]^{3+}$	DMSO	k_0	83	+22	+16	+0.22	28
$[Al(tmpa)_6]^{3+}$	TMPA–CH_3NO_2	k_0	85	+38	+23	+0.20	35
$[Al(CH_3CN)_6]^{3+}$	CH_3CN	k_0	80	+40			30

[a] $k_0 = k_1 + k_2[H_2O]$; k_0, observed first-order rate constant. [b] No k_1 path in toluene. [c] k_{rac}, rate constant of racemization. [d] V_s^0 (cm^3 mol^{-1}), partial molar volume of the ligand.

but to a much smaller extent than does the proton transfer rate. In so far as k_b is subject only to the deuterium isotope effect, and k_{bH}/k_{bD} falls in the range 2–10, the ratio k_b/k_{-a} is calculated from the observed k_{1H}/k_{1D} value (1.6) to be 0.5–0.9. Hence $k_a \ll k_{-a} < k_b$, and the first substitution should be rate determining. Since k_1 and k_2 have similar activation parameters and deuterium isotope effects, both paths must have a similar rate-determining step, i.e. the water molecule gives **IV** more easily than Hacac gives **III**, and **IV** is converted into **III** quickly. For the tris(acetylacetonato) complexes of quadrivalent ions such as those of silicon, germanium and tin the intermediate **III** seems more stable, and sometimes the proton transfer can be rate determining [20–24].

The activation volume is a useful quantity for elucidating the activation mode (Ia or Id) of ligand substitution [27]. Figure 2 exemplifies the dependence of k_0 on water concentration under different pressures, and Fig. 3 plots of k_1 (intercept) and k_2 (gradient) vs. pressure respectively for the ligand exchange of this complex in Hacac at 25 °C. A dissociative mechanism was proposed for the exchange of a unidentate ligand molecule such as DMSO [28], DMF [29], acetonitrile [30] and water [31] on the basis of positive (+5.7 to +23 cm^3 mol^{-1}) activation volume and this suggests mechanism Id, while the modestly negative $\Delta S^{\neq}$ implies mechanism Ia.

Use of the ratio $\Delta V^{\neq}/V_s^0$, where V_s^0 is the partial molar volume of the solvent molecule [27], may be useful in resolving this ambiguity. A larger absolute value of the ratio is claimed to indicate a more enhanced associa-

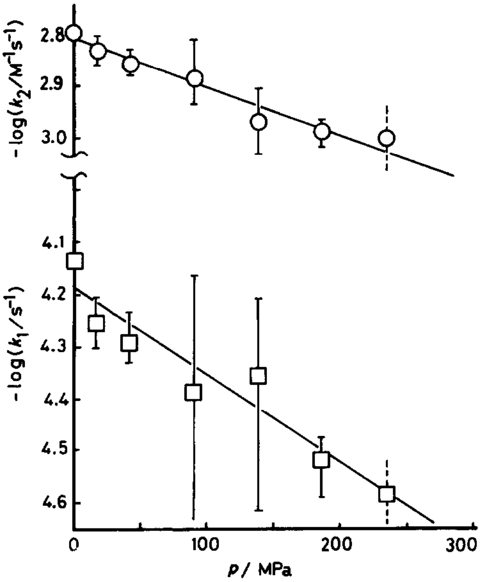

Fig. 3. Pressure dependence of k_1 and k_2 for the ligand isotopic exchange of [Al(acac)$_3$] in acetylacetone at 25° C: □, k_1; ○, k_2.

tive (A) or dissociative (D) character. Our system gives the ratio 0.1, whereas the unidentate ligand systems give ratios of ca. 0.2. Hence a less dissociative nature of the rate-determining step is implied in our system, i.e. more significant participation of the incoming Hacac is feasible in the formation of **III** from **I**. Another interpretation can be encountered in our system by considering more seriously the fact that the leaving ligand remains within the coordination sphere as a unidentate ligand. The leaving ligand is not entirely free after the M–O bond is broken, so that the increase in entropy accompanied by the bond breakage may not be large enough to give a positive activation entropy.

It also appears that steric factors play a significant role in determining the $\Delta V^{\neq}$ value [32]. Bulky solvent molecules such as DMSO and DMF repel each other in the coordination sphere, thereby decreasing the contribution of the incoming ligand at the transition state. The enolate ring of coordinated acac$^-$ is planar and provides less crowding in the coordination sphere than DMSO and DMF. Stacking of the solvent Hacac molecule on the acac$^-$ ligand may be possible both at the ground and transition state, to bring about a more enhanced contribution of the incoming ligand on going to the transition state.

In less-polar solvents such as toluene, EtOAc and THF, the activation enthalpy (80–90 kJ mol^{-1}) and entropy (-50 to -15 J mol^{-1} K^{-1}) do not differ much from those in Hacac. The k_0 values are independent of the Hacac concentration (0.02–0.2 M) in these solvents [17]. Therefore the substitution mechanism does not seem very different from that in Hacac. The acid catalysis may be understood as facilitating the proton transfer at the intermediate **III**.

This complex was resolved and the rate of racemization was measured in mixtures of isopentane and ethanol (1 + 1 v/v) and isopentane and diethyl ether (1 + 5 v/v) in the absence of free Hacac. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are large and positive (Table 2). A mechanism involving an intermediate with coordination number five was postulated, in which one of the Al–O bonds is dissociatively broken and internal rearrangement follows [33]. This result indirectly supports our view that free Hacac participates in the formation of transition state **II** in neat Hacac, but does not affect the rate.

(iii) Reaction mechanism of [Co(acac)$_3$]

Ligand substitution reactions of cobalt(III) complexes are understood to proceed generally via a dissociative mechanism. The isotopic exchange of this complex was studied in Hacac [11] and compared with the racemization rate in chlorobenzene [34] (Table 3). Large positive $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values and the absence of a deuterium isotope effect ($k_H/k_D = 1$) suggest a dissociative mechanism for both reactions. The overall process for the exchange should be similar to that given in Fig. 1, and the branching ratio (eqn. (7)) should be almost unity. On going from **I** to **III**, however, another intermediate **II′** should be involved; this contains one unidentate acac$^-$ and has a coordination number of five (Fig. 4). (Intermediate **II′** has a similar structure to that of **II**, but **II′** is an intermediate and **II** is a transition state.) A polar solvent molecule may occupy the sixth coordination site to give an apparent coordination number of six, but its coordination does not affect the rate, so that the process from **I** to **II′** is thought to be purely dissociative. The rate k_x of formation of **II′** from **I** by a purely dissociative mechanism should be rate determining, and the observed k_1 value should correspond to k_x. The value of k_{-x} is large, and cannot be much larger than k_y. The racemization was claimed to proceed via an intermediate of coordination

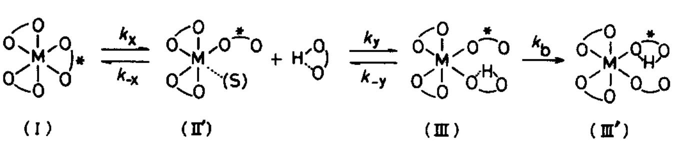

Fig. 4. Plausible mechanism of ligand isotopic exchange of [Co(acac)$_3$] in acetylacetone. Asterisks denote ^{14}C labelling.

TABLE 3

Rate constants and activation parameters for the ligand isotopic exchange of [M(III)(acac)$_3$] in acetylacetone

M	Rate constant	t (°C)	k (10^{-5} s^{-1})	k_H/k_D	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	Ref.
Al	k_1	25	9.1	1.6	85	−38	18
	k_2	25	1.5 ^{a}	1.5	79	−34	18
	k_r ^{b}			–	133	+227	33
Cr	k_1	117	5.6	1.5	120	−21	12
	k_h ^{c}	166	0.27 ^{a}	–	94	−104	11
	k_i ^{c}	166	1.4	ca. 2	159	ca. 0	11
	k_w ^{c}	166	0.94 ^{d}		126	−2	11
	k_r ^{d}	98	0.17	–	143	+29	
Co	k_1	93	2.3	1.0	153	+80	11
	k_r ^{d}	93	4.0	–	140	+59	34
Ru	k_1	150	5.2	–	115	−61	11
Rh	k_1	185	2.4	1.4	119	−80	11
V	k_1	25	13.6	1.0	73	−73	9
	k_2	25	0.66 ^{a}		75	−53	9
	k_1 ^{c}	33.5	5.0	1.0	ca. 80	ca. −59	9
	k_2 ^{c}	33.5	0.33 ^{a}		ca. 67	ca. −88	9
Ga	k_1	25	160	1.9	67	−71	19
In	k_1	25	2×10^{4} ^{c}	5	47	−84	12
Sc	k_2 ^{f}	50	3.6×10^{4} ^{a,c}	5	36	−88 ^{e}	8
Fe	k_1	16	135	1.0	60	−92	14
Tc	k_1	123	5.2	2.3	119	−27	12
Mo	k_1	25	0.35	–	–	–	12
Mn	k_1	25	10^{5} ^{c}	–	–	–	12

[a] k_2 in 10^{-3} M^{-1} s^{-1}. [b] In $C_5H_{12}+C_2H_5OH$. [c] In CH_3CN. [d] Racemization in C_6H_5Cl. [e] The value may increase when the enol concentration is used. [f] Determined by NMR.

number five containing one unidentate acac$^-$. The mechanism through which the Co–O bond is broken should be similar for both the racemization and isotopic exchange.

(iv) Reaction mechanism of [Cr(acac)$_3$]

The kinetics were studied in detail in Hacac [11] and acetonitrile [10]. Substitution mechanisms of chromium(III) complexes are generally thought to depend on the kind of ligand and the reaction conditions. Such complexity is reflected in the kinetics of the isotopic exchange reaction in neat Hacac and acetonitrile.

(a) Acetylacetone

No influence of water concentration was observed in Hacac. The values of $\Delta S^{\neq}$ and the ratio k_H/k_D are similar to those for [Al(acac)$_3$] in Hacac (Table 3). A mechanism similar to that for [Al(acac)$_3$] (Fig. 1) should operate, i.e. an interchange mechanism with a slightly associative nature. The high $\Delta H^{\neq}$ value must reflect the difficulty with which the Cr–O bond is broken to give the transition state **II** and is responsible for the inertness of this complex.

(b) Acetonitrile

Figure 5 shows the relationship between the observed k_0 (equal to R/[complex]) and the concentration of free Hacac on a logarithmic scale. The plot consists of two regions. In the region where the concentration of Hacac in acetonitrile is greater than 0.1 M, log k_0 increases almost linearly with increasing log b and is unaffected by water concentration. The high negative $\Delta S^{\neq}$ value indicates a mechanism of an associative nature, and the second-order rate constant k_h must represent the rate of nucleophilic attack of Hacac upon the complex. As shown below, k_0 is exactly expressed by $k_0 = k_m + k_h b$. The contribution of k_m is, however, not significant under the given experimental conditions.

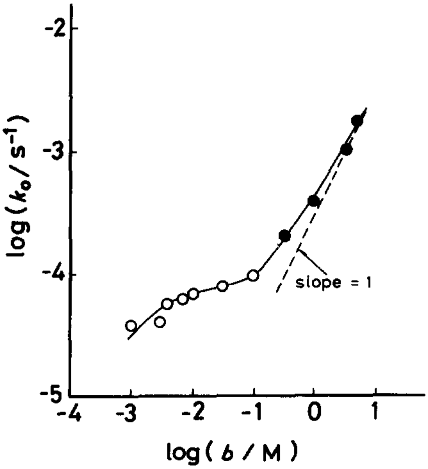

Fig. 5. Log–log plot of the observed isotopic exchange rate constant k_0 of [Cr(acac)$_3$] vs. the concentration of free ligand (b) in acetonitrile at 166 °C: [H$_2$O] = 0.70 ± 0.005 M.

In the region where $b < 0.03$ M the concave curve is analysed by use of the reciprocal plot. The linear relation between $1/k_0$ and $1/b$ indicates that the plot is expressed in terms of eqn. (8), and A and k_m were calculated as 630 M^{-1} and 8.0×10^{-5} s^{-1} respectively at 166 °C:

$$k_0 = k_m Ab/(1 + Ab) \tag{8}$$

In the range $b = 0.01$–0.03 M, k_0 is independent of b and almost equal to k_m. However, k_0 increases linearly with increasing water concentration (0.02–0.15 M):

$$k_m = k_i + k_w[H_2O] \tag{9}$$

If A represents the equilibrium constant k_a/k_{-a} (Fig. 1) for the formation of **III** from **I** and Hacac, a significant amount of **III** should be present in the reaction mixture to result in an appreciable change in the absorption spectrum. The realization of additivity between the absorption pattern of the complex and that of Hacac in the reaction mixture rules out this possibility. It must be assumed that another intermediate (**II′** in Fig. 4) exists between **I** and **III**, in which one of the three $acac^-$ ligands is in the unidentate $\overline{acac}$ form, $[Cr(acac)_2(\overline{acac})]$. (The presence of a solvent molecule at the sixth coordination site is not clear.) The A value is thus understood to show the ratio of the rate of formation of **III** from **II′** and Hacac and that to revert to **I** from **II′** unimolecularly (k_y/k_{-x}). The k_m term is then understood to be the product of the first-order rate constant k_x to give **II′** from **I** and the branching ratio of **III** to undergo proton transfer to give **III′** or to go back to **II′**, $k_x k_b/(k_{-y} + k_b)$. The terms k_w and k_i represent the values with and without the aid of water respectively.

Since the deuterium isotope effect amounts to ca. 2, the contribution of the proton transfer rate to the observed rate should not be ignored. Nevertheless, a rather high $\Delta H^{\neq}$ and virtually zero $\Delta S^{\neq}$ value for k_i and k_w suggest a dissociative mechanism to give **II′** from **I**. It can now be seen that the ligand substitution mechanism of $[Cr(acac)_3]$ depends on the reaction conditions.

(v) Reaction mechanism of other complexes

The ligand isotopic exchange rates of ruthenium(III) and rhodium(III) complexes are very small compared with those of cobalt(III) and iron(III) [11]. The relatively low $\Delta H^{\neq}$ values and negative $\Delta S^{\neq}$ values of these exchanges suggest an associative interchange mechanism (Table 3). Recent studies of the volume of activation of water exchange of $[Ru(H_2O)_6]^{3+}$ (-8.3 cm^3 mol^{-1}) also support an associative mechanism [36]. The low k_H/k_D value for the rhodium complex also supports this view. The iron complex gives a low $\Delta H^{\neq}$ value and a negative $\Delta S^{\neq}$ value, and there is no deuterium isotope effect. Thus an associative rate-determining step is suggested.

The vanadium(III) complex gives much higher rates in Hacac and acetonitrile [9]. No deuterium isotope effect is seen in either solvent (Table 3). Rather low $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ values indicate the associative nature of the rate-determining first step from **I** to **III** in Fig. 1. The k_0 value in acetonitrile increases with increasing Hacac concentration (1–8 M), not linearly with [Hacac] but with the concentration of the enol form of Hacac. We have tacitly considered the participation of Hacac in the enol form in the exchange throughout all the systems. For the relatively inert complexes of tervalent cobalt, chromium, ruthenium and rhodium, the tautomeric equilibrium between the keto and enol forms of free Hacac is established much faster than the slow isotopic exchange, so that the total concentration of Hacac contributes to the exchange. The vanadium(III) complex gives a faster exchange, and only the enol form can participate in the exchange.

The tervalent gallium complex gives a much higher rate than the aluminium complex and the rate-determining step k_a (Fig. 1) seems to be of an associative nature [12,19] (Table 3). The exchange of scandium [8] and indium [12] proceeds too fast to allow the use of the isotope labelling technique, and the rate was measured using the NMR method in acetonitrile. Low $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ values suggest an associative rate-determining step. Dependence of the observed rate upon the concentration of Hacac in the enol form supports this view. The technetium complex gives a very low rate [13] and the activation parameters indicate an associative rate-determining step. The molybdenum(III) complex gives an even lower rate than the technetium complex, but the difference is more modest compared with that between chromium(III) and manganese(III) complexes. The labile manganese(III) complex provides only limited information [12].

We have discussed the mechanism of exchange of acetylacetonate in organic solvents. Although the available information is limited, we can find common features in the process and understand that the rate-determining step is the formation of an intermediate species containing two bidentate $acac^-$ and one each of unidentate $acac^-$ and Hacac ligands. Proton transfer from the incoming Hacac to the leaving $acac^-$ is essential, but the rate is not important in determining the overall velocity of exchange. The associative nature of the rate-determining step was rather conspicuous throughout the kinetic studies, although there are cases in which the rate of bond breakage between the metal ion and ligating oxygen atom seems responsible. In so far as the interchange mechanism operates for the ligand substitution of coordination compounds, the associative and dissociative character should be considered continuous. This point will be discussed further when the experimental results are compared with the results of theoretical calculations.

D. METAL ION LABILITY CONSTANT

The overall trend in the tendency of transition metal complexes to undergo ligand substitution reactions has been discussed by several authors [4,6]. A clear linear free energy relationship has been found between the rate constant of ligand exchange of acetylacetonate in organic solvents and that of water exchange in aqueous solution [37] for tervalent main group and transition metal complexes. On the basis of such an observation we propose an empirical parameter, the "metal ion lability constant" σ, which reflects the intrinsic lability of these metal ions. The σ values are compared below with ligand field activation energies calculated using the angular overlap model, and the correlation is discussed.

(i) Linear free energy relationship between ligand exchange of [M(acac)$_3$] and aqua complexes of M(III)

First-order rate constants of the ligand exchange reactions of tris(acetylacetonato) complexes in neat Hacac and of water exchange of hexaaqua complexes in aqueous solution are listed in Table 4 and plotted in Fig. 6 on a log–log scale. Since both sets of data are not always available for individual tervalent metal ions, other data had to be included [37].

(a) The ordinate

In acetylacetone the first-order rate constants, k_1, in neat acetylacetone (eqn. (4)) are listed in Table 4 under the heading (A) and plotted with open symbols in Fig. 6. The values for chromium, molybdenum, technetium, iron, ruthenium, cobalt and rhodium are extrapolated to those at 25 °C by use of the observed $\Delta H^{\neq}$ values. The values for scandium and indium are those in mixed solvents of acetonitrile and Hacac. They are extrapolated to 9.7 M Hacac, shown in parentheses in Table 4, and plotted with half-solid symbols in Fig. 6. Such an extrapolation gives values very similar to the observed k_1 values in Hacac for vanadium, chromium, iron, cobalt and aluminium complexes where experimental values under both conditions were available.

In acetonitrile the k_0 values under the same conditions, [complex] = 0.001–0.01 M (0.05 M for scandium), [Hacac] = 0.1–2 M and [H_2O] = 0.01–0.1 M, are listed under heading (B) in Table 4, and plotted with solid symbols in Fig. 6. Manganese gives a rather complicated kinetic formula, and only the lowest limit is shown in Table 4 and Fig. 6 at [Hacac] = 0.02 M.

TABLE 4

First-order rate constants of ligand exchange and substitution reactions of $[M(acac)_3]$, $[M(H_2O)_6]^{3+}$ and $[M(NH_3)_5(H_2O)]^{3+}$ at 298 K

M	k_1(acac) (s^{-1})		$k_1(H_2O)$ [a] (s^{-1})				References					
			$[M(H_2O)_6]^{3+}$		$[M(NH_3)_5(H_2O)]^{3+}$							
	In Hacac (A)	In CH_3CN [b] (B)	Exchange of water (C)	Anation [c] (D)	Exchange of water (E)	Anation [c] (F)	A	B	C	D	E	F
Sc	(60) [d,m]	4		5×10^{7} [e,i]				8		38		
V	1.4×10^{-4}	2.0×10^{-5}	5.0×10^{2}	1×10 [h]			9	9	39	40		
Cr	4×10^{-10} [d]	9×10^{-11}	2.5×10^{-6} [h]	1×10^{-6} [h]	5.2×10^{-5}	1×10^{-7} [g]	11	10	41 [k]	43	44	45
Mo	3.5×10^{-6}			5×10^{-4} [g,l]			12			46		
Mn		1		10^{4}–10^{5} [j]				12			47	
Tc	2×10^{10} [d]						13					
Fe	3.3×10^{-3}	2×10^{-4} [f]	1.6×10^{2}	1 [g]			14	14	48	48		
				10^{1} [h]						49		
Ru	3×10^{-11} [d]		5×10^{-6}		2.3×10^{-4}	1×10^{-5} [g]	11		36		50	51
Co	2×10^{-10} [d]	1×10^{-10}			5.9×10^{-6}	2×10^{-8} [g]	11	15			52	53
Rh	8×10^{-13} [d]		3×10^{-8}		8.4×10^{-6}	7×10^{-7} [g]	11		54		44	55
Al	9.1×10^{-5}	4.6×10^{-5}	1.3				18	18	31			
Ga	1.6×10^{-3}		4.0×10^{2}				12		56			
In	(2) [d,m]	2×10^{-1}	4×10^{4}	2×10^{5} [i]				12	57	38		

[a] In acid aqueous solution. [b] Observed first-order rate constant under a common condition. [c] Reported second-order rate constant was divided by an assumed outer-sphere association constant. [d] Extrapolated from the data obtained at different temperatures. [e] At 286 K. [f] At 283 K. [g] Anation of Cl^-. [h] Anation of NCS^-. [i] Anation of Murexide. [j] Estimated for the anation of F^-. [k] Also ref. 42. [l] For [h], 3×10^{-2}. [m] Extrapolated from the data in acetonitrile (see text).

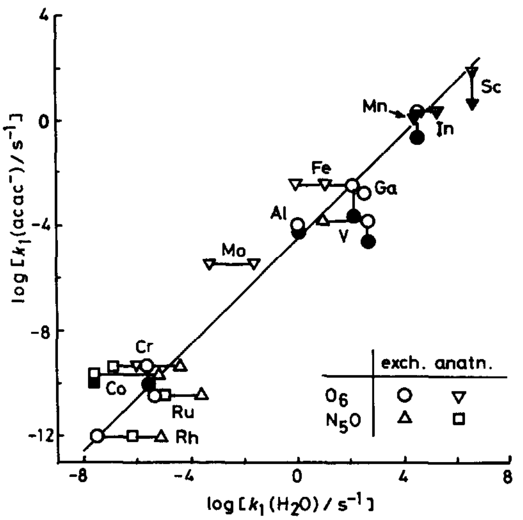

Fig. 6. The linear free energy relationship between ligand isotopic exchange rates of [M(III)(acac)$_3$] and aqua complexes of M(III) at 25 °C. Ordinate, k_1 for [M(acac)$_3$]: ○, △, ▽, □, in Hacac; ▼, in mixed solvent; ●, ▼ ■, in acetonitrile. Abscissa: first-order rate constants for water exchange (○) and anation (▽) of $[M(H_2O)_6]^{3+}$, and water exchange (△) and anation (□) of $[M(NH_3)_5(H_2O)]^{3+}$ in acid aqueous solution.

(b) Abscissa

The reported first-order rate constants for the water exchange of hexaaqua and aquapentammine complexes of the tervalent ions are listed in Table 4 under headings (C) and (E) and plotted in Fig. 6 with circles and triangles respectively. The anation rate constants for these sets of complexes were calculated from the observed second-order rate constants for the replacement of an aqua ligand with Cl^- or NCS^- (or inevitably Murexide) and an assumed outer-sphere association constant of 10 M^{-1} which is estimated by the Fuoss equation for the ion pairs with Cl^-. The values are listed under headings (D) and (F) in Table 4 and plotted with inverted triangles and squares in Fig. 6 respectively. No reliable data were available for the water exchange and anation reactions of $[Mn(H_2O)_6]^{3+}$, and the only available datum of Diebler's work on the formation of $[Mn(H_2O)_5F]^{2+}$ was adopted [47].

Whenever data under headings (A) and (C) are available, those under headings (B), (D), (E) and (F) might be considered to be of minor importance in the following discussion. However, it is remarkable that the plots in Fig. 6 do show much scatter despite the variety of reactions and the reaction environment. The deviation of $k_1(H_2O)$ values for a given metal ion from one another is rather modest. The use of the averaged values for calculating the gradient of the straight line (vide infra) gives no significant difference from the use of the values for water exchange of hexaaqua complexes (open circles). The k_1(acac) values in neat Hacac (A) are consistently larger than those in acetonitrile (B) by about one order of magnitude. Hence the former data were exclusively used for the following calculation.

(c) Empirical formula

The least-squares treatment for the k_1(acac) vs. the $k_1(H_2O)$ values gives the empirical relationship

$$\log k_1(\text{acac}) = (0.98 \pm 0.08) \log k_1(\text{H}_2\text{O}) - (4.5 \pm 0.4) \qquad (10)$$

at the 70% confidence level with a correlation factor of 0.95. Thus the gradient of the line is unity, and k_1(acac) is shifted by ca. $10^{-4.5}$ compared with $k_1(H_2O)$ (eqn. (10)):

$$\log k_1(\text{acac}) = \log k_1(\text{H}_2\text{O}) - 4.5 \qquad (11)$$

(ii) Metal ion lability constant

It is noteworthy that such a linear free energy relationship with a gradient of unity is found for various octahedral complexes of tervalent metal ions, despite the difference in overall charge, dentate number of the ligand and the solvent. The difference in the free energy of activation ($\Delta G^{\neq}$) between the two kinds of reaction of a given metal ion is small (ca. 25 kJ mol^{-1}). The change in $\Delta G^{\neq}$ with variation of tervalent metal ions is more or less similar for these two kinds of reaction. In other words, the way in which the central metal ion governs the reaction rate remains similar for the reactions given.

By choosing an optional standard ion, eqn. (11) is converted into eqn. (12), and a Hammett-type equation (eqn. (13)) is obtained:

$$\log k_1(\text{acac})_{\text{std}} = \log k_1(\text{H}_2\text{O})_{\text{std}} - 4.5 \qquad (12)$$

$$\log \frac{k_1(\text{acac})}{k_1(\text{acac})_{\text{std}}} = \log \frac{k_1(\text{H}_2\text{O})}{k_1(\text{H}_2\text{O})_{\text{std}}} = \sigma \qquad (13)$$

An empirical parameter, the "metal ion lability constant" σ, is thus introduced to reflect the effect of the metal ion on the lability of the ligand substitution reactions. The values are estimated by taking the arithmetic mean of the first and second terms of eqn. (13):

$$\sigma = \tfrac{1}{2}[\log\{k_1(\text{acac})\} + 4.5 + \log\{k_1(\text{H}_2\text{O})\}] \qquad (14)$$

where the units of k_1 are reciprocal seconds. The values, rounded to the nearest integer or half-integer, are given in Table 5.

TABLE 5

Metal ion lability constant σ for tervalent metal ions

M(III) [a]	log k_1(acac) [b] (s^{-1})	4.5 + log k_1(acac) (s^{-1})	log k_1(H_2O) [c] (s^{-1})	σ
Sc	1.8 [d]	6.3	6.7	6.5
Mn (HS)	ca. 1 [e]	5.5	4.5	5
In	0.3 [d]	4.8	5.0	5
Ti			ca. 5 [g]	(5) [h]
Ga	−2.8	1.7	2.6	2
Fe (HS)	−2.5	2.0	1.1	1.5
V	−3.9	0.6	1.9	1
Al	−4.0	0.5	0.1	0.5
Mo	−5.5	−1.0	−2.5	−1.5
Tc (LS)	−9.5 [f]	−5.0		(−5) [i]
Cr	−9.4	−4.9	−5.7	−5.5
Ru (LS)	−10.5	−6.0	−4.7	−5.5
Co (LS)	−9.7	−5.2	−6.4	−6
Rh (LS)	−12.1	−7.6	−6.3	−7

[a] HS, high spin; LS, low spin. [b] In acetylacetone. [c] Average value of $k_1(H_2O)$ values in Table 4 for each M(III). [d] Extrapolated from data at different temperatures. [e] In acetonitrile. [f] Ref. 13. [g] Ref. 58. [h] Estimated from $k_1(H_2O)$ only. [i] Estimated from k_1(acac) only.

(iii) Verification and usefulness of the parameter

The observed k_1 values are plotted against the calculated σ values in Fig. 7. The lines for the ligand isotopic exchange reactions of tris(acetylacetonato) complexes and for $[ML_5(H_2O)]^{3+}$ are expressed in terms of eqn. (15), where $\kappa = 0$ for $k_1(H_2O)$, $\kappa = -4.5$ for k_1(acac), and k_1 is in reciprocal seconds:

$$\log(k_1) = \sigma + \kappa \tag{15}$$

All the plots are good straight lines. The κ value reflects the susceptibility of a given substitution reaction towards the influence of the central metal ion; it corresponds to log $k_{1,\mathrm{std}}$ of the given reaction, i.e. the log k_1 value for a metal ion with $\sigma = 0$.

The appropriateness of the σ values may be demonstrated by plotting first-order rate constants of a third ligand isotopic exchange reaction against the σ values. Several k_1 values are available for the exchange of DMF molecules of $[M(dmf)_6]^{3+}$ in DMF [59–65]; these are plotted (solid circles) in Fig. 7. The plot is almost parallel to the other two lines, and the κ value is estimated to be −1. It is thus seen that σ and κ contribute to the k_1 values independently of each other.

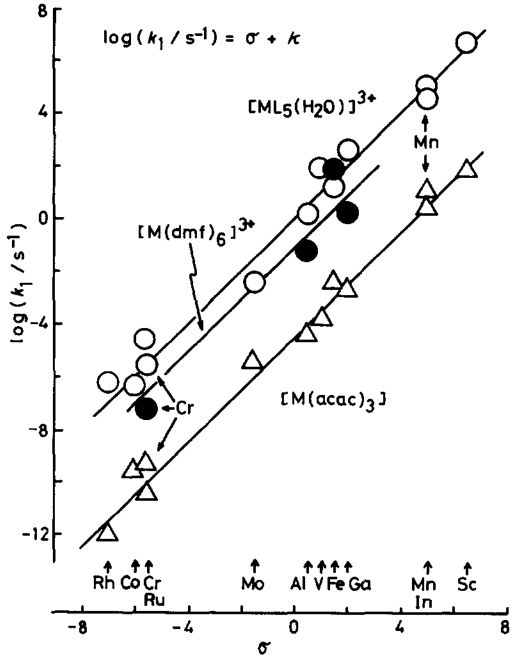

Fig. 7. Plot of log k_1 (s^{-1}) vs. σ: ○, water exchange (and anation); △, ligand exchange of [M(acac)$_3$]; ●, ligand exchange of [M(dmf)$_3$].

Equation (15) can be considered as a modified form of the Hammett equation, $\log(k/k_0) = \rho\sigma$. We have shown that the reaction constant ρ is unity. This fact indicates that the central metal ion strongly affects the lability of the present ligand substitution reactions in a similar way for each reaction. The k_1 values depend also on κ, which reflects the reaction conditions, including the nature of the incoming, leaving and non-substituting ligand, that of the solvent, and the charge of the complex. Realization of eqn. (15), however, suggests that the nature of the central metal ion is not concealed or significantly modified by the variety of substitution reactions.

Since bivalent metal ions give fast substitution reactions, their σ values should be positive. It is remarkable that none of the metal ions studied here have σ values between -5 and zero. When Taube first presented the idea of substitution lability and inertness in 1952 [4], the available kinetic data were far more limited than at present. Nevertheless his rather bold distinction between these two categories was quite correct. Since the rates of diverse reactions are also governed by κ, it is reasonable to classify the lability of metal complexes into three groups, as in Table 1.

When the σ values of tervalent metal complexes are compared within the same family of the periodic table, those with d^0 and d^{10} electron configurations and in the high spin state exhibit larger σ values as the atomic number increases ($\sigma_{Al} < \sigma_{Ga} < \sigma_{In}$, $\sigma_{Cr} < \sigma_{Mo}$). However, ions in the low spin state show the reverse trend ($\sigma_{Mn} > \sigma_{Tc}$, $\sigma_{Fe} > \sigma_{Ru}$, $\sigma_{Co} > \sigma_{Rh}$). The large differences in σ between manganese and technetium, and iron and ruthenium are due to the difference in the spin states of these metal ions.

(iii) Comparison with theoretical considerations

The metal lability constant may be correlated with the ease or difficulty with which the transition state is reached in the substitution reactions. Various kinds of sophisticated theoretical considerations have been proposed on the basis of different assumptions [5]. The usefulness of the angular overlap model in discussing the electronic state of transition metal complexes has been demonstrated for the interpretation of *d–d* transition energies [66]. Yamatera calculated the ligand field activation energy (LFAE) for substitution reactions of various octahedral complexes as a function of the number and spin state of *d* electrons by use of the angular overlap model [67]. He assumed various stereochemistries for the transition state (C_{4v}, D_{3h}, D_{5h} and C_{2v} (octahedral wedge)) and also different (σ-antibonding, π-bonding and π-antibonding contributions) and gave various diagrams for the calculated LFAE plotted against the number of *d* electrons.

Yamatera found a very good correlation between the rate of water exchange of hexaaqua complexes of bivalent transition metal ions of the fourth period in aqueous solution and an LFAE diagram of the transition state with a square pyramidal structure (C_{4v} symmetry). Water exchange of these metal ions is understood to proceed via an Id mechanism with a plausible transition state of C_{4v} symmetry, but there are cases (e.g. manganese(II)) in which an associative exchange mechanism is postulated [68]. The fact that the LFAE calculated for the C_{4v} transition state can account for the experimental results for bivalent transition metal ions may infer that the difficulty with which the metal–O bond is broken is an important factor and a useful parameter in determining the rate of water exchange in aqueous solution.

We have discussed above that most of the present complexes as well as the hexaaqua complexes of tervalent metal ions undergo ligand isotopic exchange through an interchange mechanism with a rather associative character. Among the models of the transition states used by Yamatera, the C_{2v} octahedral wedge structure with half-strength of the metal–ligand bonds between the central metal ion and the sixth and seventh ligating atoms (at the coordination sites forming the wedge) seems to be most appropriate.

Figure 8 shows the plot of our σ values vs. the number of *d* electrons, in high and low spin states, for the elements of the fourth (Fig. 8B) and the

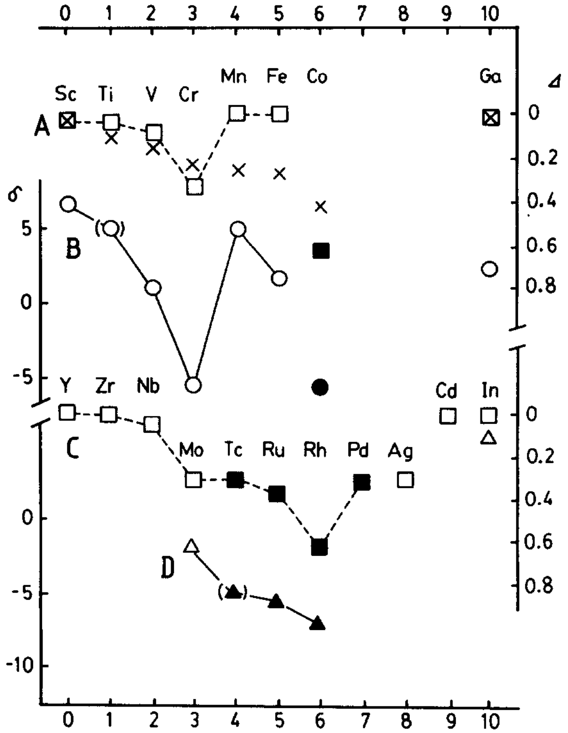

Fig. 8. Comparison of empirical σ values with theoretical ligand field activation energy (LFAE) calculated using the angular overlap model for fourth period elements (plots A and B) and for fifth period elements (plots C and D): open symbols, high spin state; solid symbols, low spin state; □, ■, calculation using octahedral wedge model with C_{2v} symmetry and a coordination number of seven; × calculation using square pyramidal model with C_{4v} symmetry and a coordination number of five for high spin state and without π interactions; △, ▲, ○, ●, σ values.

fifth period (Fig. 8D) of the periodic table respectively. (Plots for low spin complexes are given with solid symbols.) Figure 8 also shows Yamatera's plots of LFAE vs. the number of *d* electrons for the C_{2v} octahedral wedge model (squares) and the C_{4v} pyramidal model without π interactions (crosses) (Figs. 8A and 8C). His LFAE values for these transition states were calculated by assuming only one kind of electron configuration at the transition state. Participation of π-bonding and π-antibonding orbitals to different extents changes the pattern of the diagram only slightly. Since his ordinate indicates the LFAE scale relative to the ligand field stabilization energy Δ, only a qualitative comparison can be made with our empirical σ values.

Although the discussion is limited, our diagram can be satisfactorily interpreted by Yamatera's angular overlap model. The gradual decrease in σ on going from scandium to chromium and the marked increase on going from chromium to manganese are well represented by the maximum on the LFAE diagram at chromium (Fig. 8B). (The relative σ values for scandium, high spin iron and gallium, which are unaffected by LFAE, are understood by considering the ionic radii.) Qualitatively, our σ vs. d electron number diagram seems also to be interpreted by the LFAE values calculated on the C_{4v} square pyramidal model. The difference between the LFAE values calculated on the C_{2v} octahedral wedge and on the C_{4v} model is most noticeable at d^4-manganese(III). Unfortunately, the empirical σ value for d^4-manganese is very poor (vide supra). Hence detailed discussion cannot be warranted. However, we have seen the importance of the difficulty with which the metal–O bond is broken in determining the rate of ligand exchange of bivalent transition metal ions. The same trend is also seen for our tervalent metal ions where both the results of a calculation based on the C_{2v} octahedral wedge and on the C_{4v} transition state account for the σ values. Since the strength of the metal–ligand bond at the sixth and seventh coordination sites was taken as half that of other metal–O bonds on the C_{2v} octahedral wedge model, the patterns of the theoretical diagrams may not differ much from each other.

Comparison with the data for fifth-period elements is much more limited because of the small number of experimental points, but no contradiction is seen. (Figure 8C shows only the result of the calculation on the C_{2v} octahedral wedge model.)

E. CONCLUSION

Tris(acetylacetonato) complexes of tervalent metal ions enabled us to study the kinetics of ligand exchange in organic solvents by the isotope labelling method. A common reaction route was observed in which an intermediate with two bidentate acac$^-$ ligands and one each of unidentate acac$^-$ and Hacac ligands undergoes proton transfer to result in ligand exchange. Discussion on the basis of activation parameters and the deuterium isotope effect suggested an interchange mechanism with an associative nature for most complexes, but the extent of participation of the incoming ligand in the formation of the transition state differs from one element to another.

A comparison of our results with those of the water exchange of tervalent metal ions in aqueous solution gave a good linear free energy relationship. A new parameter, the "metal ion lability constant" σ, has been postulated on the basis of a Hammett-type equation. Conventional crystal field activation energy cannot account for the σ vs. d electron number diagram. The usefulness of the ligand field activation energy calculated on the basis of the angular overlap model was demonstrated. The σ values are appropriate for use as empirical parameters, indicating an approximate intrinsic lability for the tervalent metal ions towards ligand substitution reactions.

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REFERENCES

1 J.C. Bailar, Jr., and W. Auten, J. Am. Chem. Soc., 56 (1934) 774.
J.C. Bailar, Jr., F.G. Jonelis and E.H. Hoffman, J. Am. Chem. Soc., 58 (1936) 2224.
J.C. Bailar, Jr., and D.F. Peppard, J. Am. Chem. Soc., 62 (1940) 820.
2 F. Basolo, Coord. Chem. Rev., 100 (1989) 47.
3 H.R. Hunt and H. Taube, J. Chem. Phys., 19 (1951) 602.
A.W. Adamson, J.P. Welker and M. Volpe, J. Am. Chem. Soc., 72 (1950) 4030.
A.W. Adamson, J.P. Welker and W.B. Wright, J. Am. Chem. Soc., 73 (1951) 4786.
J. Long, J. Am. Chem. Soc., 73 (1951) 537.
J.E. Johnson and N.F. Hall, J. Am. Chem. Soc., 70 (1948) 2344.
4 H. Taube, Chem. Rev., 50 (1952) 69.
5 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd edn., Wiley, New York, 1967.
6 K. Saito, Stereochemistry of Octahedral Complexes, Kagaku Sosetsu, 13 (1976) 178 (in Japanese).
7 K. Saito, Pure Appl. Chem., 30 (1974) 325.
8 Y. Hatakeyama, H. Kido, M. Harada, H. Tomiyasu and H. Fukutomi, Inorg. Chem., 27 (1988) 992.
9 A. Watanabe, H. Kido and K. Saito, Inorg. Chem., 27 (1981) 1107.
10 H. Kido and K. Saito, Inorg. Chem., 16 (1977) 397.
11 H. Kido, Bull. Chem. Soc. Jpn., 53 (1980) 82.
12 H. Kido and K. Saito, unpublished results.
13 H. Kido and Y. Hatakeyama, Inorg. Chem., 27 (1988) 3623.
14 H. Kido and K. Saito, Bull. Chem. Soc. Jpn., 53 (1980) 424.
15 K. Saito and M. Murakami, Bull. Chem. Soc. Jpn., 45 (1972) 2472.
H. Kido and K. Saito, Bull. Chem. Soc. Jpn., 52 (1979) 3545.
16 K. Saito and K. Masuda, Bull. Chem. Soc. Jpn., 41 (1968) 384.
17 K. Saito and K. Masuda, Bull. Chem. Soc. Jpn., 43 (1970) 119.
18 A. Nagasawa, H. Kido, M. Hattori and K. Saito, Inorg. Chem., 25 (1986) 4330.
19 C. Chatterjee, K. Matsuzawa, H. Kido and K. Saito, Bull. Chem. Soc. Jpn., 47 (1974) 2809.

20 M. Nishizawa, H. Kido, I. Kinoshita, Y. Soma and K. Saito, Bull. Chem. Soc. Jpn., 49 (1976) 819.
21 T. Inoue and K. Saito, Bull. Chem. Soc. Jpn., 46 (1973) 2417.
22 A. Nagasawa and K. Saito, Bull. Chem. Soc. Jpn., 51 (1978) 2015.
23 F.B. Ueno, A. Nagasawa and K. Saito, Bull. Chem. Soc. Jpn., 52 (1979) 1363.
24 A. Nagasawa and K. Saito, Bull. Chem. Soc. Jpn., 49 (1976) 3079.
25 H.A.C. McKay, Nature (London), 142 (1938) 997.
26 W.H. Saunders, Jr., in E.S. Lewis (Ed.), Investigation of Rates and Mechanisms of Reactions, 3rd edn., Wiley, New York, 1974, Chapter V, p. 211.
27 A.E. Merbach, Pure Appl. Chem., 54 (1982) 1479.
28 A.E. Merbach, P. Moore, O.W. Howarth and C.H. McAteer, Inorg. Chim. Acta, 39 (1980) 129.
29 C. Ammann, P. Moore, A.E. Merbach and C.H. McAteer, Helv. Chim. Acta, 63 (1980) 268.
30 J.F. O'Brien and M. Alei, J. Phys. Chem., 74 (1970) 743.
31 D. Hugi-Cleary, L. Helm and A.E. Merbach, Helv. Chim. Acta, 68 (1985) 545.
32 K. Ishihara, S. Funahashi and M. Tanaka, Inorg. Chem., 24 (1983) 3589.
S.F. Lincoln, A.M. Hounslow, D.L. Pisaniello, B.G. Doddledge, J.H. Coates, A.E. Merbach and D. Zbinden, Inorg. Chem., 23 (1984) 1090.
33 B. Nordén and I. Jonås, Inorg. Nucl. Chem. Lett., 12 (1976) 33.
34 R.C. Fay, A.Y. Girgis and U. Klabunde, J. Am. Chem. Soc., 92 (1970) 7056.
35 C. Ammann and A.E. Merbach, Inorg. Chim. Acta, 40 (1980) X98.
36 P. Bernard, L. Helm, I. Rapaport, A. Ludi and A.E. Merbach, J. Chem. Soc., Chem. Commun., (1984) 302.
I. Rapaport, L. Helm, A.E. Merbach, P. Bernhard and A. Ludi, Inorg. Chem., 27 (1988) 873.
37 H. Kido and K. Saito, J. Am. Chem. Soc., 110 (1988) 3187.
38 G. Geier, Ber. Bunsenges. Phys. Chem., 69 (1965) 617.
39 A.D. Hugi, L. Helm and A.E. Merbach, Helv. Chim. Acta, 68 (1985) 508.
40 B.R. Baker, N. Sutin and T.S. Welch, Inorg. Chem., 6 (1967) 1948.
W. Kruse and D. Thusius, Inorg. Chem., 7 (1968) 464.
41 D.R. Stranks and T.W. Swaddle, J. Am. Chem. Soc., 93 (1971) 2783.
42 F.-C. Xu, H.H. Krouse and T.W. Swaddle, Inorg. Chem., 24 (1985) 267.
43 C. Postmus and E.L. King, J. Phys. Chem., 59 (1955) 1216.
44 T.W. Swaddle and D.R. Stranks, J. Am. Chem. Soc., 94 (1972) 8357.
45 N.V. Duffy and J.E. Earley, J. Am. Chem. Soc., 89 (1967) 272.
46 Y. Sasaki and A.G. Sykes, J. Chem. Soc., Dalton Trans., (1975) 1048.
47 H.Z. Diebler, Z. Phys. Chem. (Neue Folge), 68 (1969) 64.
48 R.E. Connick and C.P. Coppel, J. Am. Chem. Soc., 81 (1959) 6389.
T.W. Swaddle and A.E. Merbach, Inorg. Chem., 20 (1981) 4212.
M. Grant and R.B. Jordan, Inorg. Chem., 20 (1981) 55.
49 J.F. Below, R.E. Connick and C.P. Coppel, J. Am. Chem. Soc., 80 (1958) 2961.
50 H. Doine, K. Ishihara, H.R. Krouse and T.W. Swaddle, Inorg. Chem., 26 (1987) 3240.
51 J.A. Bloomhead and L. Kane-Maguire, Inorg. Chem., 10 (1971) 85.
52 H.R. Hunt and H. Taube, J. Am. Chem. Soc., 80 (1958) 2642.
53 G.R.H. Jones, R.C. Edmondson and J.H. Taylor, J. Inorg. Nucl. Chem., 32 (1970) 1752.
54 W. Plumb and G.M. Harris, Inorg. Chem., 3 (1964) 542.
55 A.J. Poe, K. Shaw and M.J. Wendt, Inorg. Chim. Acta, 1 (1967) 371.
56 D. Hugi-Clearly, L. Helm and A.E. Merbach, J. Am. Chem. Soc., 109 (1987) 4444.

57 G.E. Glass, W.B. Schwabacher and R.S. Tobias, Inorg. Chem., 7 (1968) 2471.
58 A.M. Chmelnick and D. Fiat, J. Chem. Phys., 51 (1969) 4238.
59 F.W. Breivogel, Jr., J. Phys. Chem., 73 (1969) 4203.
60 J. Hodgkinson and R.B. Jordan, J. Am. Chem. Soc., 95 (1973) 763.
61 F.K. Meyer, A.R. Monnerat, K.E. Newman and A.E. Merbach, Inorg. Chem., 21 (1982) 774.
62 L.S. Frankel and E.R. Danielson, Inorg. Chem., 11 (1972) 1964.
63 W.G. Morius and N.A. Matwiyoff, Inorg. Chem., 8 (1969) 925.
64 C. Ammann, P. Moore, A.E. Merbach and C.H. McAteer, Helv. Chim. Acta, 63 (1980) 268.
65 S.T.D. Lo and T.W. Swaddle, Inorg. Chem., 14 (1975) 1878.
66 C.E. Schäffer and C.K. Jørgensen, Mol. Phys., 9 (1965) 401.
67 H. Yamatera, Bull. Chem. Soc. Jpn., 31 (1958) 95; La Nature et les Propriété des Liaisons de Coordination, Colloques Internationaux de CNRS, No. 191 (1970) 73.
68 M. Tanaka, Inorg. Chim. Acta, 54 (1981) L129.