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Isotopic Exchange Kinetics between Trisacetylacetonatocobalt(III) and Acetylacetone-^{14}C in Organic Solvents

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The isotopic exchange proceeds faster than the decomposition of the complex at more than 80°C and below 120°C. McKay plot gives a linear diagram at the initial stage of isotopic exchange. The rate is expressed by $R=[\text{complex}](k_1+k_2[\text{acacH}])$, where acacH stands for free acetylacetone. The Arrhenius activation energy decreases in the order anisole (25 kcal per mole), chlorobenzene (21), and toluene (18) and is subject to acid catalysis with a strong acid as trichloroacetic. Comparison of the data with those of racemization of this complex, and isomerization and inversion of tris(benzoylacetonato)cobalt(III) suggested that k_1 represents dissociation mechanism through a five coordinate intermediate containing a unidentate acetylacetonate anion, and the k_2 an association mechanism involving association of free acacH with the intermediate.

In order to extend our studies of isotopic exchange kinetics of β-diketonato complexes,[1,2] exchange reaction between tris(acetylacetonato)cobalt(III) [Co(acac)$_3$] and acetylacetone (acacH) labelled with ^{14}C has been examined in organic solvents. This complex was claimed to be substitution inert on a qualitative experiment,[3] and to undergo decomposition at higher temperatures.[4] We have found that this complex decomposes to bis(acetylacetonato)-cobalt(II) at more than 130°C in gaseous state within several minutes. On the other hand, in organic solvents the cobalt(III) complex gave brown precipitate on prolonged heating at more than 70°C (*e.g.* after 30 hr at 90°C). Infrared absorption spectrum of the precipitate in KBr pellet disclosed that it consists mainly of polymeric acetylacetonatocobalt(III) complex and does not contain cobalt(II) complex. The visible and ultraviolet absorption spectrum of the remaining reaction mixture suggested that [Co(acac)$_2$] is appreciable, when the reaction mixture was heated so long as to give the precipitate.

McKay plot[5] in toluene and anisole at 80 to 97°C (Fig. 1) gave a straight line at the initial stage of the exchange reaction, where the absorption spectrum remained unchanged. With progress of the reaction, however, the apparent rate gradually decreased accompanied by change in absorption spectrum and eventually with formation of the brown precipitate. The apparent rate of exchange (R) was reproducible in the initial stage at 85 to 100°C and seemed to suit for kinetic studies.

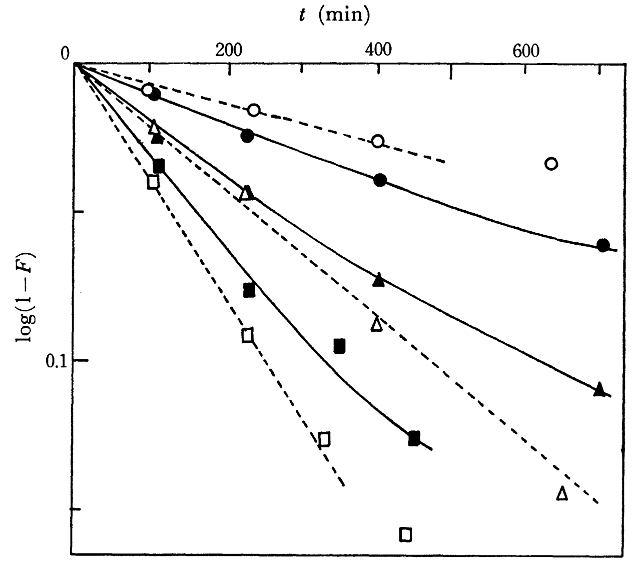

Fig. 1. McKay plots in toluene and anisole. [complex]=[acacH]=0.05 M, ○ 80; △ 90; □ 97°C. Open marks in anisole and solid marks in toluene.

Results

Figure 2 shows the relationship between the log of initial concentration of the complex and log R values in anisole and toluene. The diagram has a gradient

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

[2] K. Saito and M. Takahashi, *ibid.*, **42**, 3462 (1969).

[3] R. W. Kluiber, *J. Amer. Chem. Soc.*, **82**, 4839 (1960).

[4] R. C. Fay, A. Y. Girgis, and U. Klabunde, *ibid.*, **92**, 7056 (1970).

[5] H. A. C. McKay, *Nature*, **142**, 997 (1938).

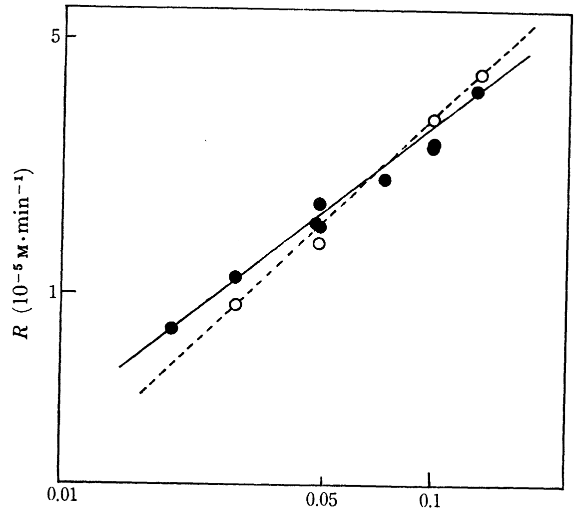

Fig. 2. Relationship between R and the initial concentration of complex.
90°C, —●— in toluene, --○-- in anisole, [acacH] =0.05 M.

near to unity in both solvents and the rate is expressed by Eq. (1).

$$R = k_0[\text{complex}] \tag{1}$$

Figure 3 gives the relationship between R and the concentration of the free ligand in anisole and toluene. The diagram indicates that the k_0 consists of two terms, one of which is independent of and the other dependent on the concentration of acacH. (Eq. 2)

$$R = [\text{complex}](k_1 + k_2[\text{acacH}]) \tag{2}$$

The k_1 and the k_2 are known from the intercept and the gradient of the lines, respectively, and listed in Table 1. The Arrhenius activation energy is known from the data in Table 1 and listed together. Because of the big error involved in the determination of k_1 and k_2 values by extrapolation, only overall E_a values are significant. The influence of acid and base on the exchange rate in toluene and anisole is shown in Table 2. Addition of the bivalent cobalt(II) complex [Co(acac)$_2$] did not affect the rate. Toluene was almost saturated with water, and its content was changed within a limited range (0.008 to 0.019 M) in the given temperature region. However, no significant change in R values was observed. The water content remained practically unchanged (within ±0.001 M) during kinetic runs.

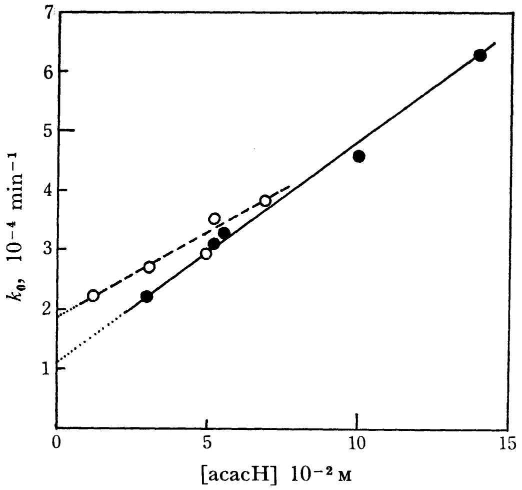

Fig. 3. Relationship between k_0 and the initial concentration of free acetylacetone-^{14}C.
90°C, —●— in toluene, --○-- in anisole.

Discussion

As the McKay plot indidates, isotopic exchange reaction predominates at the early stage of reaction without being involved by the irreversible decomposition. It appears as if the linear range on the McKay plot is larger at a higher temperature. It is presumably because the temperature coefficients of the rates of isotopic exchange and the decomposition differ from each other.

TABLE 1. FIRST ORDER RATE CONSTANTS AND THE ARRHENIUS ACTIVATION ENERGY[a)]

Solvent	Temp. °C	k_0 min^{-1}	E_a kcal/mol
Toluene	80	1.6×10^{-4}	
	85	2.2×10^{-4}	
	90	3.2×10^{-4} b)	18
	97	4.6×10^{-4}	
Anisole	80	1.1×10^{-4}	
	90	2.8×10^{-4} c)	25
	97	6.0×10^{-4}	
Chlorobenzene	80	1.2×10^{-4}	
	90	2.4×10^{-4}	21
	97	5.0×10^{-4}	
(Racemization)	98.2	4.8×10^{-3}	34.8 d)
(Isomerization of [Co(bzac)$_3$])	96.1	7.6×10^{-3}	33 e)
(Inversion of [Co(bzac)$_3$])	96.1	1.3×10^{-2}	33 e)
(Ligand interchange of [Co(bzac)$_3$])	96.1	4×10^{-6}	48 f)

a) [complex]=[acacH]=0.05 M. b) $k_1=1.85\times10^{-4}$ min^{-1}, $k_2=3.05\times10^{-3}$ M^{-1} min^{-1}. c) $k_1=1.1\times10^{-4}$, $k_2=3.2\times10^{-3}$. d) Ref. 4. e) Average of *cis*- and *trans*-isomers, Ref. 6. f) Exchange of benzoylacetonate between [Co(bzac)$_3$] and [Co(bzac-d_4)$_3$], Ref. 6.

TABLE 2. INFLUENCE OF ACIDS AND BASE UPON THE RATE

Solvent	Acid or base	Concn (M)	R mol·min^{-1}	k_0 min^{-1}
Toluene	*m*-Toluic acid	0.01	1.1×10^{-5}	4.2×10^{-4}
	Trichloroacetic acid	0.01	8.3×10^{-5}	16.6×10^{-4}
	Pyridine	0.02	1.2×10^{-5}	2.4×10^{-4}
	(None)		1.6×10^{-5}	3.6×10^{-4}
Anisole	*m*-Toluic acid	0.01	1.8×10^{-5}	3.6×10^{-4}
	Trichloroacetic acid	0.01	12.5×10^{-5}	25.0×10^{-4}
	Pyridine	0.02	1.2×10^{-5}	2.4×10^{-4}
	(None)		1.4×10^{-5}	2.4×10^{-4}

[complex] = [acacH] = 0.05 M, 90°C.

The k_1 Path. The first term of Eq. (2) seems to represent a mechanism in which the break of metal-ligand bond is the rate-determining step. This path can be interpreted in two ways. In one of them, break of the first metal-oxygen bond at one of the chelate rings is the rate-determining step, and the remaining metal-oxygen bond breaks fast. The second way is to consider that the first bond breaks and forms rapidly so that an intermediate state involving unidentate acetylacetonate can survive for a significant lapse of time, and the break of the remaining bond is the rate-determining step.

Girgis and Fay[6] studied the kinetics of ligand interchange between tris(benzoylacetonato)cobalt(III) [Co(bzac)$_3$] with the same complex labelled with ^{2}H in chlorobenzene at 96.1°C, and compared the rate and activation parameters with those of the inversion and isomerization of this complex (Table 1). The ligand interchange proceeds slower by one order or two, and they proposed a predominating intermediate involving axial trigonal bipyramidal structure with a unidentate ligand. Their k_0 value for ligand interchange was obtained in the absence of excessive ligand, and can be compared with our k_1 values. Although the experimental conditions are different, our k_1 values are larger than theirs by *ca.* two orders. This fact would be due to the smaller basicity of acetylacetonate than benzoylacetonate.

Fay, Girgis, and Klabunde measured the rate of racemization of partly resolved [Co(acac)$_3$] in chlorobenzene at 78 to 108°C.[4] The results are included in Table 1. Although their experimental condition is not exactly equal to ours, the isotopic exchange rate is smaller than the rate of racemization by one order.

In order to account for the mechanisms of isotopic exchange and racemization in consonance, we tend to consider an intermediate involving a unidentate ligand. Fig. 4 gives a probable scheme for the mechanism of the present isotopic exchange. One of the cobalt(III)-oxygen bonds in one of the three ligands can break and restore rapidly. The vacant coordination site could be occupied either by the solvent molecule or free acetylacetone. The latter case will be discussed later. The intermediate can also rearrange to give trigonal bipyramidal structure. Whenever the remaining bond of the unidentate ligand breaks spontaneously, the ligand would be liberated and the labelled free acetylacetone would combine with cobalt(III) rapidly to give a first order rate term corresponding to k_1. Contribution of this term would depend on how easily the free end of unidentate ligand recombines with cobalt(III). A polar solvent such as anisole would occupy the vacant site more easily than less polar solvents (*e.g.* toluene) do, and retard the recombination to increase the contribution of k_1. This is what was experimentally found.

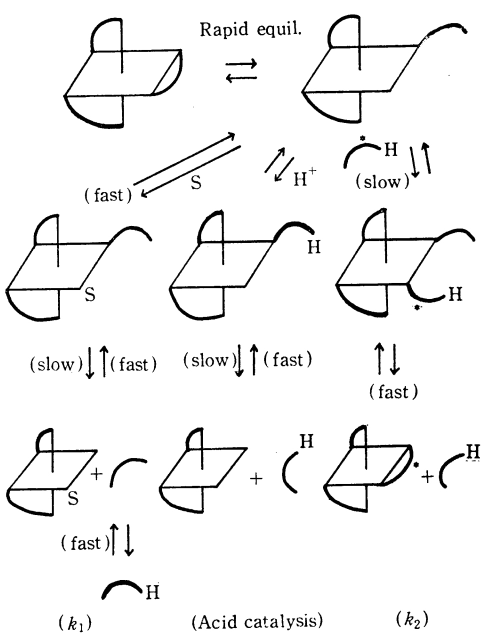

Fig. 4. Probable mechanism for the isotopic exchange. S, solvent molecule; the arc-form represents acac$^-$.

An alternative explanation could be encountered by considering the role of water in the solvent. However, water content did not affect the rate, although the examined range of concentration was rather small, and its participation could be excluded.

The acid catalysis could be understood by considering the protonation at the free end of unidentate ligand, which increases the difficulty with which the free end recombines with cobalt(III) to restore the original complex. Only a strong acid such as trichloroacetic acid seems to be eligible of bringing about such an effect. Contribution of free acetylacetone (p$K\simeq6$) as acid catalyst is ruled out, because a stronger acid, *m*-toluic acid (pK=4.27) is not useful as acid catalyst.

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[6] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).

If an acetylacetonate ligand were liberated whenever its first bond with cobalt(III) was broken, this would result in simultaneous racemization and isotopic exchange. Hence the fact that racemization is faster than isotopic exchange (Table 1) should be interpreted by an intra-molecular twist mechanism without liberation of the ligand. The activation enthalpy of the racemization is close to those of inversion and isomerization of [Co(bzac)$_3$], and there seems to be no reason to exclude such a twist mechanism for the racemization of [Co(acac)$_3$].

The k_2 Term. The second term of Eq. (2) is also interpreted in two ways. One is to reckon a rate-determining nucleophilic attack of acetylacetone upon the intermediate containing a unidentate acetylacetonate. The other is to consider a preliminary equilibrium between free acetylacetone and the intermediate, and regard the break of remaining cobalt(III)-oxygen bond of the original ligand as rate-determining step. In this case the k_2 term is written as $k_2'K_2$[acacH], where K_2 and k_2' stand for the apparent association constant and the rate of bond break in the adduct, respectively.

Such an interaction was first proposed by Graziano and Harris,[7] and later modified by Llewellyn, O'Connor and Odell[8] for the isotopic exchange of trioxalatochromate(III) with oxalic acid-^{14}C. Neither of them, however, distinguished these two mechanisms. It is generally understood that a dissociative mechanism gives higher E_a values than an associative mechanism does. The E_a values in Table 1 decreases in the sequence, anisole, chlorobenzene, and toluene. Because of experimental difficulty E_a values for the k_1 and the k_2 path were not obtained separately. Anisole, with the biggest contribution of the k_1 term, gives the biggest E_a, whilst toluene with the smallest contribution of k_1 gives the smallest E_a. Chlorobenzene will have less affinity toward cobalt(III) than anisole despite of its bigger dipole moment.

This fact seems to be in favor of the first mechanism reckoning rather associative nature of the k_2 term. Dielectric constants of organic compounds decrease with rise of temperature, and the rather ionic interaction involved in the preliminary equilibrium between free acetylacetone and the intermediate will be facilitated at a higher temperature. This would give rise to increase in K_2 values with rise of temperature and the the dissociative $k_2'K_2$ values might bring about bigger temperature coefficient for the k_2 term. Such a tendency does not seem to suit for interpretation of the experimental results, and we tend to reckon the rather associative interpretation more appropriate, although nothing decisive can be stated at the present stage.

Experimental

Materials. The labelled compound, acetylacetone-^{14}C was prepared as reported before.[1] The specific activity was 0.02 mCi per mg. Tris(acetylacetonato)cobalt(III) was synthesized from cobalt(II) carbonate, commercial acetylacetone, and hydrogen peroxide, and recrystallized from hot benzene by addition of petroleum ether and cooling.[8] When the recrystallized [Co(acac)$_3$] was sublimed at 3 mm-Hg at 120°C, the product gave the same kinetic result. Hence the product was regarded sufficiently pure. Impure complex can give erroneous results.

Toluene was shaken with concentrated sulfuric acid, washed with water and sodium hydroxide solution, dried with calcium chloride and then with metallic sodium and distilled. Anisole was washed with sodium hydroxide solution and water, dried with calcium chloride and then with sodium and distilled. Chlorobenzene was washed with 1% sodium carbonate solution and water, dried with calcium chloride and distilled. The water contents of these solvents were *ca.* 0.012, 0.035, and 0.0046 M, respectively, on Karl Fischer titration in a mixture of pyridine and propyleneglycol. *m*-Toluic and trichloroacetic acid were sublimed *in vacuo*, and pyridine was distilled by the usual method.

Measurement. A known amount of labelled acetylacetone was added to the thermostated complex solution ($\simeq 10^{-2}$ M, 10 or 15 m*l*) to produce $\simeq 10^{-2}$ M solution and kept in a thermostat. Aliquots ($\simeq$2 m*l* each) were taken out of the solution at appropriate intervals, added to cold petroleum ether (*ca.* 20 m*l*), and set aside in a cold Dewar vessel. Green needles appeared within 3 hr. The mother liquor was decanted, the precipitate washed with petroleum ether and dried at 80°C. A portion (3 to 7 mg) was dissolved in anisole containing 0.4% *p*-terphenyl and 0.01% POPOP (30 m*l*) to prepare liquid scintillator and the counting rate measured by use of the photomultiplier pulse due to β rays.[1] The quenching effect of the colored solution was corrected by use of a calibration curve. (*e.g.* the apparent counting rate decreases to 72% in the liquid scintillator containing 3 mg of [Co(acac)$_3$] per 30 m*l*.) Acids and bases were added to the original complex solution in advance.

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[7] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

[8] D. R. Llewellyn, C. O'Connor, and A. L. Odell, *J. Chem. Soc.*, **1964**, 4627.