

# ISOTOPIC EXCHANGE AND RACEMIZATION OF SOME TRIS- $\beta$ -DIKETONATO COMPLEXES OF TYPICAL ELEMENTS OF GROUPS III AND IV

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## ABSTRACT

In organic solvents the isotopic exchange between  $\beta$ -diketone- $^{14}\text{C}$  and its tris complexes with  $\text{Al}^{\text{III}}$ ,  $\text{Ga}^{\text{III}}$  and  $\text{In}^{\text{III}}$  proceeds at a greater rate in the order given, and with decrease in  $\text{p}K_{\text{a}}$  of the ligand. There seems to be a rapid equilibrium between the complex and an intermediate with one of the ligands as unidentate, and the break of the remaining bond appears to be the rate-determining step. Similar tris-complexes of  $\text{Si}^{\text{IV}}$  and  $\text{Ge}^{\text{IV}}$  give an immeasurably slow rate of such an exchange up to  $80^{\circ}\text{C}$ . They undergo racemization in dehydrated organic solvents and the rate is governed by the ease of  $\text{M}-\text{O}$  bond break and the probability of intramolecular rearrangement to give a symmetrical intermediate. Comparison of the order of ease of intermolecular isotopic exchange with that of intramolecular site-exchange of a variety of  $\beta$ -diketonato complexes reveals a dominating contribution of the charge of the central ion upon the intermolecular change.

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## INTRODUCTION

In the last decades a large amount of work was done concerning kinetics of substitution reactions of metal complexes. Taube first proposed to classify metal complexes according to the rate of their substitution reactions, i.e. substitution labile and substitution inert<sup>1</sup>. Mechanism of substitution reactions has been mostly discussed with substitution inert complexes, e.g. trivalent cobalt, rhodium, chromium etc. with octahedral structure and bivalent palladium, platinum etc. with square planar structure<sup>2</sup>.

Most typical elements give substitution labile complexes, and the knowledge relating to their substitution reaction mechanism is far less. Eigen, in the plenary lecture of XI ICCC in 1968, reviewed the kinetics and mechanism of reactions of main group metal ions with biological carriers<sup>3</sup>. 'Specialist Periodical Reports' of the Chemical Society, 'Inorganic Reaction Mechanisms Vol. 1' has a chapter concerning complex formation with labile metals and reactions of biological interest<sup>4</sup>. Some other useful reviews are also published in other countries. The most precisely studied variety of substitution reactions of labile elements would be solvent exchange between coordinated solvent molecule and bulk solvent, and the replacement of coordinated water by some other anionic ligands.

Substitution reactions in water are definitely most important, because water is the most common solvent and many reactions of major interest take place in water. Water is, however, a very strong ligand for various metal ions and overwhelms other ligands in concentration. Hence, the aqueous system is a less convenient medium for discussing the kinetics and mechanism of substitution reactions involving other ligands. Little information is, however, available concerning reaction kinetics of typical elements in non-aqueous solvents.

The elements which are mainly dealt with in this article belong to Groups III<sub>B</sub> and IV<sub>B</sub> of the Periodic Table, the formal charge being +3 and +4, respectively. They have relatively high surface charge<sup>4</sup>. Mechanism of their substitution reactions is least known even among other labile metal ions. Tervalent aluminium and gallium have a relatively small rate of water<sup>5,6</sup> and dimethylformamide<sup>7,8</sup> exchange,  $10^0$  to  $10^3$  s<sup>-1</sup> at room temperature. The activation parameters were very different for Al<sup>III</sup> and Ga<sup>III</sup> and it was claimed that they involve dissociative and associative reaction paths, respectively. The present author found that when these ions are chelated with multidentate ligands such as edta<sup>4-</sup>, their isotopic exchange with aquo metal ions was extremely slow, and reported detailed kinetics by use of radioisotopes of Ga<sup>9</sup>, In<sup>10</sup> and Tl<sup>11</sup>. It was thus demonstrated that even 'substitution labile' ions can give slow reaction kinetics, whenever they are chelated with bi- or multi-dentate ligands.

Isotopic exchange in liquid systems was first kinetically treated by McKay in 1939<sup>12</sup>. When two compounds A (molar concentration  $a$ ) and B ( $b$ ) containing  $m$  and  $n$  moles of exchanging species, respectively, undergo isotopic exchange, the rate of exchange is expressed by equation (1):

$$R = -2.303 \frac{ma \cdot nb}{(ma + nb)} (\log [1 - F])/t \quad (1)$$

where  $t$  is the lapse of time and  $F$  the fraction of exchange. By use of a radioisotope,  $F$  is written as  $x_i/x_\infty$ , where  $x_i$  and  $x_\infty$  are the specific activity of A (or B) at time  $i$  and infinity, respectively.  $R$  is not a rate constant but a function of  $a$  and  $b$ . Examination of the relation between  $R$ , and  $a$  and  $b$ , reveals the reaction kinetics and the reaction mechanism can be discussed. Since isotopic exchange is examined in the chemically equilibrated state, the kinetics give a good measure for the lability of given complexes and useful information concerning the reaction mechanism.

Acetylacetone (2,4-pentanedione; Hacac) is one of the most common bidentate ligands and its enol form gives anions  $acac^-$  with a  $pK_a$  value ca. 11 in water. Bis-, tris- and tetrakis-acetylacetonato complexes with six-membered chelate rings are known with a variety of metal ions and very often they are chargeless. This  $\beta$ -diketone has many homologues, in which 2- and 3-positions are substituted. They are also in keto-enol equilibrium and the enol forms have different  $pK_a$  values depending on the nature of the substituting groups.

## ISOTOPIC EXCHANGE OF TRIS- $\beta$ -DIKETONATO COMPLEXES OF III<sub>B</sub> ELEMENTS

Tervalent cations of the Group III<sub>B</sub> elements give one to three complexes

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with various  $\beta$ -diketonates which are chargeless and soluble in various organic solvents. The isotopic exchange between  $[M(\text{acac})_n]$  and  $\text{Hacac-}^{14}\text{C}$  was first examined briefly by Klüber in 1960<sup>13</sup>. He gave approximate percentages of exchange within 10 min in chloroform and dioxane in concentrated solutions of several complexes.

We have found that most of the chargeless  $\beta$ -diketonato complexes are insoluble in light petroleum, and recovered crystalline free from excessive ligand by adding the reaction mixture in organic solvents into chilled light petroleum<sup>14</sup>. A known amount of the crystalline complex is dissolved in a liquid scintillation counter and submitted to the measurement of specific counting rate. We extended the kinetic study since 1965 and precisely discussed the mechanism of isotopic exchange.

Table 1. Approximate isotopic exchange rate of tris- $\beta$ -diketonato complexes of trivalent ions of Group IIIb elements in tetrahydrofuran

	$t/^\circ\text{C}$	$R/\text{Ms}^{-1} a$
$[\text{Al}(\text{acac})_3] > [\text{Al}(\text{bzac})_3] > [\text{Al}(\text{dbm})_3]^b$	50	$10^{-6}$
$[\text{Ga}(\text{acac})_3] > [\text{Ga}(\text{bzac})_3] > [\text{Ga}(\text{dbm})_3]$	0	$10^{-7}$
$[\text{In}(\text{dbm})_3]$	0	$10^{-4}$

<sup>a</sup>  $R$  values for dibenzoylmethane complexes.  $[\text{complex}] = [\text{Hdbm}] = 0.07 \text{ M}$ ,  $[\text{H}_2\text{O}] = \text{ca. } 0.04 \text{ M}$ .

<sup>b</sup> Hacac, acetylacetonate; Hbzac, benzoylacetone; Hdbm, dibenzoylmethane.

Table 1 compares approximate  $R$  values. The lability of the complexes increases with increase in atomic number within a Group as in the case of water exchange in aqueous solutions<sup>7</sup>. As shown in the following, the isotopic exchange seems to proceed via a dissociative mechanism. Their metal-ligand bond must be of ionic nature and decrease in ionic radius will increase the charge density at the central metal ion to make the bond break more difficult. For a given metal ion, the exchange is slower when the basicity of the ligand increases. The exact  $\text{p}K_a$  values of their conjugate acids are not known in tetrahydrofuran (THF), but they are *ca.* 11.7, 12.0 and 13.0 for acetylacetonate, benzoylacetone and dibenzoylmethane in methanol containing 0.1M tetramethylammonium perchlorate.

Details of the isotopic exchange mechanism were studied with aluminium complexes of acetylacetonate (Hacac) and dibenzoylmethane (Hdbm) in various solvents<sup>15, 16</sup>. The reaction mixtures containing  $10^{-2}$  to  $10^{-1}\text{M}$  each of the complexes and the labelled ligands in THF, ethylacetate and toluene gave identical absorption spectra during kinetic runs, and they were equal to the sum of the absorption curves of the complexes and the ligands. The McKay plots gave straight lines for several half periods of isotopic exchange. Hence the isotopic exchange took place without net chemical change.

For all the systems studied, the  $R$  values are proportional to the complex concentration so that equation (2) holds:

$$R = k_0 [\text{complex}] \quad (2)$$

The exchange is slower than the keto-enol equilibrium of Hacac and Hdbm†. One of the remarkable features of the kinetics is that the exchange is catalysed by water and acid. *Figures 1-3* illustrate the dependence of  $k_0$  upon the water concentration in various solvents. Since the reagents and the solvents contain certain amounts of water, the experiments cannot be carried out in the absence

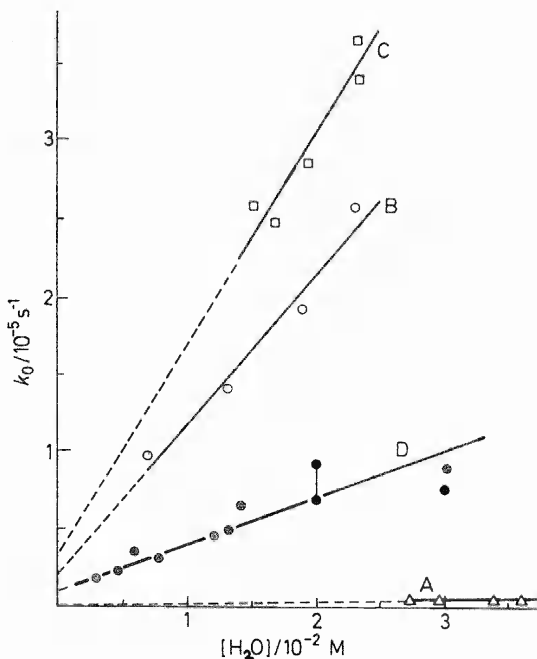


Figure 1. Relationship between  $k_0$  and water concentration for  $[\text{Al}(\text{acac})_3]$  in ethylacetate (A,B,C) and tetrahydrofuran (D). A, 0°C; B, 30°C; C, 35°C; C, 35°C; D, 25°C.

of water. In the given concentration ranges the rate constant  $k_0$  is proportional to water concentration. (In the presence of larger amounts of water, the complexes are hydrolysed to give a gelatinous precipitate.) When the straight lines are extrapolated to zero concentration, the lines in *Figure 1* have intercepts, whereas those in *Figures 2* and *3* do not ( $k_1 = 0$ ):

$$k_0 = k_1 + k_2[\text{H}_2\text{O}]$$

*Figure 4* shows the dependence of  $k_0$  upon the water concentration in the presence of acids. Whereas  $[\text{Al}(\text{acac})_3]$  is catalysed by both strong and weak acids,  $[\text{Al}(\text{dbm})_3]$  is only by a strong acid like trichloroacetic. All the lines

† The time required for the equilibrium to be reached is not known in the organic solvents. Eigen gave a rate *ca.*  $10^{-2} \text{ s}^{-1}$  for the slowest step, enolate to keto form in water<sup>17</sup>. Recent results (not published) in some organic solvents suggest that tautomerism is reached more quickly than the present isotopic exchange.

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have intercepts. The rate increases with increase in acid concentration, and at a given concentration of water, with increase in water concentration. No base catalysis was observed with pyridine. Hence  $k_0$  is expressed by equation (3) in lower concentration ranges of acid and water:

$$k_0 = k_1 + k_2[\text{H}_2\text{O}] + k'_3[\text{acid}] + k_3[\text{H}_2\text{O}][\text{acid}] \quad (3)$$

All the rate constants are known from the intercepts and the gradients of the diagrams.

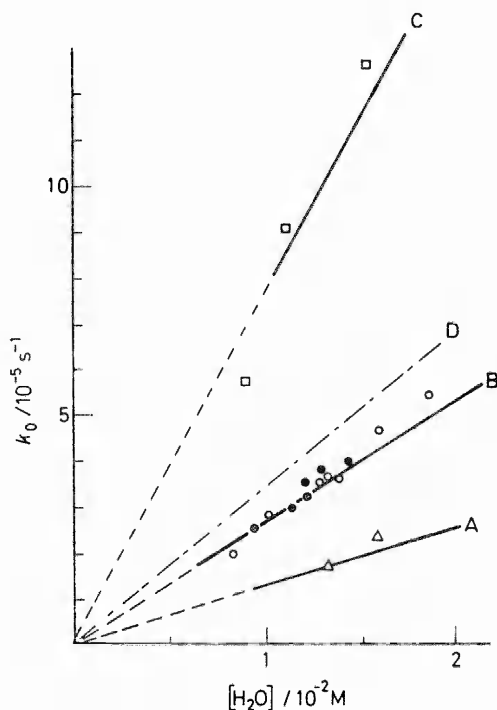


Figure 2. Relationship between  $k_0$  and water concentration for  $[\text{Al}(\text{acac})_3]$  in toluene (A,B,C) and xylene (D). A,  $0^\circ\text{C}$ ; B,  $25^\circ\text{C}$ ; C,  $35^\circ\text{C}$ ; D,  $25^\circ\text{C}$  in three isomers of xylene. Open marks,  $[\text{Hacac}] = 0.070 \text{ M}$ ; full marks,  $[\text{Hacac}] = \text{varying}$ .

Another characteristic of the present exchange reaction is that Arrhenius plots are parallel for various  $k$ s and give equal  $\Delta H^\ddagger$  for each rate constant. Some of the  $k$ s were obtained by extrapolation and their activation parameters may involve bigger errors. Table 2 summarizes the rate constants and activation parameters. Because of the smaller solubility of  $[\text{Al}(\text{dbm})_3]$  in organic solvents, the kinetics were studied only in THF. The concentration of the added ligand has no influence on the rate. (For  $[\text{Al}(\text{dbm})_3]$  there is a small influence, which will be discussed later.)

On the basis of these results, a plausible reaction mechanism is illustrated

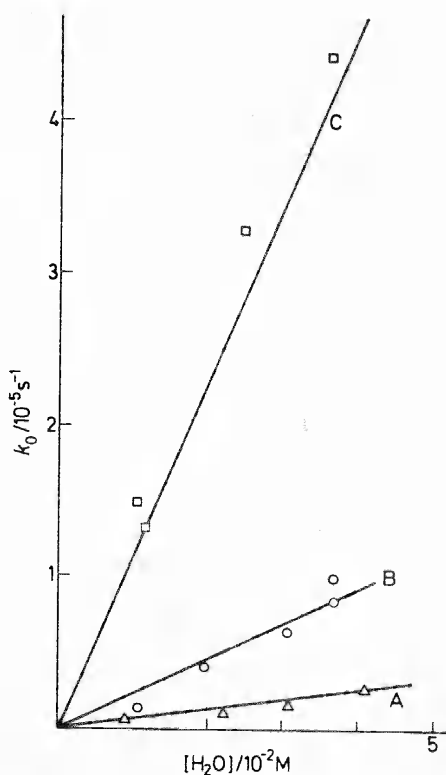


Figure 3. Relationship between  $k_0$  and water concentration for  $[\text{Al}(\text{dbm})_3]$  in tetrahydrofuran. A, 30°C; B, 40°C; C, 50°C

Table 2. Rate constants and activation parameters for the isotopic exchange of  $[\text{Al}(\text{acac})_3]$  and  $[\text{Al}(\text{dbm})_3]$  in organic solvents (25°C).

$$\text{Rate} = [\text{complex}](k_1 + k_2[\text{H}_2\text{O}] + k_3'[\text{acid}] + k_3[\text{acid}][\text{H}_2\text{O}])$$

Solvent	Complex			THF
	Ethylacetate	Toluene	THF	
$k_1/10^{-6} \text{ s}^{-1}$	1.1	0	1.0	0
$k_2/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	4.6	26.7	3.3	0.32
$k_3'/10^{-4} \text{ M}^{-1} \text{ s}^{-1b}$	9.0	15.8	1.55	0.20
$k_3/10^{-2} \text{ M}^{-2} \text{ s}^{-1b}$	5.0	21.7	2.0	0.091 <sup>c</sup>
$\Delta H^\ddagger/\text{kcal mol}^{-1d}$	21.4	19.2	21.4	25.6
$\Delta S^\ddagger/\text{cal K}^{-1} \text{ mol}^{-1e}$	+0.04	-3.8		-1.8

<sup>a</sup>  $k$  values converted into those at 25°C with the aid of  $\Delta H^\ddagger$ . <sup>b</sup> *m*-Toluic acid for  $[\text{Al}(\text{acac})_3]$  and trichloroacetic acid for  $[\text{Al}(\text{dbm})_3]$ .

<sup>c</sup> See text. <sup>d</sup> Practically equal for all the  $k$ s. <sup>e</sup> For  $k_2$ .

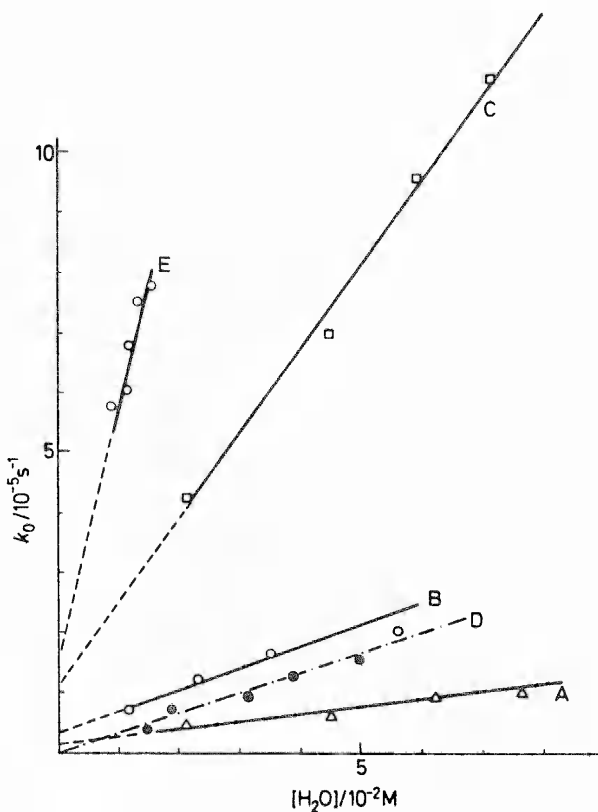


Figure 4. Influence of water upon the exchange rate of  $[\text{Al}(\text{dbm})_3]$  (A,B,C,D) and  $[\text{Al}(\text{acac})_3]$  (E) in the presence of acids. A, 30°C, B, 40°C, C, 50°C in THF,  $[\text{trichloroacetic acid}] = 0.029 \text{ M}$ ; D, 40°C in THF,  $[\text{acid}] = 0.0021 \text{ M}$ ; E, 25°C in toluene,  $[m\text{-toluic acid}] = 0.090 \text{ M}$ .

in Figure 5. Whenever a bidentate ligand is replaced, there are two possible rate-determining steps. One is the break of the first bond so that the second bond breaks rapidly. The other mechanism presumes a rapid equilibrium between the bidentate and the unidentate state of the ligand and reckons the break of the second bond as rate-determining.

In the present systems, the second mechanism seems to be more appropriate. The catalytic actions of water and acid are understood by considering that they occupy the vacant coordination site of the intermediate and the free end of the unidentate ligand, respectively, to retard the recombination of unidentate ligand. The fact that the activation enthalpies for all the kinetic terms are equal will be accounted for by such occupations affecting the break of the remaining bond less. If break of the first bond were the rate-determining step, catalytic action by water or acid would bring about a larger difference in enthalpy of activation.

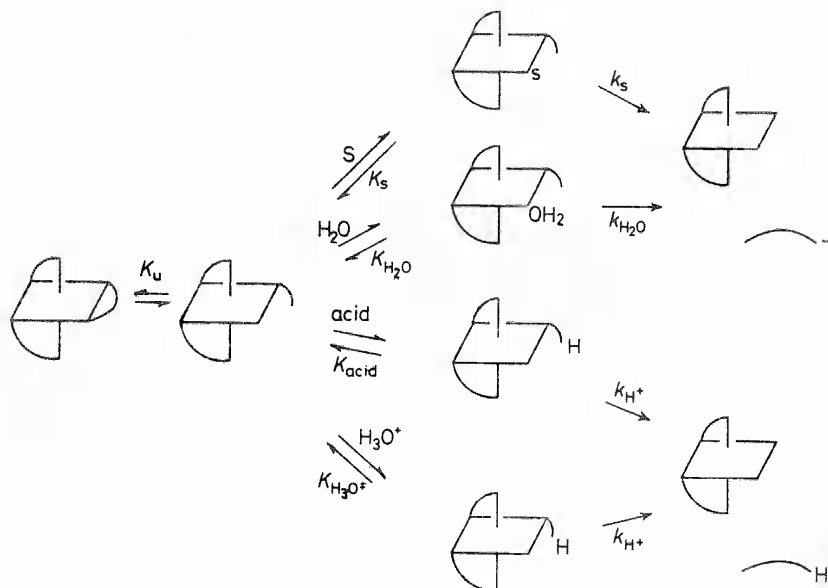
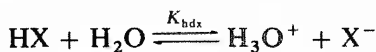


Figure 5. Plausible reaction mechanism for the isotopic exchange of  $[\text{Al}(\beta\text{-dik})_3]$  in organic solvents. Capital  $K$ s, equil. const.; small  $k$ s rate const. at the rate-determining step; arcs,  $\beta$ -diketone anion in enol form; S, solvent molecule.

When the equilibrium and the rate constants are designated as in Figure 5, the kinetic terms are expressed as follows:

$$\begin{aligned} k_1 &= k_s K_u K_s & k_2 &= k_{\text{H}_2\text{O}} K_u K_{\text{H}_2\text{O}} \\ k'_3 &= k_{\text{H}^+} K_u K_{\text{acid}} & k_3 &= k_{\text{H}^+} K_u K_{\text{H}_3\text{O}^+} \end{aligned}$$

The terms  $k'_3$  and  $k_3$  represent acid catalysis with different proton carriers. Proton is transferred to  $\text{H}_3\text{O}^+$  from the acid according to the equilibrium



Dibenzoylmethane (Hdbm) gives stronger conjugate base  $\text{dbm}^-$  than acetylacetone does  $\text{acac}^-$ , and  $[\text{Al}(\text{dbm})_3]$  is reasonably more inert than  $[\text{Al}(\text{acac})_3]$ . Absence of a  $k_1$  term for  $[\text{Al}(\text{acac})_3]$  in toluene and isomers of xylene must be due to small  $K_s$  values in these non-polar solvents. Bigger  $k_2$  values for  $[\text{Al}(\text{acac})_3]$  in toluene and xylenes than in THF and ethylacetate will be understood by considering that water will be present more around the complex in non-polar solvents than in polar solvents.  $[\text{Al}(\text{dbm})_3]$  may have bigger  $K_{\text{acid}}$  and  $K_{\text{H}_3\text{O}^+}$  values than  $[\text{Al}(\text{acac})_3]$ , but its much smaller  $k_{\text{H}^+}$  would overwhelm the influence of  $K_{\text{acid}}$  and  $K_{\text{H}_3\text{O}^+}$  to give smaller  $k'_3$  and  $k_3$ .

The small influence of ligand concentration upon the exchange rate of  $[\text{Al}(\text{dbm})_3]$  in Figure 6 will be due to the attack of Hdbm on the intermediate. Less basic Hacac will have smaller affinity towards the intermediate and fail to exhibit influence.



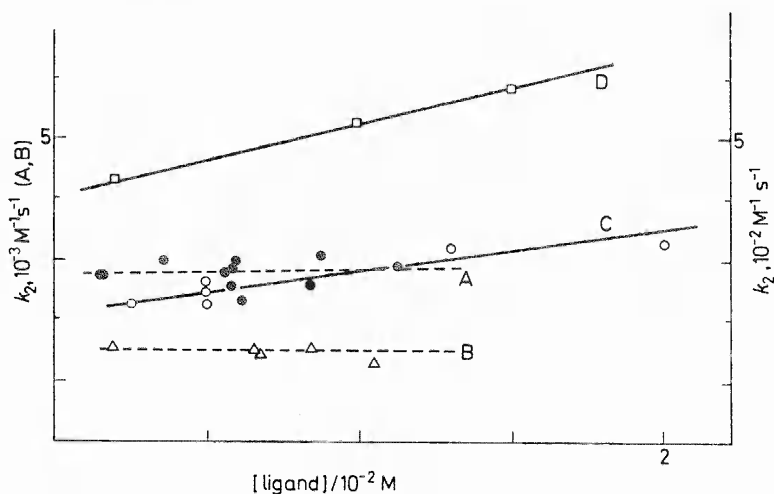
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Figure 6. Influence of the ligand concentration upon the rate of  $[Al(acac)_3]$  (A,B) and  $[Al(dbm)_3]$  (C,D). A, 35°C in toluene; 25°C in ethylacetate; C, 40°C and D, 50°C in THF.

Table 3 summarizes the influence of various factors on the exchange rate of various acetylacetonato complexes. Influence of free ligand was observed for  $Ga^{III}$ <sup>21</sup>,  $Pd^{II}$ <sup>18</sup> and  $Co^{III}$  complexes<sup>19</sup>. Barabás also observed such a term for  $Be^{II}$ <sup>20</sup>. Palladium(II) and beryllium(II) complexes with coordination number 4 will involve  $S_N2$  attack by the free ligand. Rate-determining

Table 3. Influence of various factors on the isotopic exchange rate of various acetylacetonato complexes

Ion	Solvent	$k_1$	$[H_2O]$	[acid]	[ligand]
$Al^{III}$	polar	○	○	○	×
	non-polar	×	○	○	×
$Ga^{III}$	polar	○	○	○	○
$Pd^{II}$	non-polar	○	×	○	○
$Co^{III}$	non-polar	○	×	×	○
$Be^{II}$ <sup>a</sup>	both	○			○

<sup>a</sup> Barabás, ref. 20.

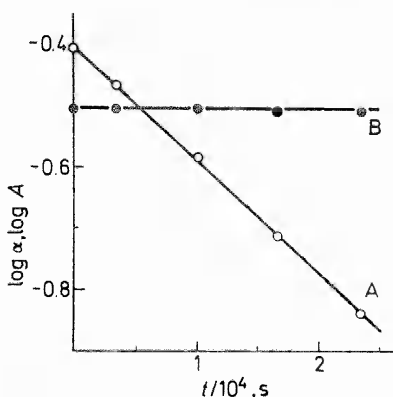
○. Contribution appreciable; ×, contribution not appreciable.

attack of  $\beta$ -diketone upon an octahedral complex seems more probable at the vacant coordination site of the intermediate with one of the ligands as unidentate, whenever the break of the remaining bond takes place with some difficulty as a rate-determining step. Participation of this term in gallium(III) complexes may be compared to the solvent exchange of this ion<sup>6</sup>, which is claimed to involve associative path<sup>21</sup>.

**RACEMIZATION AND ISOTOPIC EXCHANGE OF  
TRISACETYLACETONATO-SILICON(IV) AND  
-GERMANIUM(IV)**

Silicon(IV) and germanium(IV) give various compounds analogous to organic carbon compounds, and much work has been done with their tetrahedral compounds. They also give octahedral compounds, but their dynamic properties are least known. Kirschner *et al.* first resolved  $[\text{Si}(\text{acac})_3]^+$ <sup>22</sup>, and studied the hydrolysis, methanolysis and loss of optical activity. They concluded that the loss of optical activity was mainly due to solvolysis<sup>23</sup>. Pearson, Edgington and Basolo proposed a possible  $\text{S}_{\text{N}}2$  displacement mechanism for the base hydrolysis of the same complex<sup>24</sup>, and suggested the participation of racemization on the basis of the difference in rates of hydrolysis and loss of optical activity. Muetterties and Wright studied the base hydrolysis of  $[\text{Si}(\text{dbm})_3]^+$  and trispropolonato-silicon(IV) in  $^{18}\text{O}$ -labelled water, and suggested a nucleophilic attack of hydroxide ions on the carbonyl carbon<sup>25</sup>.

We have resolved homologous compounds  $[\text{Si}(\text{dbm})_3]$  and  $[\text{Ge}(\text{acac})_3]^+$  by a similar method to that for  $[\text{Si}(\text{acac})_3]^+$ . It was found that  $[\text{Si}(\text{acac})_3]\text{ClO}_4$ ,  $[\text{Si}(\text{dbm})_3]\text{ClO}_4$  and  $[\text{Ge}(\text{acac})_3]\text{ClO}_4$  undergo intrinsic racemization in carefully dehydrated organic solvents such as tetrachloroethane (TCE) and acetonitrile (AN) without being involved by solvolysis or hydrolysis. *Figure 7* shows the change of optical rotation at Na D line and of extinction



*Figure 7.* Change of optical rotation at Na D line (A) and of extinction at 305 nm (B) in tetrachloroethane.

at 305 nm (absorption peak) of  $[\text{Si}(\text{acac})_3]^+$  in tetrachloroethane with time. The rate of racemization was measured at varying temperatures and the results ( $k_1$ ) are summarized in *Table 4*<sup>26</sup>.

The racemization rate is not affected by change in concentration of free  $\beta$ -diketone and water under the given conditions. In tetrachloroethane, the rate increased in the presence of strong acids such as trichloroacetic, but not with a base like pyridine. The pyridinium salt of trichloroacetate had no

Table 4. Rate of racemization of  $[\text{Si}(\text{acac})_3]^+$ ,  $[\text{Si}(\text{dbm})_3]^+$  and  $[\text{Ge}(\text{acac})_3]^+$  in organic solvents

Solvent	Tetrachloroethane			Acetonitrile		
	Complex	$[\text{Si}(\text{acac})_3]^+$	$[\text{Si}(\text{dbm})_3]^+$	$[\text{Si}(\text{acac})_3]^+$	$[\text{Si}(\text{dbm})_3]^+$	$[\text{Ge}(\text{acac})_3]^+$
$k_1/s^{-1}a$		$9.5 \times 10^{-7}$	$5.1 \times 10^{-6b}$	$1.1 \times 10^{-5}$	$1.6 \times 10^{-5}$	$8.0 \times 10^{-6}$
$k_2/M^{-1} s^{-1}a$		$3.6 \times 10^{-5c}$	$2.3 \times 10^{-5b,c}$	$6.5 \times 10^{-2d}$	0 <sup>e</sup>	$9.0 \times 10^{-5e}$
$\Delta H^\ddagger/\text{kcal mol}^{-1} (k_1)$		$31.6 \pm 0.1$	$32.4 \pm 0.6$	$25.7 \pm 0.2$	$25.0 \pm 0.2$	$24.2 \pm 1.0$
$(k_2)$		$29.3 \pm 1.9$	$25.0 \pm 0.7$	<i>ca.</i> 18		$23.0 \pm 1.1$
$\Delta S^\ddagger/\text{calK}^{-1} \text{mol}^{-1} (k_1)$		14.6	14.3	0.53	-0.8	-4.5
$(k_2)$		14.2	-5.1	-5.8		-3.5

<sup>a</sup> All complexes as perchlorate; at 40°C except for *b*. <sup>b</sup> At 60°C. <sup>c</sup> Acid catalysis with trichloroacetic acid. <sup>d</sup> Base catalysis with 2,6-lutidine;  $k_2$  for pyridine is  $1.5 \times 10^{-4} M^{-1} s^{-1}$  at 40°C.

<sup>e</sup> Base catalysis with pyridine.

influence, and the catalytic action should be due to proton catalysis. In acetonitrile, on the other hand, no acid catalysis was observed but a base like pyridine accelerated the racemization. Again its salts had no influence. Aliphatic amines changed the absorption spectrum, and Schiff base formation with the ligand was observed.

The catalytic action increases with increase in acid or base concentration and the rate formula is expressed by equation (8):

$$k_0 = k_1 + k_2 [\text{acid or base}] \quad (8)$$

Table 4 includes  $k_2$  values for acid and base catalysis, and the corresponding activation parameters.

Intermolecular isotopic exchange between  $\text{Hacac-}^{14}\text{C}$  and  $[\text{Si}(\text{acac})_3]^+$  and  $[\text{Ge}(\text{acac})_3]^+$  was examined in tetrachloroethane and acetonitrile by a similar method to that for the aluminium complex. The  $\beta$ -activity of  $^{14}\text{C}$  was measured by a gas-flow counter. No appreciable exchange was observed in all the systems mentioned above for several half times of racemization. Presence of acid and base did not affect the result.

It is clear that the racemization takes place via an intramolecular mechanism. Since no net chemical change was involved, some kind of twisting mechanism should be operating. Intramolecular racemization can proceed either with or without break of one of the metal-oxygen bonds. The mechanism maintaining coordination number 6 was interpreted by Ray and Dutt<sup>27</sup> and by Bailar<sup>28</sup> in slightly different ways, and summarized by Sievers<sup>29</sup>.

Racemization of the present compounds, however, seems to be more appropriately understood by considering an intermediate with coordination number 5. A twist mechanism without bond break will be less sensitive towards acid and base catalysis. An intermediate with coordination number 5 can be either a trigonal bipyramid or square pyramid but should have a plane of symmetry with the unidentate ligand at the apical position. Figure 8 shows a possible route of intramolecular racemization.

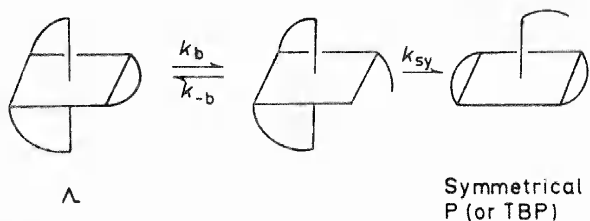


Figure 8. Plausible reaction mechanism of racemization of  $[\text{Si}(\text{acac})_3]^+$ ,  $[\text{So}(\text{dbm})_3]^+$  and  $[\text{Ge}(\text{acac})_3]^+$  in organic solvents.

Two possible rate-determining steps can be encountered, whenever an intermediate with coordination number 5 is involved. One is to reckon the bond break to give the intermediate as rate-determining, and the probability of intramolecular rearrangement is expressed by  $k_{sy}/(k_{sy} + k_{-b})$ . The rate is expressed by equation (9):

$$\text{Rate} = k_b \cdot k_{sy}/(k_{sy} + k_{-b}) \quad (9)$$

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An alternative is to consider that one of the bonds of a given ligand breaks and forms quickly and the rearrangement will be the rate-determining step.

Table 5 shows the change of  $k_1$  of various tris- $\beta$ -diketonato-silicon complexes in tetrachloroethane. Introduction of ethyl and phenyl at R and R' in place of methyl decreases the rate to a small extent. The  $pK_a$  values of the

Table 5. Rate of racemization of substituted  $\beta$ -diketonato complexes of silicon(IV) in tetrachloroethane at 50°C

R	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
R'	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
R''	H	H	H	CH <sub>3</sub>	CH <sub>3</sub>
$k_1/10^{-6} \text{ s}^{-1}$	4.8	1.8	1.1	88	45
$\Delta H^\ddagger/\text{kcal mol}^{-1}$	31.6	32.7	32.4	25.2	25.0
$\Delta S^\ddagger/\text{cal K}^{-1} \text{ mol}^{-1}$	+15	+16	+14	+0.6	-0.8

R,R': substituents on carbonyl carbon. R'': substituents on  $\gamma$ -position.

$\beta$ -diketones increase in the same order and the slowing-down will be related to the stronger Si-O bond. The  $pK_a$  values of the R''-substituted ligands is bigger than Hacac and smaller rates of racemization might have been expected. The rapid racemization may be related to the favourable rearrangement of the unidentate ligand. These  $\beta$ -diketones are claimed to have a more stable *trans*-R'R'' isomer than *cis* in the enol form and the isomerization is very quick<sup>30</sup>. If the unidentate ligand assumes a similar electronic state to the free enol form, it is likely that the free end of unidentate ligand recombines with more difficulty on introduction of methyl to the R'' position. The increase in racemization rate is due to increase in the  $k_{sy}/(k_{sy} + k_{-b})$  term.

Table 6. Rate of racemization of  $[\text{Ge}(\text{acac})_3]^+$  in various organic solvents (50°C)

Solvent	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	DMF
$\epsilon$	8.2	35.8	37.5	36.7
$\mu/\text{Debye}$	1.85	3.17	3.44	3.86
D.N.*		2.7	14.1	27
$k_1/10^{-5} \text{ s}^{-1}$	0.4	0.42	2.8	10
$\Delta H^\ddagger/\text{kcal mol}^{-1}$	31	26.5	24.7	

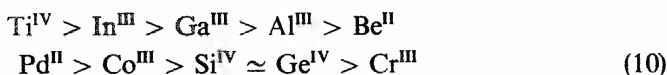
\* Gutmann's donor number; see ref. 31.

Table 6 gives the solvent effect on the racemization of  $[\text{Ge}(\text{acac})_3]^+$ . Despite a similar dielectric constant and dipole moment, nitromethane gives smaller  $k_1$ . Gutmann's donor number<sup>31</sup> can be a good measure for the solvent molecule to squeeze in the coordination sphere to facilitate the racemization. The ease of bond break is also reflected in the  $\Delta H^\ddagger$  values.

For these reasons we tend to consider that the racemization involves an intermediate with one-ended ligand.

## COMPARISON OF THE LABILITY OF ACETYLACETONATO COMPLEXES IN RELATED REACTIONS

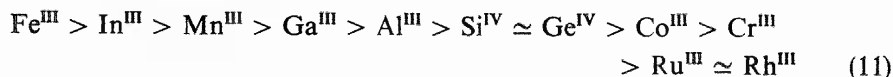
The following sequence gives the order of lability of some metal ions, both typical and transition, towards isotopic exchange:



The mechanism of intermolecular isotopic exchange of these acetylacetonato complexes has been discussed here and elsewhere. Titanium(IV) is very labile in acetonitrile but seems to involve associative path. The details will be discussed elsewhere. Chromium(III) gives intermolecular isotopic exchange at more than 140°C in organic solvents and presumably over 180°C in the gaseous phase. The beryllium complex with tetrahedral structure was studied by Barabás<sup>20</sup>.

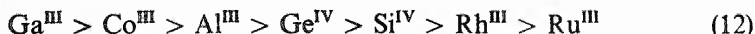
Apart from such intermolecular isotopic exchange, much work has been carried out concerning the site exchange of various tris-β-diketonato complexes<sup>32</sup>.

The following sequence very briefly summarizes the order of decreasing site-exchange rate:



There may be results by other workers too. Site exchange is accompanied by isomerization and/or racemization of complexes involving bi- or multi-dentate ligands and has many routes. It can proceed either inter- or intramolecularly. In the latter case, intramolecular rearrangement with or without bond break is feasible. It is claimed that in most cases the site exchange with β-diketonato complexes proceeds through an intermediate with a unidentate ligand, namely involving the break of one of the metal-ligand bonds. Hence the order seems to tell the order of difficulty with which the first metal-ligand bond is broken. We have considered that the racemization of the silicon and germanium complexes involves the break of one of the metal-ligand bonds, and these two ions can be included in the series. They are more inert than trivalent aluminium but more labile than the so-called inert complexes.

When the site exchange of α-diketonato complexes, e.g. tropolone derivatives (T), is compared, the order of inertness is as follows<sup>33</sup>



Trivalent cobalt is more labile than aluminium, germanium and silicon. Since these ligands have planar structure with π-electron systems, the mechanism will be a twist without bond break. Even if one metal-bond is broken, the oxygen will remain near the coordination site, and internal rearrangement will be less feasible. The lability of the cobalt(III) complex is accounted for by the small strain in the intermediate, trigonal prism structure as shown in *Figure 9*.

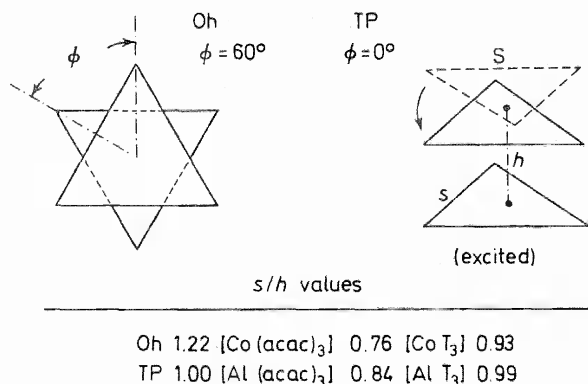
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Figure 9. Intramolecular site exchange mechanism without bond break for octahedral complexes (ref. 34).

It is claimed that in the ideal trigonal prism the ratio  $s/h$  is equal to unity, and the nearer the ratio in the intermediate state to unity, the easier the twist through this intermediate. For tropolonates the ratios are very near to unity and the site exchange seems to proceed via a twist mechanism without bond break.

The order of rate of intermolecular isotopic exchange (Sequence 10) is given with the overall rate. Some of the complexes have both dissociative and associative paths. If the order is given with the dissociative path, the sequence does not change except for titanium(IV)\*.

The experimental conditions for these experiments and those for the site exchange (sequence 11) are not equal in most cases, and the comparison should be approximate. However, the rate of site exchange is always greater than that of intermolecular isotopic exchange. The earlier discussion that the isotopic exchange rate of the dissociative path is governed by the ease of break of the second bond of a chelate is thus indirectly supported.

Sequence 10 is similar to sequence 11 for the most part, but there is a small difference. A dominating influence of the charge of the central ion is seen.  $\beta$ -Diketonato complexes of quadrivalent ions give smaller isotopic exchange rates than those of trivalent ions. This fact will be interpreted by the greater difficulty with which the remaining bond of a unidentate ligand is broken in the  $\text{Ge}^{\text{IV}}$  and  $\text{Si}^{\text{IV}}$  complexes. (Inertness of  $\text{Cr}^{\text{III}}$  will be understood by its high affinity with oxygen donors in general.) This fact seems to reflect the dominating influence of the charge in determining the strength of single  $\text{M}-\text{O}$  bonds.

The studies introduced now are joint work with the following co-workers: K. Matsuzawa (nee Masuda), M. Takahashi, H. Kido, T. Inoue, A. Nagasawa, M. Murakami and C. Chatterjee. We thank Nishina Memorial Foundation for financial support.

\* The isotopic exchange of titanium(IV) is measurable at  $-10^\circ\text{C}$ . but there seems to be a big contribution of an associative path and the dissociative cleavage of the  $\text{Ti}-\text{O}$  bond must be more difficult.

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