Isotopic Exchange Kinetics between Dibenzoylmethane-^{14}C and Its Tris-type Complex with Aluminium(III) in Tetrahydrofuran

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Isotopic exchange kinetics between [Al(dbm)$_3$] and Hdbm–^{14}C (dbm$^-$, anion of dibenzoylmethane in enol form) has been studied in tetrahydrofuran (THF) at 30 to 55 °C. During several half lives the McKay plot gives straight lines, the AB spectrum remaining unchanged. The rate is very small in the absence of catalysts, and accelerated by water and trichloroacetic acid, but not by weak acids and pyridine. The rate is expressed by

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

The Arrhenius plots of k_2, k_3', and k_3 give an equal $\Delta H^{\ne}$ value 25.6 kcal/mol. It appears one of the ligands is present as unidentate in the intermediate state, and the break of the remaining bond is the rate-determining step.

As an extension of our previous kinetic studies of isotopic exchange between acetylacetone-^{14}C (Hacac) and trisacetylacetonatoaluminium(III) ([Al(acac)$_3$]),[1] we have examined the isotopic exchange kinetics between the corresponding dibenzoylmethane (Hdbm) complex, in order to find the influence of a more basic ligand upon the kinetic formula and rate. Because of the smaller solubility of [Al(dbm)$_3$] in various organic solvents, the rate was precisely studied only in tetrahydrofuran (THF).

Experimental

Materials. *The Labelled Ligand*: Acetic acid-^{14}C imported from Radiochemical Centre, Ammersham, England, was converted into acetophenone in benzene by the Friedel-Crafts reaction, and treated with ethyl benzoate (Claisen condensation) to give Hdbm. The product with a specific activity *ca.* 10 μCi per mg was diluted with commercial Hdbm before use to obtain samples with a specific activity *ca.* 0.5 μCi per mg.

The Complex: Dibenzoylmethane (5 g) in ethanol (25 ml) was treated with aluminium chloride hexahydrate (1.5 g) in water (5 ml) and sodium acetate (3 g) in water (5 ml) to give crude [Al(dbm)$_3$] (4 g). The product was dissolved in THF (50 ml) and precipitated with a large amount of petroleum ether. The purity of these products were confirmed by elemental analysis and UV spectroscopy. Trichloroacetic acid and THF were purified as mentioned before.[1]

Kinetic Runs. The complex in THF (0.01 to 0.1 M) was mixed with Hdbm in THF (0.01 to 0.3 M) in a thermostat (total volume 10 to 15 ml) and portions (1 to 2 ml) were withdrawn into chilled petroleum ether (*ca.* 15 ml) at appropriate intervals. The complex was precipitated instantaneously in fine crystals, which were filtered off with a piece of filter paper and dried at 80 °C. A known amount of the precipitate (3 to 10 mg) was dissolved in anisole containing *p*-terphenyl and POPOP as wave length shifters and submitted to scintillation counting. The results were calculated by McKay's formula to obtain R values under various conditions.

Measurements. The counting rate was measured with an automatic apparatus from Nuclear Chicago. The AB spectra were recorded with a Hitachi 124 Double Beam Spectrometer. Karl Fischer titration was employed for the determination of water.

Results

The influence of the complex concentration upon R was examined as in Ref. 1, and a similar diagram to Fig. 1 of Ref. 1 was obtained. The influence of water content is shown in Fig. 1 at 30, 40, and 50 °C. The straight lines pass the origin, so that the k_0 values are expressed by

$$R = k_0[\text{complex}] = k_2[\text{complex}][\text{H}_2\text{O}] \qquad (1)$$

Trichloroacetic acid catalyses the exchange reaction. The extent depends on the concentration of water at a given concentration of acid. Figure 2 shows that the lines have intercepts. When the concentration of trichloroacetic acid was increased at a given concentration of water, the k_0 values increase linearly in a low acid concentration range and then the gradient decreases as the acid concentration increases. (Fig. 3) Hence the overall formula is written for low acid concentration region as Eq. (2).

$$R = [\text{complex}](k_2[\text{H}_2\text{O}] + k_3'[\text{acid}] + k_3[\text{acid}][\text{H}_2\text{O}]) \qquad (2)$$

The k_3 and the k_3' values are known from the gradients

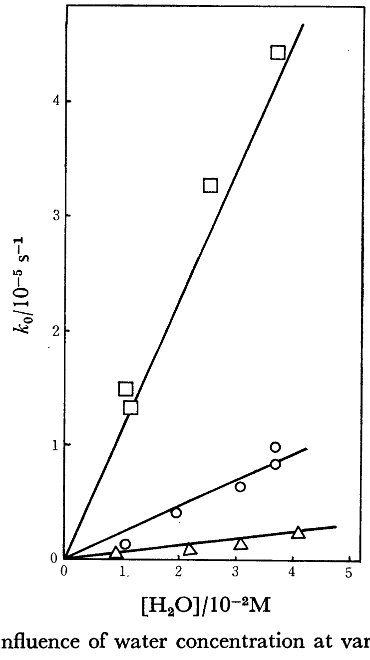

Fig. 1. Influence of water concentration at various temperatures.
(—△— 30 °C, —○— 40 °C, —□— 50 °C, [Hdbm] = 0.050 M)

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[1] K. Saito and K. Masuda, This Bulletin, **43**, 119 (1970).

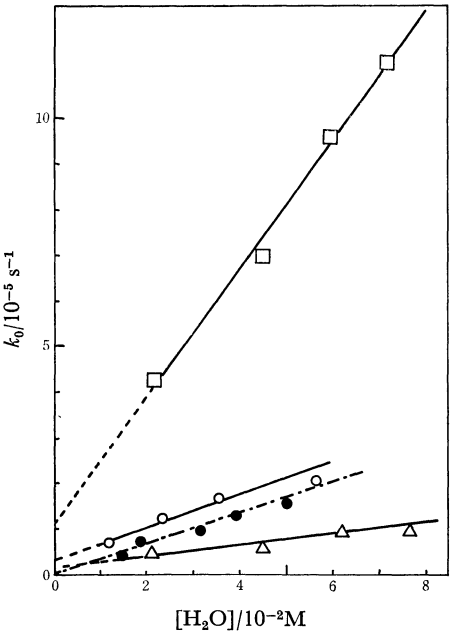

Fig. 2. Influence of water concentration in the presence of trichloroacetic acid at various temperatures.
(—△— 30 °C, —○— and —●— 40 °C, —□— 50 °C; open marks [acid]=0.0286 M, full marks [acid]=0.0021 M; [Hdbm]=0.050 M)

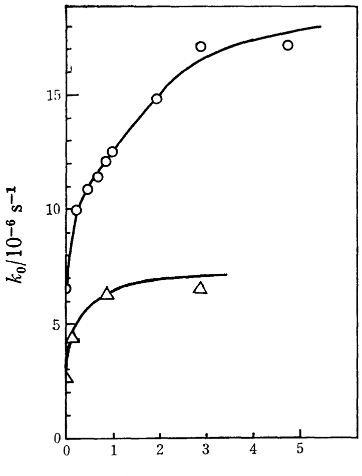

Fig. 3. Influence of concentration of trichloroacetic acid in the presence of known amounts of water.
(—△— 30 °C, $[H_2O]$=0.046 M; —○— 40 °C, $[H_2O]$=0.035 M; [Hdbm]=0.050 M)

and the intercepts of Fig. 2, respectively. Weaker acids such as *m*-toluic do not give acid catalysis. Pyridine has no influence on the exchange rate.

There is a very slight influence of the concentration of Hdbm upon the rate at given water concentrations, as shown in Fig. 4, in which $k_0/[H_2O]$ is plotted against [Hdbm]. The change in $k_0/[H_2O]$ is very small unless a large amount of Hdbm is added. The values of k's in Table 1 are those at [Hdbm]=0.05 M, and are very near to the intercepts of diagrams in Fig. 4.

Arrhenius plots of k_2, k_3', and k_3 at 30, 40, 50, and 55 °C gave parallel lines and the activation enthalpies were known to be 25.6±0.2 kcal/mol for all the terms. The k_0 values were converted into those at 25 °C and the k's tabulated in Table 1 together with those for the exchange reaction between $[Al(acac)_3]$ and Hacac-^{14}C.[1)]

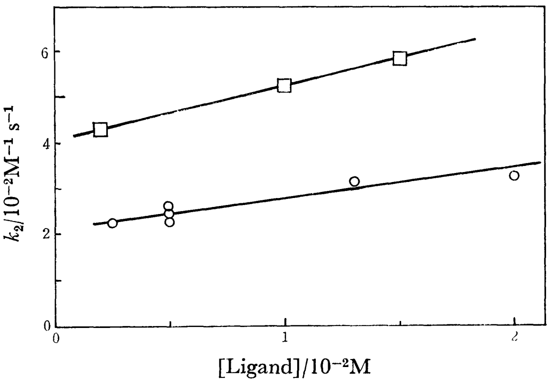

Fig. 4. Influence of concentration of free ligand.
(—○— 40 °C, $[H_2O]$=0.010 M; —□— 50 °C, $[H_2O]$=0.018 M)

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE ISOTOPIC EXCHANGE OF $[Al(acac)_3]$ AND $[Al(dbm)_3]$
(in THF, k's converted into those at 25 °C)

	$[Al(acac)_3]$	$[Al(dbm)_3]$
k_1/s^{-1}	1.0×10^{-6}	$\simeq0$
$k_2/M^{-1}s^{-1}$	3.3×10^{-4}	3.2×10^{-5}
$k_3'/M^{-1}s^{-1}$	1.6×10^{-4} a)	2.0×10^{-5}
$k_3/M^{-2}s^{-1}$	2.0×10^{-2} b)	9.1×10^{-4} c)
$\Delta H^{\ddagger}/kcal\cdot mol^{-1}$ d)	21.4	25.6
$\Delta S^{\ddagger}/cal\cdot K^{-1}mol^{-1}$ e)	−7.8	−1.8

a) k_1' in Ref. 1 b) k_2' in Ref. 1. c) at $[Cl_3CCOOH]$=0.0286 M. d) equal for all the reaction paths e) for k_0 at $[H_2O]$=0.015 M in the absence of acid.

Discussion

Since the absorption spectrum does not change during kinetic runs and McKay plots give straight lines, it is clear that the isotopic exchange takes place without involving net chemical change. It is remarkable that the exchange is very slow in the absence of water and acid. Except this the rate formula is very similar to that for $[Al(acac)_3]$, although the figures are smaller by *ca.* one order than those for $[Al(acac)_3]$. Another marked feature for the present case is that the $\Delta H^{\ddagger}$ values are the same for all the reaction paths within experimental error. This fact is again very similar to that for $[Al(acac)_3]$, although the value itself is bigger than that for $[Al(dbm)_3]$.

We consider that the rate-determining step for the three reaction paths are equal. Fig. 5 gives the plausible reaction mechanism. Although the observed k values for each-term in Eq. (2) consist of more than one constant as seen in Fig. 5, the biggest and the most remarkable contribution should come from the k's at the rate-determining step. The equality of observed $\Delta H^{\ddagger}$ values can be ascribed to the equality of activation enthalpies for the k's. The capital K's indicate equilibrium constants for the given stages, and small k's rate constants at the rate-determining steps. The complex must be in rapid equilibrium with an intermediate

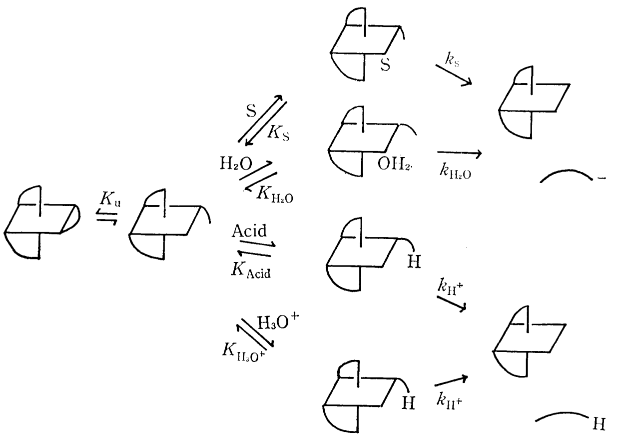

Fig. 5. Probable reaction mechanism.
(arc-like curves represent dbm$^-$; S, solvent molecule)

form, which has one of the ligands as unidentate. The break of its remaining bond is reckoned as the rate-determining step.

The catalytic action of water will be accounted for by considering that it occupies the vacant coordination site to retard the recombination of the free end of unidentate ligand. Hence k_2 is written as Eq. (3).

$$k_2 = k_{H_2O}K_uK_{H_2O} \tag{3}$$

The k_3' and the k_3 path seem to represent acid catalysis with different proton carriers. In the k_3' path, the acid itself will act as proton carrier and the following equation holds.

$$k_3' = k_{H^+}K_uK_{acid} \tag{4}$$

Addition of proton on the free end of unidentate ligand will make its recombination more difficult and increase the probability of break of the remaining bond. In the k_3 path, proton will be transferred to water according to Eq. (5) and k_3 is expressed by Eq. (6).

$$Cl_3CCOOH + H_2O \xrightleftharpoons{K_{hdx}} H_3O^+ + Cl_3CCOO^- \tag{5}$$

$$k_3 = k_{H^+}K_uK_{H_3O^+}[H_3O^+] \tag{6}$$

A characteristic feature in the present study is that the influence of acid concentration tends to show saturation. (Fig. 3) This trend is interpreted in two ways. If Eq. (5) reaches saturation in the given concentration range, further increase in acid concentration will not increase the $[H_3O^+]$. On the other hand, if all the free end of unidentate ligand were protonated, *i.e.* equilibrium $K_{H_3O^+}$ reaches saturation, further increase in $[H_3O^+]$ would not affect the rate.

Whenever HX is a weak acid, the H_3O^+ concentration is expressed by $(K_{hdx}[acid][H_2O])^{1/2}$ from Eq. (5). If so, square root of the acid concentration should have to be plotted on the abcissa in Fig. 2. Although K_{hdx} of trichloroacetic acid is not known in THF, it is a strong acid in water with a pK_a value 0.635 at 25 °C. When the acid is extremely strong, $[H_3O^+]$ is equal to acid concentration in the presence of excess of water, and equal to water concentration in the presence of excessive acid. Figure 3 gives straight lines when the acid concentration is small as compared with water concentration, and the curves approach saturated values with increase in acid concentration. Such a saturation is observed, however, before the acid concentration overwhelms the water concentration, and fails to be seen in Fig. 2. Thus we tend to consider that the saturation may be due to saturation of $K_{H_3O^+}$. Trisacetylacetonatoaluminium(III) did not exhibit such a saturation presumably owing to the smaller $K_{H_3O^+}$ value. The fact that ordinary organic acids fail to give acid catalysis is presumably because their K_{acid} and K_{hdx} values are not big enough to bring about effective protonation upon the free end.

As seen in Eqs. (3), (4), and (6), k_2, k_3', and k_3 involve various factors. The pK_a values of Hacac and Hdbm are not known in THF, but they are *ca.* 11 and 13 respectively at 25 °C in water. The smaller k's for $[Al(dbm)_3]$ than for $[Al(acac)_3]$ are understood by considering that the stronger Lewis base dbm$^-$ gives much smaller k_{H_2O} and k_{H^+} values than acac$^-$ does, and the bigger K_{acid} and $K_{H_3O^+}$ values are overwhelmed. The greater $\Delta H^{\neq}$ of $[Al(dbm)_3]$ than $[Al(acac)_3]$ is also thus accounted for. Absence of k_1 path for $[Al(dbm)_3]$ is similarly interpreted, too. Further, the effective charge of aluminium ions in $[Al(dbm)_3]$ will be smaller owing to the coordination of more basic dbm$^-$ and the equilibrium constant K_s (coordination of solvent molecule on the vacant site) would be smaller.

Another characteristics in the present kinetic study is that increase in the concentration of ligand increases the exchange rate, although the extent is very small. Such an influence was also seen in the exchange between $[Co(acac)_3]$ and Hacac-^{14}C in toluene and anisole.[2] If Hdbm attacks the vacant coordination site of the intermediate as rate-determining step, increase in Hdbm concentration will increase the rate of exchange. However, the gradients of lines in Fig. 4 are very small, and the contribution of ligand concentration is appreciable only at a high concentration range. The k_2 values at the ligand concentration 0.05 M are very near to that at null ligand concentration, and was not included in the main kinetic formula. If Hdbm behaved as an acid and gave proton to the free end of the unidentate ligand in the intermediate, a similar kinetic result would be obtained. This is not probable, however, because a stronger acid, *m*-toluic acid, does not exhibit acid catalysis. Further, $[Al(acac)_3]$ failed to show such a tendency. If acid catalysis were operating, a stronger acid, Hacac, should give a bigger influence on a more labile $[Al(acac)_3]$. Hence the effect in Fig. 4 should be due to the nucleophilic attack of Hdbm upon the complex, probably in the intermediate state. The basicity of Hdbm must be bigger than Hacac even in the protonated state.

Thus all the differences in kinetics between $[Al(dbm)_3]$ and $[Al(acac)_3]$ are understood by taking the difference in basicity of the ligands into account. Our present results seem to support and reinforce the reaction mechanism postulated in Ref. 1, that the complex is in rapid equilibrium with an intermediate with one of the ligands as unidentate and break of the remaining Al–O bond is the rate-determining step.

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[2] K. Saito and M. Murakami, This Bulletin., **45**, 2472 (1972).