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Kinetics of Isotopic Exchange between Acetylacetone-^{14}C and Tris-acetylacetonatoaluminum in Tetrahydrofuran

Kazuo SAITO and Kazuyo MASUDA

Chemistry Department, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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Tris-acetylacetonatoaluminum [Al(acac)$_3$] is precipitated crystalline from tetrahydrofuran (THF) solution containing an excess of acetylacetone (acacH) by adding chilled petroleum ether. This fact enables a kinetic study of isotopic exchange of acac$^-$ between [Al(acac)$_3$] and acacH with the aid of acetylacetone-^{14}C. The exchange rate is independent of the concentration of acacH and dependent on that of water. The rate formula at 25°C is as follows:

$$R = [\mathrm{Al(acac)_3}](6\times10^{-5} + 2.0\times10^{-2}[\mathrm{H_2O}])\ \mathrm{mol}\ l^{-1}\ \mathrm{min}^{-1}$$

This exchange reaction is catalysed by acids; the stronger the acid, the greater the catalytic effect. One of the acetylacetonate ligands would be present with one end free, and break of the remaining bond of unidentate acetylacetonate seems to be the rate determining step. Water can occupy the vacant coordination site of aluminum ion to retard recombination of the unidentate ligand. The donation of proton to the free end of acetylacetonate appears to impede the recombination, too, and facilitate the exchange. Hydronium ion seems to be the unique proton carrier.

Little information is available concerning the isotopic exchange of organic ligands of non-electrolytic complexes in organic solvents. Such kinetic studies with complexes of typical elements seem very interesting, because no influence is expected from charge, ligand field stabilization energy, hydrolytic decomposition, and ionic strength. One of the present authors measured the exchange rate of radioactive indium between its tris-acetylacetonato- and tris-8-quinolinolato (oxinato) complex in chloroform and found that it is measurable at room temperature (*e. g.* half period

11 min at 25°C).¹⁾ He also found that the exchange between the corresponding zinc complexes is very fast.²⁾ These experiments exemplified that complexes of tervalent typical elements can undergo slow isotopic exchange under certain conditions, but failed to give further information concerning the mechanism.

The difficulties involved in carrying out such studies are to separate one of the participants in the exchange reaction free from the other, and to measure the specific activity (or specific counting rate) with reasonable accuracies. The present authors have examined the solubility of acetylacetone (acacH) and tris-acetylacetonatoaluminum [Al(acac)$_3$] in a variety of organic solvents, and found that the latter is precipitated crystalline free from the former in tetrahydrofuran solution (THF) on addition of petroleum ether at a low temperature. By use of acetylacetone labelled with ^{14}C, they have succeeded in studying the isotopic exchange kinetics at room temperature, and have posturated a reasonable reaction mechanism.

Experimental

Materials. Acetylacetone-^{14}C was synthesized by the method given in Ref. 3, slightly modified to suit for a small scale synthesis. Metallic sodium powder (4.6 g) was refluxed with ethanol (12 m*l*) for 7 hr in ethylether, the ether evaporated off, the product treated with ethylacetate (80 m*l*), acetone-1, 3-^{14}C (0.5 mCi, 0.11 mg) and acetone (15 m*l*) for 1 hr with reflux, and set aside for 20 hr at room temperature. The product was treated with water (170 m*l*), the ether layer discarded, and the aqueous solution made acid with dilute sulfuric acid. The liberated acetylacetone-1, 3, 5-^{14}C was extracted with ethylether, dried with anhydrous sodium sulfate for 24 hr, and distilled to collect a fraction boiling at 120 to 134°C. The distillate was further dried with potassium carbonate, diluted with inactive acetylacetone to adjust the specific activity to the order of 0.02 μCi/mg, and distilled (boiling point 134 to 136°C). The water content of the product was estimated to be 0.31 and 0.71 M (two batches) as mentioned below.

Tris-acetylacetonatoaluminum was synthesized by the ordinary method,⁴⁾ from commercial aluminum sulfate made free from iron and inactive acetylacetone, and sublimed at 5 mmHg at 165°C, to give colorless crystals. Water content of the sublimate was *ca.* 0.06 M. Commercial extra pure THF was refluxed with sodium for 1 hr, distilled and the distillate further dehydrated with lithium aluminum hydride, and distilled. The product contained less than 0.005 M water, and preserved in a desiccator as long as two weeks without being contaminated by atmospheric moisture. *m*-Toluic acid, trichloroacetic acid and phenol were sublimed at 5 mmHg at 105, 50 and 35°C respectively and dissolved in THF without being in contact with air. The concentration and the water content were determined by alkalimetric and Karl Fischer titration, respectively.

Commercial anisole was shaken with sodium hydroxide solution, dried with calcium chloride, refluxed with sodium and distilled. *p*-Terphenyl was recrystallized from xylene. *p*-Di-(5-phenyl-2-oxazolyl)-benzene (POPOP) was of scintillation grade and used without further purification. Other chemicals were of chemically pure grade.

Experimental Procedure. A given amount of tris-acetylacetonatoaluminum (0.2 to 0.7 g) was dissolved in anhydrous THF (10.0 m*l*) and the acetylacetone-^{14}C (0.02 to 0.2 g) was added, the amounts being known from the weight difference. Other reagents such as acids and water were added to the THF in advance, whenever necessary, and their amounts known from the weight difference. The water content thus determined coincided well with those measured by Karl Fischer titration within an erorr less than 0.003 M in the reaction mixture.

The reaction mixture was kept in a thermostat at 25 or 35°C, and an aliquot (*e. g.* 1 m*l*) was added to chilled petroleum ether (−20°C) at appropriate intervals. Crystalline [Al(acac)$_3$] separated out on standing at −20°C for 4 hr. The standing time did not affect the results, and there was no appreciable zero-time exchange. The supernatant was decanted, the precipitate washed with petroleum ether and dried at 80°C. Its weighed portion (4 to 15 mg) was dissolved in anisole (15.0 m*l*), mixed with POPOP (0.02%) and *p*-terphenyl (0.8%) in anisole (15.0 m*l*) and the counting rate measured by the scintillation technique. Five to six aliquots were taken during one kinetic run and about 70 runs were carrierd out under various conditions as mentioned below.

The absorption spectra of reaction mixtures coincide with the sum of those of tris-acetylacetonatoaluminum and acetylacetone. Hence the reaction mixture does not undergo any reaction other than isotopic exchange, regardless of the presence of other ingredients such as water and organic acid.

Since water accelerates the exchange and the reaction mixture absorbs water slightly, the water content was carefully determined during the course of exchange reaction, to find that the change in content of water is less than 0.1 mg per m*l*, *i. e.* less than 0.005 M. In extreme cases, the mean value before and after the exchange reaction was used for calculation.

Measurement of Radioactivity. A coincidence liquid scintillation counter, made by Institute for Nuclear Study, the University of Tokyo was used for the β-ray counting. The quenching effect was examined with standard ^{14}C-benzoic acid and inactive acetylacetone and tris-acetylacetonatoaluminum, to find that it is negligible in the presence of less than 20 mg per 30 m*l* anisole under the given conditions. The counting rate was proportional to the amount of carbon-14 in the range from 10^{-3} to 10^{-2} μCi of either acetylacetone or tris-acetylacetonatoaluminum. The counting rate at the end of exchange reaction (infinite time) was calculated from that of the acetylacetone-^{14}C and the used amounts of the respective compounds.

Other Measurements. The NMR spectra were recorded with Varian A 60 Spectrometer (60 mega

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1) K. Saito and M. Tamura, *J. Inorg. Nucl. Chem.*, **13**, 334 (1960).

2) K. Saito and M. Tamura, This Bulletin, **32**, 532 (1959).

3) "Organic Synthesis," **20**, 7 (1940).

4) "Inorganic Synthesis," **2**, 25 (1946).

cycle) at room temperature. The absorption spectra in the visible and ultraviolet region were measured with Hitachi EPU-2A Spectrometer. Karl Fischer titration apparatus of Mitsubishi Kasei type with electric end-point indicator was used for the analysis of water; propyleneglycol containing 25% (v/v) pyridine was the useful titration medium.

Results

The experimental data were treated in accordance with McKay's formula,⁵⁾

$$R = -2.303 \cdot \frac{3ab}{3a+b} \cdot \frac{\log(1-F)}{t} \qquad (1)$$

where a and b are the molar concentrations of trisacetylacetonatoaluminum (containing three moles of exchangable acetylacetonate per mole) and acetylacetone, respectively, F is the fraction of reaction and t the lapse of time in minutes.

Influence of the Concentration of Complex, Free Ligand and Water. The influence of a upon R is illustrated in Fig. 1, which clearly shows that R is proportional to a in the given concentration range. More dilute solutions did not yield the precipitate on addition of chilled petroleum ether.

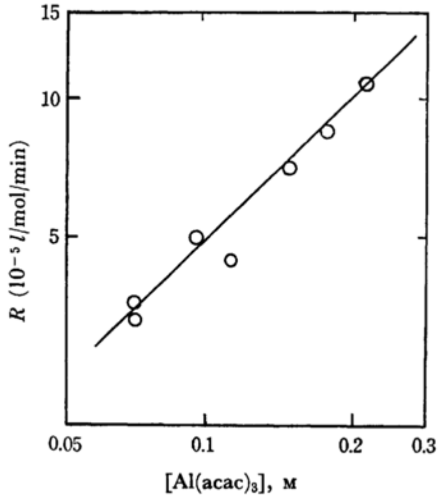

Fig. 1. Influence of the concentration of trisacetylacetonatoaluminum on the exchange rate. [acacH], 0.070 M; [H_2O], 0.027 M; 25°C

Water in the reaction mixture accelerates the exchange reaction. So far as its concentration was kept constant, however, the rate was independent of b, as seen from Table 1. Hence R is expressed as

$$R = k_0 a \qquad (2)$$

Table 1. Influence of concentration of acetylacetone-^{14}C on the exchange rate

[H_2O], M	[acacH], M	k_0, min^{-1}
0.0046	0.067	1.3×10^{-4}
0.0047	0.144	1.4×10^{-4}
0.045	0.031	1.1×10^{-3}
0.046	0.051	1.1×10^{-3}
0.046	0.066	1.1×10^{-3}
0.047	0.095	1.2×10^{-3}

[Al(acac)$_3$], 0.070 M; 25°C

Since the acetylacetone-^{14}C contained a small amount of water, which cannot be removed by accessible dehydrating agents, change in b also brought about change in concentration of water in the reaction mixture. However, such a contribution is negligible, when the amount of added water in THF is large. The difference in water content coming from varying amounts of the complex *etc.* is even smaller and can be ignored.

When R was measured in THF solutions containing varying amounts of water at given a and b values, the R *vs.* [H_2O] diagram was almost a straight line on log-log scale (Fig. 2). On the other hand, when R was measured with varying b values in the absence of added water in THF containing a given amount of the complex, the diagram really indicates the influence of water concentration. Both the diagrams coincide with each other, to reconfirm that R is independent of b. By extrapolating the anti-logarithmic diagram corresponding to Fig. 2 to zero concentration, the k_0 value in the absence of water, k_1, is known. The accuracy of the concentration of water is low especially in less than 0.01 M solution, and only an approximate amount of k_1 is known by extrapolation, to be less than 6×10^{-5} min^{-1} or less. When this value is subtracted from the measured k_0 values and the difference plotted against [H_2O], a straight line of a gradient 45° is obtained on log-

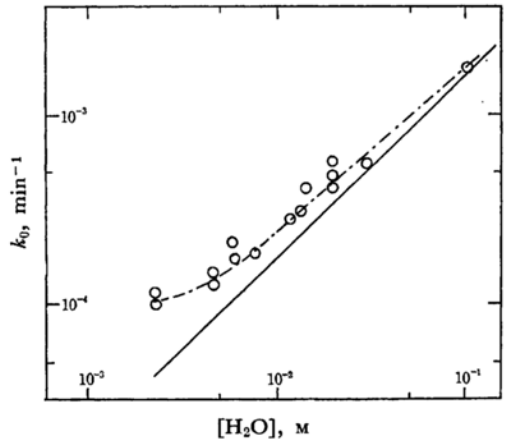

Fig. 2. Influence of the concentration of water on the exchange rate constant. [Al(acac)$_3$], 0.070 M; [acacH], 0.070 M; 25°C

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5) H. A. McKay, *Nature*, **142**, 997 (1939).

TABLE 2. THE INFLUENCE OF VARIOUS ACIDS ON THE EXCHANGE RATE

No.	Acid (pK)	Concn. of acid (10^{-2} M)	Concn. of water (10^{-2} M)	k_0 10^{-4} min^{-1}	k_2'' l^2 mol^{-2} min^{-1}
1	Trichloroacetic (pK=0.635)	2.5	2.5	13.3	12
2		2.5	1.9	10.0	11
3		2.5	1.4	7.9	12
4	m-Toluic (pK=4.272)	1.5	3.0	12.3	1.3
5		1.5	1.6	9.0	2.1
6		1.5	1.0	6.8	2.8
7		0.27	1.6	5.8	2.2
8	Phenol (pK=9.998)	0.36	3.5	10.6	2.5
9		1.1	3.5	16.5	2.2
10		1.6	3.5	21.1	2.5
11		0.45	2.3	7.7	2.5
12		1.2	2.3	14.0	3.2

[Al(acac)$_3$], 0.070 M; [acacH], 0.070 M; 25°C

log scale, as seen in Fig. 2. Hence Eq. (2) is written as Eq. (3).

$$R = k_0 a = a(k_1 + k_2[\mathrm{H_2O}]) \qquad (3)$$

At 25° Eq. (3) is numerically expressed as Eq. (4).

$$R = [\text{complex}](6\times10^{-5} + 2.0\times10^{-2}[\mathrm{H_2O}]) \quad (\text{mol } l^{-1}\text{ min}^{-1}) \qquad (4)$$

Acid catalysis. The exchange is accelerated by acids, although the variety of useful acids is very much limited because of their solubility in THF. The influence of acid concentration in the presence of a given amount of water is shown in Fig. 3.*1 It is seen that the rate increases with increase in concentration of a particular acid. Figure 4 illustrates the influence of the concentration of water in the presence of a given amount of particular acids. Since water is contained more or less in the reagents and solvent, experiments in the absence of water could not be substantiated. However, when the diagrams are exptraporated to zero concentration, the intercept would indicate the rate in the absence of water.

The reaction kinetics is expressed by Eq. (5).

$$R = a\{k_1 + k_1'[\text{acid}] + [\mathrm{H_2O}](k_2' + k_2''[\text{acid}])\} \qquad (5)$$

The accuracy of the extrapolated values is low and

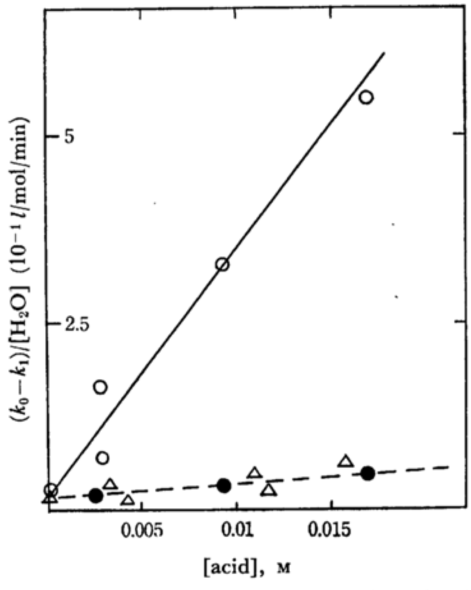

Fig. 3. Influence of the concentration of acids on the reaction rate.
[Al(acac)$_3$], 0.070 M; [acacH], 0.070 M; 25°C
—○— Trichloroacetic acid
--△-- m-Toluic acid
--●-- Phenol

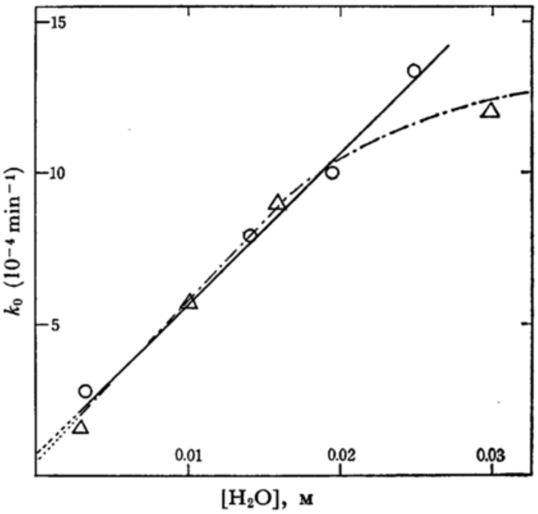

Fig. 4. Influence of the concentration of water on the rate constant in the presence of acids.
[Al(acac)$_3$], 0.070 M; [acacH], 0.070 M; 25°C
——○—— Trichloroacetic acid 2.5×10^{-3} M
·—·△·—· m-Toluic acid 1.5×10^{-2} M

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*1 The absolute water content is known only within an error *ca.* 0.003 M, but experience showed that the relative error for one sets of reaction mixtures simultaneously prepared was much less than that.

it remains uncertain whether the difference between the intercept of Fig. 4 (the second term of Eq. (5)) and k_1 in the absence of acid catalysis is really significant or not. Nevertheless it is quite clear that its contribution is of far less importance as compared with that of the last term of Eq. (5), when the mechanism of acid catalysis is discussed. The k_2'' values are listed in Table 2 together with the acid dissociation constants.

Temperature Dependence. The R values were measured at 0, 25 and 35°C to find the Arrhenius activation energy to be 22 kcal per mole in the presence of 0.020 M water. Since the contribution of k_1 is very small, this value is regarded as corresponding to that of water catalyzed exchange.

Discussion

Dissociation Mechanism. The experimental results indicate that the exchange mechanism is of dissociative nature and the rate determining step is the liberation of coordinated acetylacetonate from the complex. The second term of Eq. (3) corresponds to the catalytic action of water in THF. Since simultaneous break of two metal-oxygen bonds of one ligand is not probable, a possible reaction mechanism can be presented as shown in Fig. 5.

One of the three ligands can be present as unidentate and the break of its remaining bond will bring about the exchange of ligand. Thus the constant k_1 is expressed by $k_b{}^+ \cdot k_u{}^+ / k_b{}^-$, where $k_b{}^+$, $k_u{}^+$ and $k_b{}^-$ are the rates of bond break of bidente and unidentate acetylacetonate and of bond formation to give bidentate acetylacetonate, respectively. The small value of k_1 reflects the ease with which the free end of unidentate ligand recombines with aluminum rather than the remaining bond is broken to result in isotopic exchange, in the absence of catalyst.

Function of Water. In the presence of water, it can occupy the vacant coordination site of aluminum formed by break of one of the Al–O bonds to retard the recombination and to facilitate the exchange (Fig. 5).

The k_1 is rather small as compared with $k_2[\mathrm{H_2O}]$; especially when the water concentration is higher than 0.01 M as in most cases in experiments in atmosphere, the contribution of the former is negligible. In other words, the second term is really of great importance, unless the exchange reaction takes place under extraordinally dehydrated media. When tris-acetylacetonatoaluminum was to be precipitated on addition of petroleum ether to the THF solution containing a large amount of water (*e. g.* more than 0.1 M) gelatinous precipitate of aluminum was formed, which appeared to be hydrated aluminum oxide. This suggests that the water is present rather coordinated in the reaction intermediate. The same fact makes a kinetic run under such a condition impossible. Experiments with tris-acetylacetonatogallium and -indium under similar conditions could not be substanciated because gelatinous precipitate of the metal ions were formed. These findings could be also related with the ease with which water is substituted for acetylacetonate ligand even in such a medium as THF.

Acid Catalysis. As mentioned in "Results", the contribution of the second term of Eq. (5) would be very small, even if it were significant. The k_2'' values calculated by Eq. (5) without considering the contribution of the second term are practically constant for each of the three acids, (Table 2) to indicate that such a simplification is quite reasonable. The last term of Eq. (5) reflects the establishment of the following equilibrium,

$$\mathrm{HX} + \mathrm{H_2O} \rightleftarrows \mathrm{X^-} + \mathrm{H_3O^+} \qquad (6)$$

where $\mathrm{X^-}$ stands for the acid anion. Rapid establishment of this equilibrium is also demonstrated by proton nuclear magnetic resonance (NMR) spectra of the acids in 1 M water solution in THF. They all give one sharp or broad band due to acid proton. The fact that the apparent k_2'' values calculated in No. 4—6 experiments in Table 2 decreases with increase in water concentration would indicate that an equilibrium as Eq. (6) should be attained for such a weak acid as *m*-toluic, when the concentrations of acid and water are comparable.

As illustrated in Fig. 5, hydronium ions give up proton to the free end of unidentate ligand to facili-

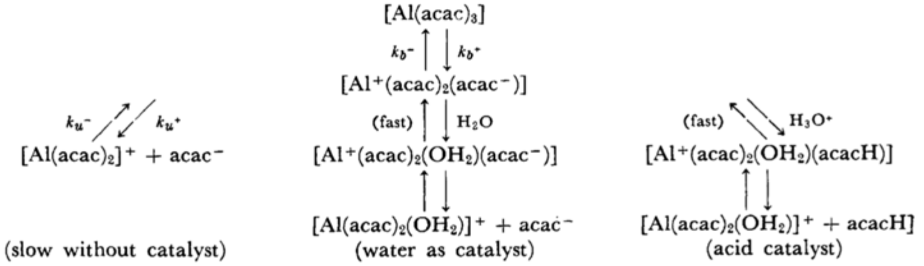

Fig. 5. A possible reaction mechanism of isotopic exchange reaction between tris-acetylacetonatoaluminum and acetylacetone-^{14}C in THF.

tate its liberation to a greater extent than water does. The difficulty of direct transfer of protons from the acid molecule, *i. e.,* the rather specific proton transportion by hydronium ions, could be understood by considering that the free end of unidentate acetylacetonate would remain in the neighborhood of the metal ion owing to electrostatic attraction, and that only a small particle like H_3O^+ can approach the end and hand over the proton to the negatively charged oxygen. Examination with molecular structure models discloses such a circumstance clearly.

Table 2 indicates that a strong acid accelerates the reaction more than a weak acid does. However, the Brønsted plot does not give a straight line. Some other factors, *e. g.* structural, could be operating. Further, free acetylacetone, being an acid with an acid dissociation constant 1.5×10^{-6}, could have acted as an acid catalyst. As carefully examined in Table 1 and Fig. 2, however, its concentration does not affect the rate of exchange at all, and this fact should be related to a structural factor, too.

Proton magnetic resonance spectrum of acetylacetone in THF has a sharp peak at 5.45 ppm and a very broad band at 14.5 ppm to indicate that this compound is present mainly in enol form and hydrogen bonded. The NMR spectrum of water has a sharp peak at 2.75 ppm to suggest a rapid exchange of protons with THF. An equimolar mixture of acetylacetone and water gives a broad band at 6.00 ppm and the peaks of water at 2.75 and of acetylacetone at 14.5 ppm disappear. The peak of vinyl proton remains at 5.35 ppm almost unchanged.

These spectra indicate that there could really be an interaction between acetylacetone and water in THF. However, the effective acid strength of acetylacetone in THF containing water to give H_3O^+ must be much weaker than that expected from its dissociation constant measured in water. Thus its failure to behave as an acid catalyst under the experimental condition would be ascribed to the difficulty with which proton is transferred from acetylacetone to water molecule. This "difficulty" certainly reasons rather thermodynamic sense than kinetic, because the proton exchange seems to occur at a rate of the order of 10^7 per sec as indicated by NMR studies at 60 Mc. The rather poor correlation between the acid dissociation constant and the k_2'' values is similarly accounted for by considering the different ease with which proton is transferred from the acid to water in THF. This ease is qualitatively parallel to the acid dissociation constant for the acids used, but would not be quantitatively.

An entirely different reaction mechanism could be encountered by considering direct attack by water, or proton transfer from hydronium ion upon the oxygen atom coordinated to aluminum ion. However, the fact that a spontaneous liberation of coordinated acetylacetonate is possible without catalytic action, although the rate is quite small, would be more reasonably understood by considering an intermediate, in which one of the ligands is unidentated. The catalytic actions are thus interpreted more consistently.

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