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Kinetic Study on Dimerization of Chlorotris(triphenylphosphine)-rhodium(I) in Benzene

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The monomer-dimer equilibrium of $RhCl(PPh_3)_3$ in benzene has been studied with a stopped-flow apparatus under He gas pressure. The decomposition rate of a dimer, $[RhCl(PPh_3)_2]_2$, obeys pseudo-first-order kinetics with respect to the concentration of PPh_3, whereas the formation rate of a dimer obtained by diluting an equilibrium solution with benzene depends on the equilibrium concentration of a monomer, a dimer and PPh_3 in a complexed manner. The kinetic results are consistent with the following mechanism; $2RhCl(PPh_3)_3 \rightleftarrows RhCl(PPh_3)_2 + RhCl(PPh_3)_3 + PPh_3 \rightleftarrows [RhCl(PPh_3)_2]_2 + 2PPh_3$.

Chlorotris (triphenylphosphine) rhodium (I) first synthesized by Wilkinson and coworkers has been found to catalyze various kinds of reactions, such as hydrogenation, carbonylation and decarbonylation.[1-3] There have been, however, some disputes over the structures of the complexes in solution. Wilkinson and coworkers proposed the complete dissociation of $RhCl(PPh_3)_3$ into $RhCl(PPh_3)_2$ and PPh_3 on the basis of the molecular weight measurement:

$$RhClL_3 \rightleftarrows RhClL_2 + L \quad (L: PPh_3) \tag{1}$$

Based on the deviations of the absorbance of $RhCl(PPh_3)_3$ from Beer's law and the effects of added PPh_3 on the spectra, Arai and Halpern estimated the dissociation constant of Reaction 1, K_{dissoc}, to be $(7 \pm 1) \times 10^{-5}$ M.[4] On the other hand, Tolman and coworkers recently observed that the ^{31}P NMR signal of chlorotris(tri-*p*-tolylphosphine)rhodium(I), $RhCl[P(p\text{-tolyl})_3]_3$, in toluene becomes weak on raising temperature with the appearance of other sharp resonances. The new resonances were identical with those of the dimer form of the complex, $[RhCl[P(p\text{-tolyl})_3]_2]_2$, which was prepared independently.[5,6] Thus it was concluded that $RhCl(PPh_3)_3$ reversibly dimerized according to

$$2RhClL_3 \rightleftarrows [RhClL_2]_2 + 2L. \tag{2}$$

Tolman and coworkers determined the dimerization constant of Eq. 2, K_{dimer}, using the same results of the electronic spectra as obtained by Halpern *et al.*; $K_{\mathrm{dimer}} = (3.3 \pm 0.4) \times 10^{-4}$ M in benzene.[6] Although ^{31}P NMR spectra unambiguously showed the reversible interconversion between a monomer and a dimer, a number of kinetic investigations on the catalytic actions of the complexes still suggests the presence of the intermediate, $RhClL_2$.[1] The present work describes the kinetics of the monomer-dimer equilibrium in benzene with the purpose to settle down the problems concerning the origin of the intermediate complex, $RhClL_2$.

Experimental

$RhCl(PPh_3)_3$ was prepared in the usual manner from $RhCl_3 \cdot 3H_2O$ and PPh_3.[1] Found: C, 70.12; H, 4.79; Cl, 3.94%. Calcd for $C_{54}H_{45}ClP_3Rh$: C, 70.10; H, 4.90; Cl, 3.83%. PPh_3 was recrystallized from ethanol. Reagent grade benzene was distilled. The solution was prepared by dissolving $RhCl(PPh_3)_3$ and PPh_3 under vacuum after rigorously excluding oxygen from solvents.

The absorbance of $RhCl(PPh_3)_3$ in benzene was measured by a Hitachi EPS-3T recording spectrophotometer. Ten ml of a PPh_3 solution (9.64×10^{-3} M) was added gradually to 10 ml of a $RhCl(PPh_3)_3$ solution (5.16×10^{-4} M). Equilibrium constant based on the dimerization equilibrium was calculated from the absorbance change at 430 nm. Equilibrium shift due to dilution was so small that it could be neglected.

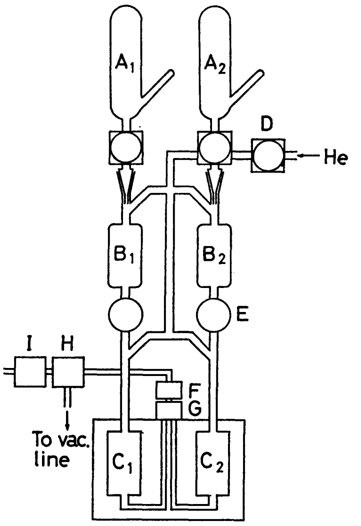

Fig. 1. Schematic diagram of the stopped-flow apparatus. A, B, and C, reservoir; D, Teflon stopcock; E, greaseless valve; F, cell; G, mixing chamber; H, three-way tap; I, air valve.

Kinetic measurements were made using a Union Giken RA 102 stopped-flow apparatus. The mixing part of the apparatus is made of glass and Teflon (Fig. 1). The samples were dissolved in (A) under vacuum. After filled with He gas, (A) was mounted on the body. The body was evacuated and the samples were dropped into (B). After raising the He gas pressure up to *ca.* 2 kg/cm^2, the samples were dropped into (C). The flow was started by opening the air valve. The flow period is about 40 ms. The reaction was followed spectrophotometrically, using a quartz cell of 2 mm optical path. The nominal purity of He gas is 99.8%, thus the effect of O_2 was negligibly small.

Results and Discussion

The variation of the absorbance at 430 nm by the addition of PPh_3 to a $RhClL_3$ solution is shown in Fig. 2. The dissociation equilibrium and the dimerization equilibrium could not be distinguished only from this result.[6] But from the reasons mentioned in the

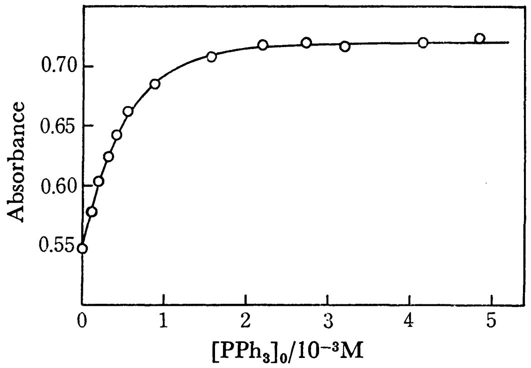

Fig. 2. Effect of added PPh_3 on the absorbance at 430 nm of a 5.2×10^{-4} M $RhCl(PPh_3)_3$ solution in benzene. 20 °C.

introduction, the dimerization equilibrium is considered to be more likely. Assuming equilibrium (2), Eq. 3 is obtained

$$K_{\mathrm{dimer}} = [(RhClL_2)_2][L]^2/[RhClL_3]^2$$
$$= \frac{(A_\infty - A)\{[L]_0^2\Delta\varepsilon + (A_\infty - A)\}^2}{2\Delta\varepsilon\left\{A - A_\infty\left(1-\frac{\Delta\varepsilon}{\varepsilon_1}\right)\right\}^2} \qquad (3)$$

where A is the absorbance, A_∞ the limiting absorbance at high PPh_3 concentrations, ε_1 and ε_2 are the extinction coefficients of $RhClL_3$ and $(RhClL_2)_2$, respectivery, $\Delta\varepsilon=\varepsilon_1-(1/2)\varepsilon_2$ and $[L]_0$ is the concentration of added PPh_3. The value of ε_1 was calculated from $\varepsilon_1=A_\infty/[RhClL_3]_0$; $\varepsilon_1=1.4\times10^3$ l mol^{-1} cm^{-1}. K_{dimer} and $\Delta\varepsilon$ were determined using the curve-fitting method; $K_{\mathrm{dimer}}=9\times10^{-5}$ M, $\varepsilon\Delta=7.1\times10^2$ l mol^{-1} cm^{-1} and $\varepsilon_2=2(\varepsilon_1-\Delta\varepsilon)=1.4\times10^3$ l mol^{-1} cm^{-1}. K_{dimer} is of the same order of magnitude as obtained by Tolman *et al.* ($(3.3\pm0.4)\times10^{-4}$ M).6)

When $RhCl(PPh_3)_3$ and PPh_3 are mixed, the time-course of the absorbance change at 430 nm gives a single exponential curve. The rate of the absorbance change at 430 nm is related to the decomposition rate of the dimer as below.

$$A_{430} = \varepsilon_1[RhClL_3] + \varepsilon_2[(RhClL_2)_2]$$
$$= \varepsilon_1[RhClL_3]_0 - (2\varepsilon_1-\varepsilon_2)[(RhClL_2)_2]$$
$$= -2\Delta\varepsilon[(RhClL_2)_2] + \text{const.}$$

Thus,

$$\frac{dA_{430}}{dt} = -2\frac{d[(RhClL_2)_2]}{dt}.$$

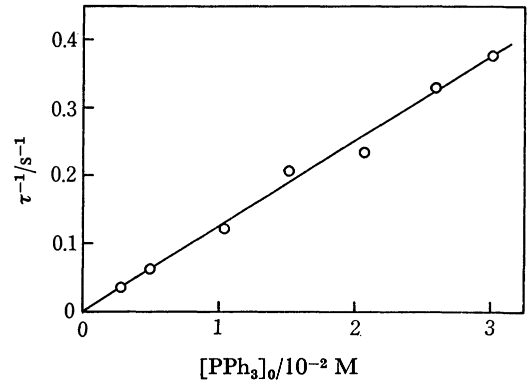

Fig. 3. The dependence of the decomposition rate of a dimer on the concentration of added PPh_3. $[RhCl(PPh_3)_3]_0=5.0\times10^{-4}$ M, at 430 nm and 20 °C.

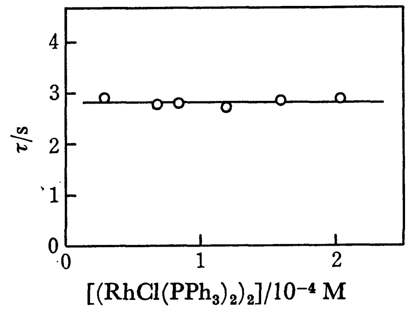

Fig. 4. The dependence of the decomposition rate of a dimer on the initial concentration of $[RhCl(PPh_3)_2]_2$. $[PPh_3]_{add}=3.0\times10^{-2}$ M, at 430 nm and 20 °C.

Figure 3 shows the dependence of the decomposition rate on the concentration of added PPh_3. Figure 4 shows the dependence of the decomposition rate on the concentration of a dimer. It shows the first-order dependence of the rate on $[RhCl(PPh_3)_2]_2$. Summarizing the above results, the decomposition rate is expressed by Eq. 4.

$$-\frac{d[(RhClL_2)_2]}{dt} = k[(RhClL_2)_2][L] \qquad (4)$$

When the solution containing the equilibrium concentrations of a monomer and a dimer is diluted by pure benzene, the equilibrium (2) shifts to the right-hand side. Therefore the formation of a dimer can be followed by mixing the equilibrium solution with pure benzene. Figure 5 shows the dependence of the formation rate of a dimer on the concentration of added PPh_3. It shows that the formation rate of a dimer increases with the concentration of $RhCl(PPh_3)_3$. Equation 4 suggests that the rate-determining step in the dimer decomposition is the first attack by PPh_3 on a dimer. Thus the following mechanism is proposed in interpreting the present kinetic results:

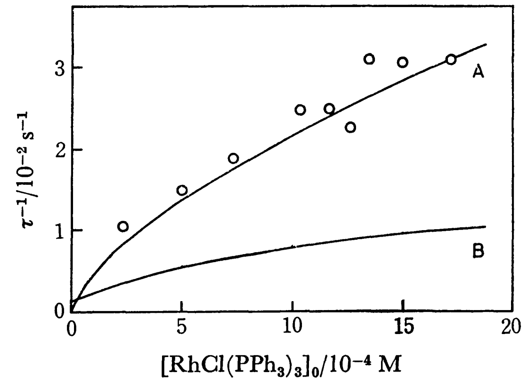

Fig. 5. The dependence of the reciprocal of the relaxation time for dilution experiments on the total concentration of $RhCl(PPh_3)_3$. 20 °C.
Solid lines show calculated curves; A from Eq. 6 and B from dissociation mechanism.

$$2RhClL_3 \overset{K_1}{\rightleftarrows} RhClL_2 + RhClL_3 + L$$
$$\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (RhClL_2)_2 + 2L \qquad (5)$$

The above mechanism assumes that the dissociation reaction (1) is present as a pre-equilibrium of the dimer formation. The rate of the concentration change of a dimer is given by Eq. 6.

$$\frac{d[(RhClL_2)_2]}{dt} = k_2[RhClL_3][RhClL_2] - k_{-2}[(RhClL_2)_2] \times \{[L]_0 + [RhClL_2] + 2[(RhClL_2)_2]\} \qquad (6)$$

where $[L]_0$ is the added PPh_3 concentration. For the decomposition experiments $[L]_0$ is so large that the second term in Eq. 6 is predominant. That is,

$$\frac{d[(RhClL_2)_2]}{dt} = -k_{-2}[L]_0[(RhClL_2)_2]$$

$$\tau^{-1} = [L]_0 k_{-2}$$

This coincides with Eq. 4, leading to $k_{-2}=k=12\ M^{-1}\ s^{-1}$. As for the dilution experiments $[L]_0$ is zero, and Eq. 6 is modified to Eq. 7.

$$\frac{d[(RhClL_2)_2]}{dt} = k_2[RhClL_3][RhClL_2] - k_{-2}[(RhClL_2)_2] \times \{[RhClL_2] + 2[(RhClL_2)_2]\} \qquad (7)$$

Applying the approximation of the vicinity of the equilibrium to each species, the pseudo-first-order rate constant for the rate of the concentration change of a dimer is given by

$$\frac{d\Delta[(RhClL_2)_2]}{dt} = -\tau^{-1}\Delta[(RhClL_2)_2]$$

where Δ[ ] is the concentration change at dilution and τ^{-1} is expressed as below.

$$\tau^{-1} = \frac{[RhClL_3]_e\{[RhClL_3]_e + 4[(RhClL_2)_2]_e\}}{2[(RhClL_2)_2]_e{}^2} K_1 k_2 + 4[(RhClL_2)_2]_e k_{-2} \qquad (8)$$

where $[\quad]_e$ denotes the equilibrium concentration of each species and $K_1=k_1/k_{-1}$. The value of τ^{-1} is calculated as a function of $[RhCl(PPh_3)_3]_0$, using Eq. 8. A solid curve in Fig. 5 is a calculated one, showing that Eq. 8 predicts the observed dependence of the rate on $[RhCl(PPh_3)_3]_0$ satisfactorily. Therefore, it is concluded that reaction mechanism (5) describes the monomer-dimer equilibrium of the complexes correctly. The present mechanism implies that an intermediate $RhClL_2$ is produced rapidly in a pre-equilibrium step leading to the dimer formation.

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