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Kinetics of Isotopic Exchange between Acetylacetone-^{14}C and Bisacetylacetonatopalladium(II) in Organic Solvents

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Bisacetylacetonatopalladium(II) [Pd acac$_2$] was precipitated crystalline free from excessive acetylacetone (Hacac) by adding the reaction mixture in anisole, benzene or 1,2-dichloroethane to chilled petroleum ether. Its specific counting rate was measured by liquid scintillation technique. The isotopic exchange rate is measurable at 40 to 80°C and the kinetics is expressed by the ordinary two term formula, Rate=[Pd acac$_2$](k_1+k_2[Hacac]). The second term corresponds to the reagent path, in which acetylacetone molecule rather than acetylacetonate anion acts as nucleophilic reagent. The first term seems to express a dissociation mechanism rather than the solvent path; the break of Pd–O bond without the aid of nucleophilic attack by the solvent molecule is responsible for determining the exchange rate. The exchange reaction is accelerated by acids, and the acid-catalyzed reaction path operates independent of the reagent path to give the following kinetic formula:

$$\text{Rate} = [\text{complex}](k_1 + k_2[\text{Hacac}] + k_3[\text{acid}])$$

Mechanism of substitution reactions involving square planar complexes of platinum(II) and palladium(II) has been discussed mainly in polar solvents such as water and alcohols.[1] These reactions generally give two term formulae [complex](k_1+k_2[Y]), where Y stands for the nucleophilic reagent which substitutes for one of the coordinated ligands. The rate constants k_1 and k_2 are considered to interpret the "solvent path" and the "reagent path", in which the solvent molecule and the reagent Y operate as nucleophilic reagent to give S_N2 reaction mechanism, respectively.

It seems interesting to examine the isotopic exchange kinetics of square planar complexes in non-polar solvents, since little information is available concerning reaction mechanism in such solvents, and isotopic exchange directly reflects the reactivity of complexes without being bothered by chemical equilibrium. We have examined the solubility of bisacetylacetonatopalladium(II) (henceforth written as [Pd acac$_2$]) and free acetylacetone (Hacac) in a variety of organic solvents and found that the complex is precipitated free from an excess of the ligand by pouring the reaction mixture in anisole, benzene or 1,2-dichloroethane into petroleum ether chilled at −20°C. Hence the experimental technique which was useful for studies with octahedral complexes such as trisacetylacetonatoaluminum(III)[2] and tris-8-quinolinolatogallium(III)[3] is also useful for the present study.

Bisacetylacetonatopalladium(II) is very inert in organic solvents, and the isotopic exchange kinetics is measurable only at elevated temperatures from 40 to 80°C in such solvents with high boiling points as mentioned above.

Experimental

Materials. Acetylacetone-^{14}C was synthesized by the same method as in a previous paper.[2] The specific activity was 0.02 mCi per mg. Bisacetylacetonatopalladium(II) was synthesized and purified by the method given in literature.[4] Extra pure grade anisole was shaken with sodium hydroxide solution, dried with calcium chloride, refluxed with sodium and distilled. The same product was used both for the solvent and the scintillator. The water content of dehydrated product was 1.7×10^{-2} M. Extra pure grade benzene was shaken with concentrated sulfuric acid until the acid layer became almost colorless, then with water, 5% sodium hydroxide solution, and water, dried with calcium chloride, refluxed with sodium and distilled. Extra pure grade 1,2-dichloroethane was shaken with 5% sodium hydroxide solution and water, dried with calcium chloride and phosphorus pentoxide, and distilled immediately before use.

Extra pure grade *m*-toluic acid and *o*-bromobenzoic

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1) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2 nd ed., John Wiley & Sons, New York (1967), p. 375.

2) K. Saito and K. Masuda, This Bulletin, **41**, 384 (1968).

3) K. Saito, M. Takahashi, Y. Miyakawa and K. Masuda, *ibid.*, **41**, 1139 (1968).

4) A. A. Grinberg and L. K. Simonova, *Zhur. Priklad. Khim.*, **26**, 880 (1953); *Chem. Abstr.*, **47**, 11060g (1952).

acid were sublimed at 90°C at 5 mmHg. Extra pure grade *p*-terphenyl was recrystallized from xylene. Scintillation grade *p*-di-(5-phenyl-2-oxazolyl)-benzene (POPOP) was used without further purification. Petroleum ether was of guaranteed grade and used without further purification.

Experimental Procedure. Weighed amount of the complex (60 to 250 mg) was dissolved in 10 m*l* of the solvent, and the ligand (10 to 150 mg) (both of the order of 10^{-2} M) added at room temperature. The amount of added reagents was known from the difference in weight of the reaction mixture before and after the addition. Other reagents such as acid and water were added to the solvent in advance, whenever necessary. The reaction mixture was then placed in a thermostat at 40 to 80°C, and aliquots (of the order of 1 m*l*) were withdrawn at appropriate intervals (several hours) and poured into chilled petroleum ether (−20°C) (20 m*l*) in order to stop the reaction. Pure [Pd acac$_2$] was separated crystalline instantaneously free from an excess of the ligand. The precipitate was swiftly filtered off with filter paper, washed with petroleum ether, dried at 60 to 70°C, and submitted to liquid scintillation counting.

The time taken for separation was about 5 min. The purity of precipitate was confirmed by chemical analysis of carbon and hydrogen, and ultraviolet absorption spectrometry. Absorption spectra of the reaction mixture also made it clear that no reaction other than isotopic exchange took place.

Measurements. The precipitate (2 to 3 mg) was dissolved in anisole (30.0 m*l*) containing 0.01% POPOP and 0.4% *p*-terphenyl as wavelength shifter, and the specific counting rate determined with a coincidence liquid scintillation counter. The complex is pale yellow and provides significant quenching effect on the scintillation. The effect was examined with standard benzoic acid-^{14}C and non-radioactive complex to obtain a calibration curve, with which the counting rate was duly corrected. The scintillation efficiency was 15% less in the presence of 2 mg per 30 m*l* of the complex as compared with that in its absence. The counting at the end of isotopic exchange reaction (infinite time) was calculated from that of the acetylacetone-^{14}C and the used amounts of the respective compounds.

Water content in the solvent and the reaction mixture was determined by Karl-Fischer titration in a mixture of pyridine and ethyleneglycol (5+1, v/v) as solvent. The ultraviolet absorption spectra were measured with a Hitachi EPU-3-spectrophotometer.

Results

The experimental data were treated with McKay's formula,

$$R = -2.303\frac{2ab}{2a+b}\cdot\frac{\log(1-F)}{t} \qquad (1)$$

where a and b denote the concentrations of the complex (containing two moles of exchangable ligands per mole) and acetylacetone, respectively. F is the fraction of reaction and t the lapse of time in minutes. The plots of $\log(1-F)$ *vs.* t were all linear to permit the treatment with Eq. (1). Zero time exchange was not observed in this isotopic exchange reaction. The relative error in R values is less than 8 %.

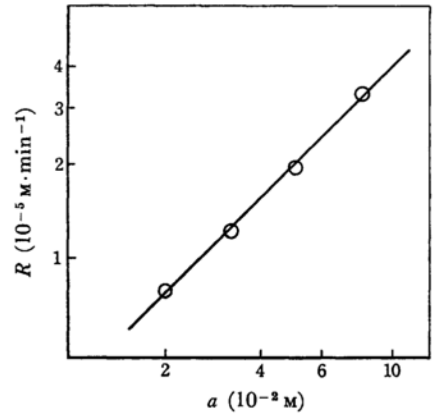

Fig. 1. Relationship between the exchange rate and the concentration of the complex. [acacH], 0.050 M, 80°C in anisole

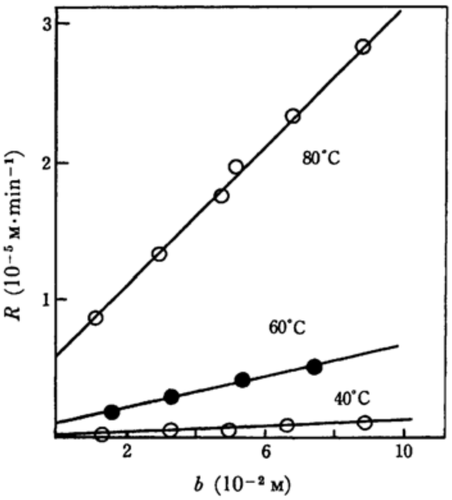

Fig. 2. Relationship between the exchange rate and the concentration of the free ligand. [Pd acac$_2$], 0.050 M, in anisole

Good first order dependence was observed between the exchange rate R and the concentration of the complex (Fig. 1). R is linearly dependent on the concentration of the free ligand (Fig. 2), but the straight line does not pass the zero point and gives a small positive intercept. Therefore R is expressed by

$$R = a(k_1 + k_2b) \qquad (2)$$

where k_1 and k_2 are rate constants.

The exchange reaction is accelerated by acids. The influence of the concentration of acids (*m*-toluic and *o*-bromobenzoic acid) was examined as shown in Fig. 3. Good first order relationship is observed over the acid concentration range. Figure 4 shows the relationship between R and b in

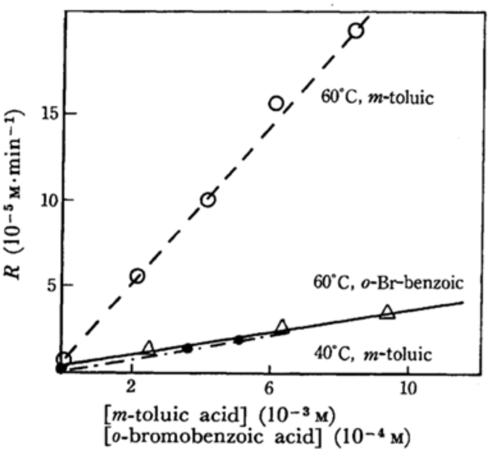

Fig. 3. Relationship between the exchange rate and the concentration of acid in anisole. [Pd acac$_2$], 0.050 M, [acacH], 4.96×10^{-2} M for *m*-toluic acid at 40°C, 4.90×10^{-2} M for *m*-toluic acid at 60°C, 5.23×10^{-2} M for *o*-bromobenzoic acid at 60°C

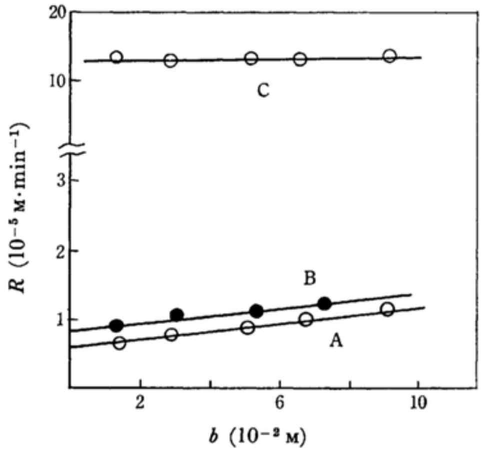

Fig. 4. Relationship between the exchange rate and the concentration of free ligand in the presence of given amounts of acids in anisole. [Pd acac$_2$], 0.050 M at 60°C. A, 0,00024 M *m*-toluic acid, B, 0.00025 M *o*-bromobenzoic acid, C, 0.0050 M *m*-toluic acid.

the presence of given amounts of the complex and the acid at 60°C. The slopes of lines are equal to the k_2 values obtained from the experiments in the absence of acids. This fact indicates that the acid-catalyzed reaction path operates independent of b.

$$R = a(k_1 + k_2b + k_3[\text{acid}]) \qquad (3)$$

So far as this formula is correct, the values of intercept in Fig. 4 should be equal to the value $a(k_1 + k_2[\text{acid}])$. Experimental values obtained from the figure are in fact equal to those obtained from Figs. 2 and 3. When the acid concentration was increased to 0.005 M, the first and the second term of Eq. (3) were overwhelmed by the third, and an apparently horizontal diagram was obtained as seen in Fig. 4 C.

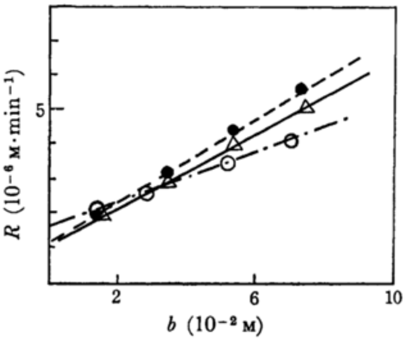

Fig. 5. Relationship between the exchange rate and the concentration of free ligand in various solvents.
[Pd acac$_2$], 0.050 M at 60°C. -△- in anisole, -●- in benzene, -○- in 1,2-dichloroethane

TABLE 1. RATE CONSTANTS IN VARIOUS ORGANIC SOLVENTS

Temp. °C	Solvent	k_1 (min^{-1})	k_2 ($\mathrm{M}^{-1}\cdot\mathrm{mol}^{-1}$)
40.0	anisole	2.0×10^{-6}	1.8×10^{-4}
60.0	anisole	2.0×10^{-5}	1.1×10^{-3}
80.0	anisole	1.2×10^{-4}	5.1×10^{-3}
E_a (kcal/mol)	anisole	23	18
60.0	benzene	2.4×10^{-5}	1.2×10^{-3}
60.0	1,2-dichloroethane	3.4×10^{-5}	7.4×10^{-4}

Figure 5 shows the relationship between R and b in various solvents. Equation (1) holds in all these solvents. The rate constants and the Arrhenius activation energy E_a are summarized in Table 1. There was no influence of water concentration upon R in the concentration range from 0.017 to 0.12 M in anisole. Because of the solubility of water in these solvents and the dehydration technique employed in this experiment, water concentration changed only within such a range.

Discussion

The k_2 Path. This reaction path is considered to be the so-called "reagent path," which proceeds with nucleophilic displacement mechanism S_N2, through direct attack by the free ligands.1) There is still a question whether acetylacetone itself or acetylacetonate anion is the nucleophilic reagent. If the anion were the effective reagent, k_2 values should be influenced by the presence of other acids, because acetylacetone is a very weak acid and only a small fraction can be dissociated in the solvents. However, they remain unchanged on addition of stronger acids, and acetylacetone molecule seems to be the nucleophilic reagent.

The k_1 Path. Generally the k_1 path is explained as the so-called "solvent path," in which the reaction proceeds with nucleophilic attack by the solvent molecule. Many experimental evidences have been postulated for reactions in polar solvents including water and methanol.5) It seems rather doubtful, however, to apply the same reaction mechanism to the k_1 path in those solvents with poor coordination ability. In the present case it appears as if the k_1 path involves a kind of dissociation mechanism. The reason is as follows.

The k_1 values do not change significantly in varying solvents (Table 1). Anisole is a relatively polar solvent ($\mu=1.35$ Debye) whereas benzene is nonpolar; the k_1 values are nearly equal in these two solvents. Since palladium(II) is a soft acid,6) it could interact with π-electrons of the aromatic solvent molecules. 1,2-Dichloroethane does not contain benzene ring, but the k_1 value in this solvent is nearly equal to those in the other two solvents. This fact indicates that the π-electron interaction between the phenyl ring and the palladium(II) complex does not affect the reaction rate appreciably.[*2]

Larger E_a values for k_1 than for k_2 and the negligible influence of water concentration upon the exchange rate seem to provide further support for the dissociative nature of the k_1 path.[*3]

The fact that k_1 in 1,2-dichloroethane is somewhat larger than that in other solvents could be interpreted by the larger dielectric constant of this solvent ($\varepsilon=10.36$, 25°C) than the other two (4.33 at 25°C for anisole and 2.28 at 20°C for benzene). Larger dielectric constant would facilitate the bond break between palladium(II) and oxygen of the ligand.

Thus the solvent molecule near the coordination sphere would have only a negligible affect on the elimination rate of the coordinated ligand, and the ease of break of the bond between the metal ion and the ligand would be responsible for determining the rate through k_1 path.

The k_3 Path. Three kinds of mechanism of acid catalysis can be considered: (i) displacement of coordinated ligand through the nucleophilic attack by acid molecule or its anion. (ii-a) dissociation of one end of chelate ligand is the rate determining step, and the other end of unidentate ligand dissociates fast. Protons attack the coordinated oxygen and accelerate the first step of bond break between palladium(II) and oxygen. (ii-b) The ligand can be present as unidentate rather stable, and the break of the remaining bond is the rate determining step. Protons trap the free end of unidentate ligand and retard its recombination to increase the reaction rate.

If the acid anion acted as nucleophilic reagent, salts of the acids should give the same catalytic effect. Unfortunately no salts of the acids, including those of lithium and tetramethylammonium have sufficient solubility in the organic solvents to permit such a comparison.

If the reaction mechanism were ii-a or ii-b, *o*-bromobenzoic acid (pK=2.85) would be the better catalyst than *m*-toluic acid (pK=4.27). If mechanism i were valid, *o*-bromobenzoic acid would be the weaker catalyst owing to its steric hindrance coming from bromine on the *o*-position. As shown in Table 2, *o*-bromobenzoic acid has greater catalytic ability. Hence mechanism ii-a or ii-b would be more appropriate.

TABLE 2. INFLUENCE OF ACID IN ANISOLE

Temp. °C	k_3 (M$^{-1}\cdot$min^{-1})	
	m-Toluic	*o*-Bromobenzoic
40.0	7.5×10^{-2}	—
60.0	4.7×10^{-1}	6.7×10^{-1}
E_a (kcal/mol)	19	

Pearson and Johnson studied the substitution reaction of [Pd acac$_2$] in water containing methanol and accounted for the acid catalysis by mechanism ii-b.7) Saito and Masuda investigated the isotopic exchange kinetics between acetylacetone-^{14}C and trisacetylacetonatoaluminum in organic solvents and interpreted the acid-catalyzed reaction path by mechanism ii-b, too, on the basis that the E_a values are identical in varying solvents and in the presence or absence of acid.8)

In the present case, however, reaction mechanism ii-a cannot be easily eliminated, because the E_a value for k_3 (19 kcal per mole in anisole) is significantly smaller than that for k_1 (23 kcal per mole in anisole). Further, bond energy between palladium-

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5) M. A. Tucker, C. B. Colvin and D. S. Martin, Jr., *Inorg. Chem.*, **3**, 1373 (1964); F. Basolo, J. Chatt, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960); R. G. Pearson, H. B. Gray and F. Basolo, *ibid.*, **82**, 787 (1960); U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *ibid.*, **87**, 241 (1965).

6) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[*2] If the k_1 path were the "solvent path," the apparent k_1 values should be divided by the molar concentration of the solvent species. They are 9.2, 11.2 and 12.7 M for benzene, anisole and 1,2-dichloroethane, respectively, and the divided values are 6.17×10^{-6}, 2.14×10^{-6} and 2.64×10^{-6} *l*/mol/min, respectively.

[*3] Dissociative nature of the k_1 path has been exemplified by use of a palladium(II) complex with a large ligand, which brings about significant steric hindrance against nucleophilic attack by the solvent molecule in water. (W. H. Bradley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964); **88**, 2944 (1966).) The present complex [Pd acac$_2$] does not seem to provide such an effect.

7) R. G. Pearson and D. A. Johnson, *ibid.*, **86**, 3983 (1964).

8) K. Saito and K. Masuda, This Bulletin, **42**, 3184 (1969).

(II) and oxygen is apparently smaller than that between aluminum(III) and oxygen as seen from their formation enthalpies, and non-polar solvents would hold the unidentate acetylacetonate less firmly than polar solvents. We would thus consider that the k_3 term is regarded as a catalytic process by protons, although neither the proton carrier nor the species subject to proton catalysis is evidently known.

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