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Mechanism of Isotopic Exchange of Trisacetylacetonatoaluminum with Acetylacetone-^{14}C in Organic Solvents

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The kinetic study concerning isotopic exchange of acetylacetone (acacH) and trisacetylacetonatoaluminum [Al(acac)$_3$] (*Bull. Chem. Soc. Jap.*, **41**, 384 (1968)) has been extended to solutions in various organic solvents. Similar catalytic actions of water and acid were observed, and the concentration of acacH did not affect the rate, so that the kinetic formula is expressed by

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

The rate constants and activation parameters are listed in Table 1. The k_1 values are zero in non-polar solvents such as toluene and xylenes, whereas the k_2 values are greater in these solvents than in polar solvents such as tetrahydrofuran and ethylacetate. The activation enthalpy is practically constant in these solvents, regardless of the participation of catalysts. The third and the fourth term seem to represent acid-catalysed reaction paths involving different proton carriers. The whole result appears to support our previous tentative conclusions that the exchange proceeds *via* an intermediate in which one of the acetylacetonate ligands is present as unidentate, and that the ease with which the free end recombines with the aluminum ion is responsible in determining the reaction rates.

In a previous paper we reported the isotopic exchange kinetics of trisacetylacetonatoaluminum [Al(acac)$_3$] and acetylacetone-^{14}C in tetrahydrofuran and postulated a plausible mechanism.[1] One of the three acetylacetonate ligands seemed to be present as unidentate with considerably long life time, and break of the remaining bond appeared to be the rate determining step. The catalytic effect of water and some acids was understood to retard the recombination of free end of the unidentate ligand by occupying the vacant coordination site of aluminum ion and the free end of unidentate acetylacetonate, respectively.

We have extended the study in other organic solvents, ethylacetate, toluene, *o*-, *m*- and *p*-xylene, in order to make clear the exchange mechanism. The exchange rate has been measured in solutions containing varying amounts of the complex, free acetylacetone (acacH), water and acids at various temperatures, and the rate formulae, rate constants and activation parameters have been discussed.

Experimental

Materials. Acetylacetone-^{14}C and trisacetylacetonatoaluminum were synthesized by the same method described previously.[1] The specific activity of the acacH was *ca.* 0.02 mCi per mg, and it contained water of the order of 10^{-1}M.

Extra pure grade ethylacetate was shaken with an aqueous solution of sodium hydrogen sulfite, water, aqueous solution of sodium carbonate and a saturated calcium chloride solution, dried with calcium chloride, distilled, further dried with phosphorus pentoxide and distilled. Toluene and xylenes were shaken with concentrated sulfuric acid, water, sodium hydroxide solution and water, dried with calcium chloride, refluxed with sodium and distilled.

m-Toluic acid and phenol were sublimed at 5 mmHg. Reagents for the scintillation counting, anisole, *p*-terphenyl and *p*-di-(5-phenyl-2-oxazolyl)-benzene (POPOP) were purified as mentioned previously.

Experimental Procedure. The method is essentially the same as that used previously.[1] Trisacetylacetonatoaluminum was precipitated crystalline within 6 hr by pouring an aliquot of the reaction mixture (*e. g.* 1 m*l*) into chilled petroleum ether (−20°C, 20 m*l*). The exchange reaction stopped instantaneously and no zero time exchange was observed.

Since the solvents and the free ligand acacH contained a significant amount of water, the water content of the reaction mixtures was determined by Karl-Fischer titration in a mixture of pyridine and ethyleneglycol (5+1). Little change in water content was observed within a given kinetic run. Five or six aliquots were withdrawn during one kinetic run, and altogether about two hundred kinetic runs were carried out.

The absorption spectra of the reaction mixtures were identical with the sum of those of [Al(acac)$_3$] and acacH in all the solvents, and no reaction other than isotopic exchange took place, regardless of the presence of water and the acids.

Measurements. Coincidence liquid scintillation counting was employed.[1] The counting rate at the

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[1] K. Saito and K. Masuda, This Bulletin, **41**, 384 (1968).

end of the exchange reaction (infinite time) was calculated from that of acacH-^{14}C and the used amounts of [Al(acac)$_3$] and acacH. The absorption spectra in the visible and ultraviolet region were measured with a Hitachi EPU-2A spectrometer.

Results

The experimental results were treated with McKay's formula

$$R = -2.3\frac{3ab}{3a+b}\cdot\frac{\log(1-F)}{t}, \qquad (1)$$

where a and b denote the concentrations of the complex with three exchangable ligands and that of the free ligand, respectively. F is the fraction of reaction and t the lapse of time in minutes. Good linear relationship was observed between $\log(1-F)$ and t in each run, and between R and a in all the solvents used. (diagram similar to Fig. 1 of Ref. 1). Hence the rate is expressed by $R = k_0 a$.

Figure 1 shows the relationship between k_0 and the concentration of water in ethylacetate solutions at various temperatures. Figure 2 gives similar relationships in toluene at various temperatures, and Fig. 3 those in o-, m- and p-xylene at 25°C. The full and the open circles in Fig. 2 denote k_0 values obtained in the presence of different amounts of free ligand. Since acacH-^{14}C contained a small amount of water, change in b brought about the change in water concentration, and the influence of b was not examined individually. However, the fact that the full and the open circles are on the same line at a given temperature clearly indicates that k_0 is independent of b. The straight lines are expressed by

$$k_0 = k_1 + k_2[H_2O]. \qquad (2)$$

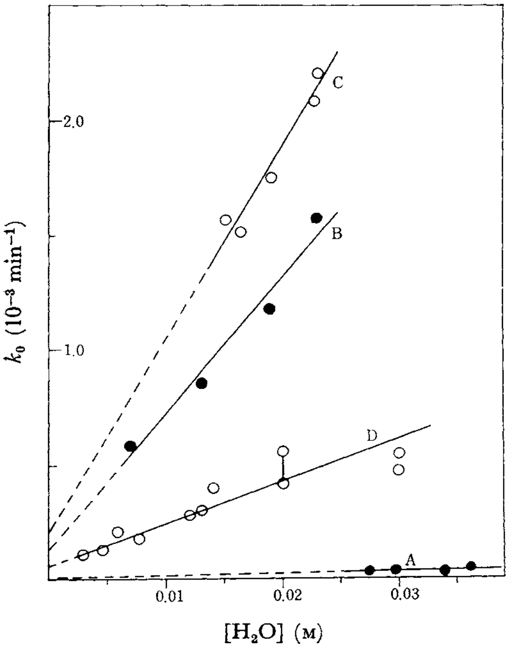


Fig. 1. Relationship between k_0 and the concentration of water in ethylacetate.
A (0°C), B (30°C), C (35°C) in ethylacetate; D (25°C) in tetrahydrofuran. (b=0.070M)

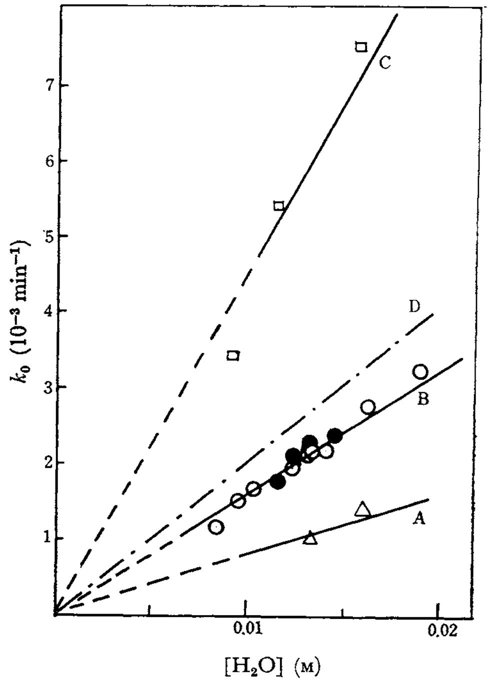


Fig. 2. Relationship between k_0 and the concentration of water in toluene.
A (0°C), B (25°C), C (35°C) in toluene; D (25°C) in xylenes (see Fig. 3).
△□○ b=0.070M ● b varying

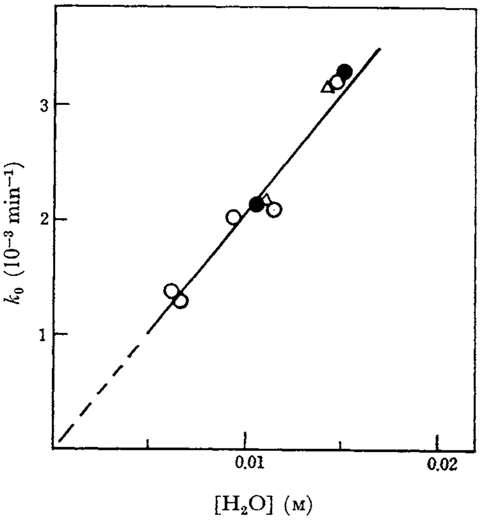


Fig. 3. Relationship between k_0 and the concentration of water in xylene isomers.
25°C, b=0.070M ○ ortho, ● meta, △ para

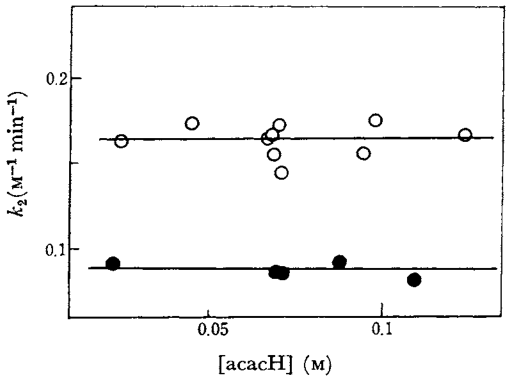


Fig. 4. Influence of the concentration of acetylacetone on the k_2 values.
○ 25°C in toluene, ● 35°C in ethylacetate

The slope and the intercept of Figs. 1, 2 and 3 correspond to k_2 and k_1, respectively, under the given conditions. The lines in Figs. 2 and 3 pass the zero point, to indicate that k_1 is almost zero in toluene and xylenes. No difference in rate constant was observed in the three isomers of xylene.

Figure 4 shows the influence of b upon k_2 in ethylacetate and in toluene. It further demostrates that k_2 is independent of b.

The exchange reaction is catalysed by acids. When m-toluic acid and phenol were used, the relationship between k_0 and acid concentration was similar to that in Fig. 3 of Ref. 1 in less than 0.021M acid in the solvents. Hence the catalytic effect increases linearly with the increase in acid concentration. Figure 5 shows the influence of water concentration upon the exchange rate in the presence of a given amount of m-toluic acid at various temperatures in ethylacetate and at 25°C in toluene.

Similar diagrams were obtained by use of phenol in place of m-toluic acid in ethylacetate. It appears as if the acid catalysis operates in two ways with and without the aid of water. The overall relationship is thus expressed by

$$k_0 = k_1 + k_2[H_2O] + k_1'[\text{acid}] + k_2'[\text{acid}][H_2O]. \quad (3)$$

The intercept and the slope of lines in Fig. 5 correspond to k_1' and k_2' of Eq. (3), respectively at a given temperature. The third and the last term of Eq. (3) express the acid catalysis operating with and without the aid of water, respectively.

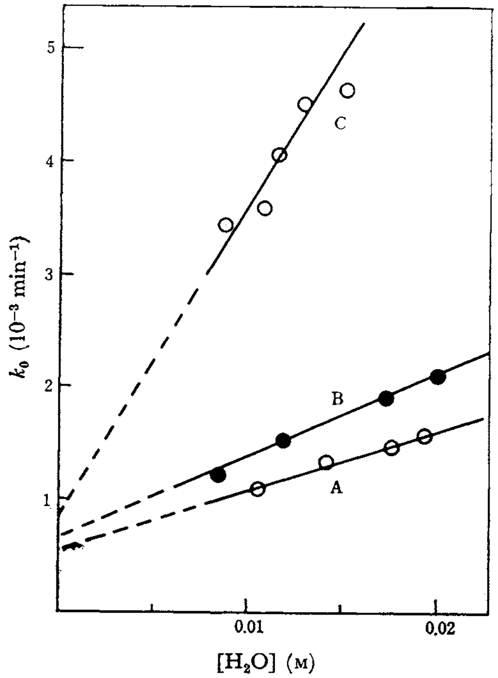


Fig. 5. Influence of the concentration of water upon the k_0 values in the presence of a given amount of m-toluic acid.
A: 25°C in ethylacetate, B: 30°C in ethylacetate, C: 25°C in toluene.
(b=0.070M, [m-toluic acid])=0.090M)

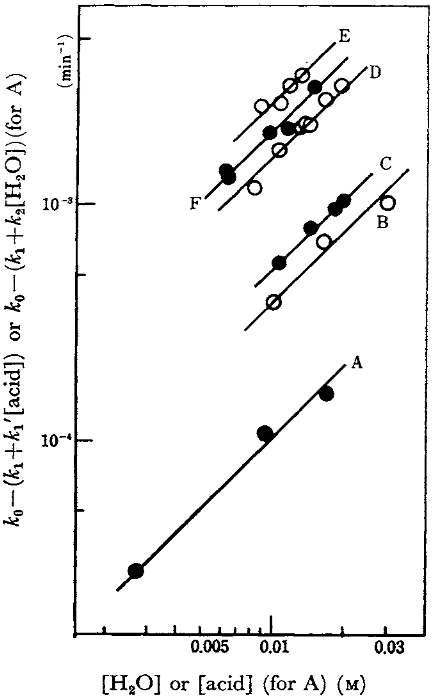


Fig. 6. Logarithmic plots indicating the influence of water in the presence of a given amount of m-toluic acid, and that of m-toluic acid in the presence of a given amount of water.
A: 25°C in tetrahydrofuran, [H_2O], 0.027M, [acid] varying;
B: 25°C in tetrahydrofuran, [H_2O] varying, [acid], 0.015M;
C: 25°C in ethylacetate, [H_2O] varying, [acid], 0.009M;
D: 25°C in toluene, [H_2O] vaying, [acid] none;
E: 25°C in toluene, [H_2O] varying, [acid], 0.004M;
F: 25°C in o-xylene, [H_2O] varying, [acid] none.

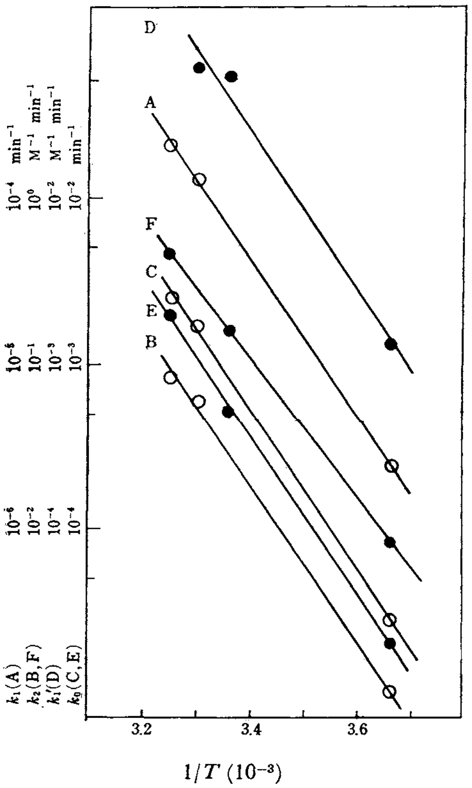


Fig. 7. Arrhenius plots of the rate constants of Eq. (3) in various solvents.
A: k_1 in ethylacetate; B: k_2 in ethylacetate;
C: k_0 in ethylacetate ($[H_2O]=0.027$M, [acid] none);
D: k_1' in ethylacetate;
E: k_0 in tetrahydrofuran ($[H_2O]=0.027$M, see the text);
F: k_2 in toluene.

Figure 6 is the log-log plots indicating the influence of water in the presence of a given amount of acid, and that of *m*-toluic acid in the presence of a given amount of water. The k_1 and the k_2 values were obtained in the absence of acid, and the k_1' values from the intercept of Fig. 5. These diagrams with a slope 45° demonstrate that Eq. (3) is quite appropriate in the present systems.

Figure 7 gives the Arrhenius plots of k_1, k_2, k_1' and k_0 in the solvents. The k_1 and k_1' values were obtained by extrapolation on Fig. 1 and Fig. 5, respectively, and their accuracy cannot be high enough. However, it is noteworthy that the values in tetrahydrofuran and ethylacetate are practically the same and that in toluene does not differ much. In tetrahydrofuran the Arrhenius activation energies were not obtained individually for k_1 and k_2. The E_a values were, however, obtained in the presence of varying amounts of water, and they were all found to be equal to 22 kcal per mole. Hence it is clear that both k_1 and k_2 have the same E_a values.

Table 1 summarizes the kinetic constants obtained in various solvents, together with the dielectric constants and dipole moments and the activation parameters in the solvents. The values for the acid-catalyzed paths do not seem very accurate, because they were obtained on the basis of extrapolated values and their approximate values are given in the footnote.

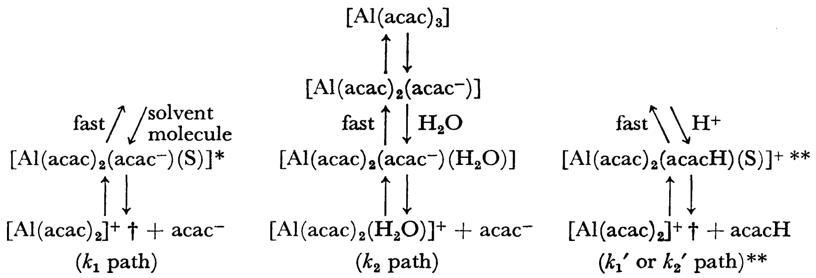
Discussion

Dissociation Mechanism. Since the exchange rate is independent of the concentration of acetylacetone, regardless of the presence of catalyst such as water and acid, the reaction must proceed through

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS AT 25°C

Solvents		Tetrahydrofuran	Ethylacetate	Toluene	Xylenes
k_0 10^{-4} min^{-1} [a]		2.5	4.75	23.8	31.0
k_1 10^{-4} min^{-1}		0.6	0.64	0	0
k_2 10^{-2} $M^{-1}min^{-1}$		2.0	2.75	16	21
k_1' 10^{-2} $M^{-1}min^{-1}$ [b]		0.93	5.4	9.5	
k_2' $M^{-2}min^{-1}$ [b]		(1.2)	(3.0)	(13)	
Dielectric const.		7.39	6.03	2.38	2.57 (*o*-)[c]
Dipole moment (Debye)		1.70	1.87	0.39	0.62 (*o*-)[d]
$\Delta H^{\neq}$ [f] (kcal/mole)	k_0[a]	21.4[e]	21.4	19.2	
	k_1	[21.4][e]	21.4		
	k_2	[21.4][e]	21.4	19.2	
$\Delta S^{\neq}$ [g] (e.u.)	k_0[a]	−7.8	−8.0	−12.2	
	k_1		−12.2		
	k_2		0.04	−3.8	

a) $[H_2O]$, 0.015M; [acid], none. b) acid, *m*-toluic c) at 20°C; *m*- 2.37; *p*- 2.27.
d) *o*-, 0.62 Debye; *p*-, non-polar. e) See text. Anticipated values in square brackets.
f) $\Delta H^{\neq}$ values in ethylacetate for k_1' and k_2' are both 21.4 kcal/mol.
g) $\Delta S^{\neq}$ values for k_1' and k_2' in ethylacetate are +1.4 and +9.5 e.u. respectively.



* S: solvent molecule ** In k_2' path, (H_2O) in place of S

† Presumably with coordinated solvent molecule (or with H_2O for the k_2' path).

Fig. 8. Plausible reaction mechanism.
(acac$^-$) denotes unidentate acetylacetonato ligand.

the dissociation mechanism, in which the break of metal-ligand bond is responsible for determining the rate. Whenever a bidentate chelate ligand undergoes isotopic exchange, two reaction mechanisms can be considered: (i) The break of one of the metal-ligand bonds is the rate-determining step, and the remaining bond breaks rapidly. The catalytic effect is understood by considering that water molecule or acid proton approaches the coordinated oxygen atom to assist the bond rupture. (ii) The ligand can be present as unidentate with considerably long life time, and break of the remaining bond is the rate-determining step. Catalytic actions can be interpreted by assuming that water molecule and the acid proton occupy the vacant coordination site of aluminum ion and the negatively charged free end of unidentate ligand, respectively, and retard recombination of the free end.

From the experimental results, we tend to conclude that mechanism (ii) is more plausible (Fig. 8). The activation enthalpies in tetrahydrofuran and ethylacetate are the same, regardless of the presence of catalysts, and that in toluene does not differ much. If (i) were operating, the ease of break of one of the metal-ligand bonds would be affected by the catalysts, and the $\Delta H^{\ddagger}$ values for k_1, k_2, *etc.* should have different values. Whenever (ii) operates, on the other hand, the rate constants are dependent on the ease with which the free end of unidentate ligand recombines with the metal ion. The transition state would involve elongation of the remaining bond of unidentate ligand, and be affected little by the protonation at the free end of the same ligand or by the occupation of coordination site on the aluminum ion by water molecule.

The k_1 Path. The fact that k_1 value is zero in toluene and xylenes, whereas it is greater in tetrahydrofuran and ethylacetate, seems to be related to the dipole moment and the dielectric constant of the solvents. We believe that activation entropy is responsible for such a difference. Polar solvents can occupy the free end of unidentate ligand or the vacant coordination site of metal ions to retard the recombination and leave more chance for the remaining bond to be broken.

Comparison of activation enthalpy, however, could also account for the difference. Since the present metal-ligand bond is regarded rather ionic, coordination of polar solvent molecule on the vacant coordination site would decrease the effective charge of the aluminum ion to make the remaining metal-ligand bond weaker, and to decrease the $\Delta H^{\ddagger}$ value. Such an interpretation is alternatively expressed as the small dielectric constants of the aromatic hydrocarbons being unfavorable for the break of aluminum-oxygen bond. These two contributions cannot be distinguished, unfortunately, because the k_1 value is zero.

The k_2 Path. The greater k_2 values in aromatic hydrocarbons than in polar solvents might be correlated with the ease with which water molecules coordinate the vacant site of the metal ion. The affinity between water and solvent molecules would be greater in tetrahydrofuran and ethylacetate than in toluene and xylenes.

In the latters, water molecules would have more chance to be present near the complex molecules and to creep in the coordination site whenever one of the aluminum-oxygen bond is broken, so that the recombination of unidentate ligand is retarded to a greater extent. Further, in these solvents, the coordination of water molecules to the vacant coordination site would decrease the effective charge of the cation and make the ionic metal-ligand bond weaker. Thus the activation enthalpy for the k_2 path could become smaller than that for the k_1 path, although the actual value for the latter cannot be known.

In polar solvents, on the other hand, the k_2 term is regarded to represent a reaction path in which water molecule occupies the vacant coordination site in place of the solvent molecule. Hence the difference in the rate constants k_1 and k_2 would not be so remarkable as in the non-polar solvents.

Acid Catalysis. The acid catalyzed reaction path operates in two ways. The k_1' path represents a reaction mechanism in which the acid acts as a proton source without cooperation with water, whereas the k_2' path that operating with the aid of water. So far as the role of acid is to provide protons to the free end of unidentate ligand, the difference between the two paths consists in the kind of proton carrier. Hydroxonium ions must be the carrier for the k_2' path, while the acid molecule itself or the solvent molecule would be the proton carrier in the k_1' path.

As seen in Table 1, acid catalysis is more marked in toluene than in ethylacetate or tetrahydrofuran. Since protons have less affinity with the solvent molecule in toluene than in the polar solvents, acid molecules themselves would be the more plausible proton carrier in the former solvent. They would have greater possibility to be present near the complex molecule, to be ready to transfer protons to the free end of unidentate ligand, and retard the recombination to a greater extent. It would be also possible that the acid anion occupies the vacant coordination site as water molecule does in the k_2 path, whenever proton transfer takes place. Such a cooperative effect cannot be expected when the solvent molecule carries proton in the polar solvents. A similar trend is observed with the k_2' values. When hydroxonium ions carry protons, proton transfer to the free end of unidentate ligand can be accompanied by the addition of water molecule to the vacant coordination site of aluminum ion, and a cooperative effect is expected with a greater probability in toluene than in the polar solvents. The relative figure of the k_1' and the k_2' values would be related to the competition between water and the acid anion or the solvent molecule as proton carrier. Such a competition would be ruled by various factors including acid strength in the non-aqueous media and also affinity of water with the solvent molecule.

Importance of the Unidentate Complex as Intermediate. Aluminum complexes are generally regarded as substitution labile,[2] except for a few cases.[1,3] Rapid establishment of ligand interchange equilibria and racemization was demonstrated by Fortman and Sievers on the basis of p.m.r. coalescence measurement with acetylacetonato, hexafluoroacetylacetonato and hexamethylacetylacetonato complexes of aluminum.[4] They postulated several possible intramolecular reaction mechanisms, but gave no conclusion as to which of them is most plausible. We have pointed out the importance of an intermediate state involving a unidentate ligand, but our result is not enough for choosing the most appropriate one. We are essentially dealing with slow reactions, and our "rapid reaction" could be slower than their reaction by several orders. Whenever the free end of unidentate ligand recombines with the aluminum ion without undergoing isotopic exchange reaction, the life time of intermediate must be long enough to allow some kinds of steric change which can bring about the inversion of individual tris complex molecules.

Although our experiment cannot provide useful information concerning the "twist mechanism," it clearly rules out any kind of intermolecular mechanism and seems to establish the importance of unidentate intermediate in considering the reaction mechanism of ligand substitution in chelate compounds.

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4) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).