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Kinetics of the Substitution of Acetonitrile in (Acetonitrile)chlorobis(triphenylphosphine)rhodium(I) by Triphenylphosphine

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Synopsis. The substitution of coordinated acetonitrile in (acetonitrile)chlorobis(triphenylphosphine)rhodium(I) by triphenylphosphine was studied in benzene by the stopped-flow method under anaerobic conditions. The reaction was found to proceed through both an associative and a dissociative path to yield chlorotris(triphenylphosphine)rhodium(I).

The catalytic activity of Wilkinson's complex, $RhClL_3$ ($L=PPh_3$), in homogeneous hydrogenations strongly depends on the nature of the solvent. The highest activities are usually observed in weakly coordinating solvents.[1] Hydrogenation is practically inhibited in a strongly coordinating solvent such as acetonitrile.[2,3] Since kinetic data on coordination of the solvent molecule to the rhodium catalyst are limited,[4,5] we have carried out a kinetic study on the coordination of an acetonitrile molecule to the Wilkinson's complex:

$$RhClL_3 + CH_3CN \overset{K}{\rightleftharpoons} RhCl(NCCH_3)L_2 + L. \qquad (1)$$

Since the direct measurement of the reaction between $RhClL_3$ and CH_3CN was difficult because of the small equilibrium constant K and partial dimerization of $RhClL_3$, $2RhClL_3 \rightleftharpoons (RhClL_2)_2 + 2L$, we measured the reverse reaction observed upon addition of PPh_3 to $RhCl(NCCH_3)L_2$ in benzene.

Equilibria. When a solution of PPh_3 is added to a solution of $RhCl(NCCH_3)L_2$, the absorption spectrum of the latter changes to that of $RhClL_3$. The equilibrium constant for Reaction 1 is expressed as follows:

$$K = \frac{[RhCl(NCCH_3)L_2][L]}{[RhClL_3][CH_3CN]} \simeq \frac{(A_\infty - A)[L]_{add}}{(A-A_0)[CH_3CN]}, \qquad (2)$$

where A, A_0, A_∞, and $[L]_{add}$ denote the absorbance at equilibrium, the initial absorbance, the limiting absorbance at high $[PPh_3]$, and the concentration of PPh_3 added, respectively. Figure 1 shows a typical change in absorbance at 500 nm at $[CH_3CN]=1.9$ mol dm^{-3}. The solid line is reproduced by assuming $K=1.0\times10^{-3}$, $A_0=0.077$, and $A_\infty=0.330$ in Eq. 2, the result showing good agreement with experimental values.

At $[CH_3CN]=1.0$ and 3.8 mol dm^{-3}, the value of K was calculated to be 1.3×10^{-3} and 0.9×10^{-3}, respectively, giving the average equilibrium constant $K_{av}=1.1\times10^{-3}$.

Kinetics. The rate of substitution of CH_3CN in $RhCl(NCCH_3)L_2$ by PPh_3 was measured at 500 nm using a single exponential change observed upon addition of a solution of PPh_3 to a solution of $RhCl(NCCH_3)L_2$. Observed rate constants, k_{obsd}, were proportional to $[PPh_3]$ at constant $[CH_3CN]$ (Fig. 2). The dependence of k_{obsd} on $[CH_3CN]$ at constant

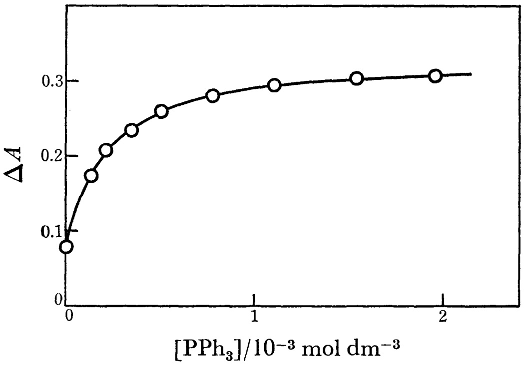

Fig. 1. Change in absorbance of the solution of $RhCl(NCCH_3)(PPh_3)_2$ by the addition of PPh_3 at 500 nm. Solid line is reproduced by assuming Eq. 2 with $K=1.0\times10^{-3}$, $A_0=0.077$, and $A=0.330$. $[RhCl(NCCH_3)(PPh_3)_2]_0=5.4\times10^{-4}$ mol dm^{-3}.

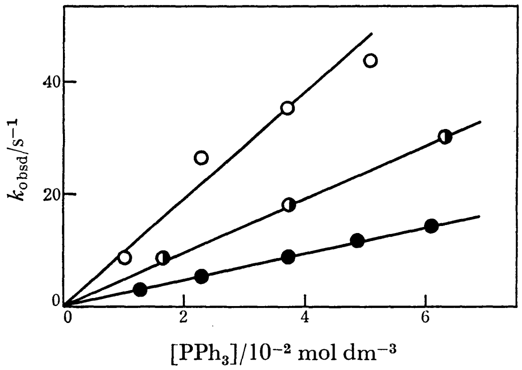

Fig. 2. The dependence of k_{obsd} on the concentration of PPh_3; $[RhCl(NCCH_3)(PPh_3)_2]_0=3.9\times10^{-4}$ mol·dm^{-3} and $[CH_3CN]=0.50$ (○), 1.0 (◑), and 2.9 (●) mol dm^{-3}.

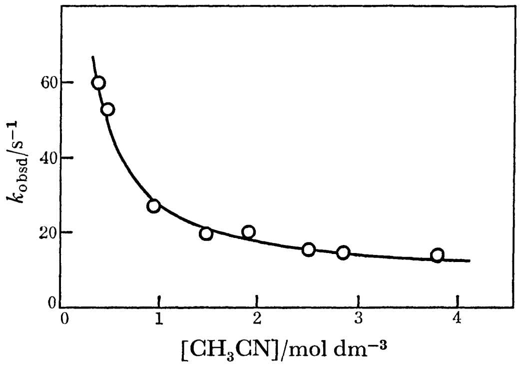

Fig. 3. The dependence of k_{obsd} on the concentration of CH_3CN. $[RhCl(NCCH_3)(PPh_3)_2]_0=4.0\times10^{-4}$ and $[PPh_3]=3.7\times10^{-2}$ mol dm^{-3}.

$[PPh_3]$ is shown in Fig. 3. From Figs. 2 and 3 the observed rate constant is given by

$$k_{\text{obsd}} = \left\{k + k'\frac{1}{[CH_3CN]}\right\}[L]. \tag{3}$$

The following reaction mechanism is postulated for the interpretation of the above relationship:

$$\begin{tikzcd}
RhClL_3 + CH_3CN \arrow[r, shift left, "k_1"] \arrow[d, shift right, "k_3"'] & RhCl(NCCH_3)L_3 \arrow[l, shift left, "k_{-1}"] \arrow[d, shift right, "k_4"'] \\
RhClL_2 + CH_3CN + L \arrow[u, shift right, "k_{-3}"'] \arrow[r, shift left, "k_2"] & RhCl(NCCH_3)L_2 + L. \arrow[l, shift left, "k_{-2}"] \arrow[u, shift right, "k_{-4}"']
\end{tikzcd} \tag{4}$$

By applying the steady-state approximation to the intermediate species, $RhClL_2$ and $RhCl(NCCH_3)L_3$, we obtain

$$k_{\text{obsd}} = \frac{k_1k_4[CH_3CN]+k_{-1}k_{-4}[L]}{k_{-1}+k_4} + \frac{k_2k_3[CH_3CN]+k_{-2}k_{-3}[L]}{k_2[CH_3CN]+k_{-3}[L]}. \tag{5}$$

The rate terms for the reaction between $RhClL_3$ and CH_3CN, $k_1k_4[CH_3CN]$ and $k_2k_3[CH_3CN]$, can be neglected, since Equilibrium 1 lies far to the left-hand side under the reaction conditions. If $k_{-3}[L]$ is small as compared with $k_2[CH_3CN]$, *viz.*, the step $RhCl(NCCH_3)L_2 \rightleftharpoons RhClL_2 + CH_3CN$ is pre-equilibrated, Eq. 5 is modified as

$$k_{\text{obsd}} = \left\{\frac{k_{-1}k_{-4}}{k_{-1}+k_4} + \frac{k_{-3}}{K_2}\cdot\frac{1}{[CH_3CN]}\right\}[L]. \tag{6}$$

The equation was found to fit the kinetic data for the values, $k_{-1}k_{-4}/(k_{-1}+k_4) = 2.4\times10^2\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ and $k_{-3}/k_2 = 3.5\times10^2\ \text{s}^{-1}$. The value of k_3 is calculated to be $0.39\ \text{s}^{-1}$ from the overall equilibrium constant $K = K_2k_3/k_{-3} = 1.1\times10^{-3}$. The value of k_3 agrees with the value $0.4\ \text{s}^{-1}$ obtained from the experiment on the substitution of a coordinated PPh_3 in $RhClL_3$ by C_2H_4,6) even when an experimental error (about 20%) is taken into consideration. The results indicate that both the associative and dissociative paths exist.

Schrock and Osborn suggested that an acetonitrile should compete with an olefin for coordination site on the central metal.5) Thus, it is expected that an olefin cannot coordinate to $RhCl(NCCH_3)L_2$ without prior dissociation of CH_3CN (Eq. 7) as observed in the case of $RhClL_3$ (Eq. 8).6) Actually, ethylene cannot coordinate to $RhCl(NCCH_3)L_2$ without dissociation of CH_3CN.7)

$$RhCl(NCCH_3)L_2 + Ol \overset{K'}{\rightleftharpoons} RhCl(ol)L_2 + CH_3CN \tag{7}$$

$$RhClL_3 + Ol \overset{K''}{\rightleftharpoons} RhCl(ol)L_2 + L, \tag{8}$$

where Ol denotes olefin. In the case of cyclohexene, K'' is too small to be determined by the spectrophotometric method; styrene has an even smaller K'' (2.4×10^{-4})8) than K for acetonitrile. Thus, Reaction 7 in the solution containing a considerable amount of acetonitrile lies far to the left-hand side under the conditions of hydrogenation. The coordination of CH_3CN suppresses the formation of olefin complexes, $RhCl(ol)L_2$ and $RhClH_2(ol)L_2$, the rate of hydrogenation of the olefins being lowered in acetonitrile.

Experimental

$RhCl(C_2H_4)(PPh_3)_2$ was prepared according to Osborn *et al.*2) A solution of $RhCl(NCCH_3)(PPh_3)_2$ was prepared by dissolving $RhCl(C_2H_4)(PPh_3)_2$ in benzene containing an appropriate amount of CH_3CN, the coordinated C_2H_4 being easily replaced by CH_3CN.9) Benzene and acetonitrile were distilled. Distilled acetonitrile contained 0.06 mol dm^{-3} of water, which affected neither the spectrum nor the reaction rate. All the measurements were carried out at 20±0.2 °C in oxygen-free benzene. Equilibrium measurements were carried out *in vacuo* with a Hitachi EPS-3T spectrophotometer. The rate of substitution of the coordinated CH_3CN in $RhCl(NCCH_3)(PPh_3)_2$ by PPh_3 was measured with a Union Giken RA-1300 stopped-flow apparatus under nitrogen atmosphere.

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