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The Rates of the Hydrogenation of the Coordinated Styrene and Acrylonitrile in a Rhodium-Olefin Complex [$RhClH_2(ol)(PPh_3)_2$]

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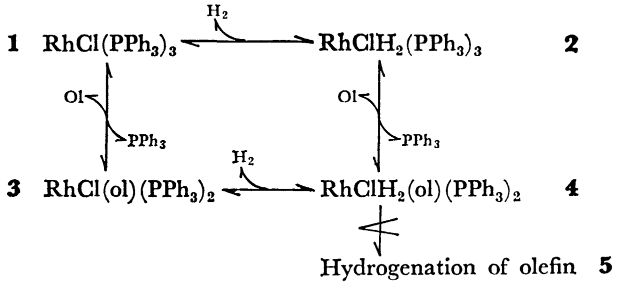
Kinetics of the hydrogenation of coordinated styrene and acrylonitrile in a rhodium-olefin complex $RhClH_2(ol)(PPh_3)_2$ (ol=styrene or acrylonitrile) was studied by stopped-flow method and by the direct measurements of hydrogen-gas uptake. The equilibrium constant of the reaction $RhCl(ol)(PPh_3)_2+H_2 \rightleftharpoons RhClH_2(ol)(PPh_3)_2$, K_{34}, and the rate of the hydrogenation of the olefin in the complex $RhClH_2(ol)(PPh_3)_2$, k_{45}, were determined to be $3.2\times10^3\ mol^{-1}\ dm^3$ and $2.7\ s^{-1}$ for styrene, and $3.5\times10^2\ mol^{-1}\ dm^3$ and $0.50\ s^{-1}$ for acrylonitrile, respectively. The differences in the values for these two olefins were discussed. The data for cyclohexene were also briefly mentioned.

The catalysis of the homogeneous hydrogenation of olefins by Wilkinson's complex $RhCl(PPh_3)_3$ has been the main subject of many investigations on the homogeneous catalyses by transition metals.[1] In recent years the detailed reaction mechanism of this system has been revealed by studying independently the individual step of the complex formation processes.[2-5] However, in most investigations concerning hydrogenation of olefins, only the overall rate of the catalytic reaction has been reported.[6-8] Since the discussions based only on the observed rate constants of the overall reaction sometimes leave significant ambiguities, we need to elucidate the detailed mechanism involving the behavior of the catalytically active intermediate species by distinguishing the information on the intermediate species from those on the overall reaction.

Though no direct evidence was reported so far, the catalytic hydrogenation of olefins is believed to proceed in the molecule of an intermediate dihydrido-olefin complex, $RhClH_2(ol)(PPh_3)_2$ (ol=olefin), the rate-determining step being suggested to be the insertion of the coordinated olefin into an Rh–H bond to yield an alkyl complex (Scheme 1).[5,9] Thus the direct measurements of the step of production of an alkane from the intermediate dihydrido-olefin complex $RhClH_2(ol)(PPh_3)_2$ would be desired.



Scheme 1.

Recently Halpern *et al.* reported the value of k_{45} for cyclohexene as an olefin measured in the presence of a large excess of the free ligand PPh_3.[9,10] Since the predominant species involved under this condition are **1** and **2**, they did not observe directly the process **4**→**5**. The value estimated by them from the small intercept, however, can include a serious error. The value obtained by them ($k_{45}=0.20\pm0.04\ s^{-1}$, at 25 °C) seems to be too small (*vide infra*).

In the previous paper on the catalytic hydrogenation of acrylonitrile, we confirmed the formation of $RhClH_2(ac)(PPh_3)_2$ (ac=acrylonitrile) in the absence of free PPh_3 added, and evaluated the value of k_{45}.[11,12] However, for the value of K_{34} only the lower limit could be determined by the stopped-flow measurements, giving consequently only an upper limit for the value of k_{45}.

In the present study, we adopted styrene as an olefin having a much lower coordinating ability than acrylonitrile. The values of K_{34} and k_{45} were determined by the stopped-flow method and the direct measurements of the hydrogen-gas uptake. The corresponding values for acrylonitrile, which had been estimated only from the stopped-flow method,[11] were also re-examined by the direct measurements of the uptake of hydrogen gas.

Experimental

Chlorotris(triphenylphosphine)rhodium(I) and chloro(ethylene)bis(triphenylphosphine)rhodium(I) were prepared according to Osborn *et al.*[6] Triphenylphosphine was recrystallized from ethanol. Benzene was distilled. Acrylonitrile and styrene were distilled under reduced pressure and used within a day. Commercial hydrogen and nitrogen were used without further purification. The concentration and the purity of hydrogen were determined by gas chromatography through Molecular sieve 5A.

All measurements were carried out at 20±1 °C in oxygen-free benzene. A solution of $RhCl(ol)(PPh_3)_2$ was prepared by dissolving $RhCl(C_2H_4)(PPh_3)_2$ in benzene containing styrene or acrylonitrile, and by removing the dissociated ethylene. The coordinated ethylene was easily replaced by the olefin, leaving a pure $RhCl(ol)(PPh_3)_2$ in benzene. The resultant solution was confirmed to contain no free PPh_3.[11]

The equilibria of the reaction were measured at 450 nm under an anaerobic condition with a Hitachi EPS-3T spectrophotometer or a Union Giken RA-1300 stopped-flow apparatus. The rates of the hydrogenation of olefins were measured by the uptake of hydrogen-gas as described previously.[11]

Results and Discussion

Styrene. *Equilibria*: The mechanism shown in Scheme 1 is proposed for the hydrogenation of olefins.[11] The steps of the complex formations are assumed to be in pre-equilibria. The hydrogenation of the coordinated olefin is the rate-determining.[5,9] The equilibrium constant for each step of the complex formations was obtained separately from the equilibrium measurements.

The value of K_{13} was obtained from the measurements carried out by the addition of the solution of PPh_3 little by little to the solution of $RhCl(st)L_2$ (st=styrene and L=PPh_3) containing no free ligand PPh_3. Figure 1 shows the dependence of the absorbance of the solution on the concentration of added PPh_3. The solid curve reproduced with the value $K_{13}=2.4\times10^{-4}$ agrees well with the experimental values.

When a benzene solution containing hydrogen was rapidly mixed with the solution of $RhCl(st)L_2$ by stopped-flow technique under the condition of $[Rh]<[H_2]_0\ll[St]$, the stepwise changes in the absorbance at 450 nm were observed. First, a rapid exponential decrease in absorbance owing to the formation of $RhClH_2(st)L_2$ was observed. The signal terminated within 0.1 s. Then the absorbance slowly increased as the hydrogen in the solution was consumed for the hydrogenation of the styrene.[11] After 20 s the absorbance was again increased to the initial value, showing the consumption of all hydrogen molecule and the reproduction of $RhCl(st)L_2$. Figure 2 shows the dependence on the concentration of hydrogen of the decrease in absorbance in the first step. The value of K_{34} was calculated from the change in absorbance. In order to ascertain the validity of the values obtained above, we compared these values with those obtained from the direct measurements of the hydrogen-gas uptake. The curve in Fig. 2 is reproduced using the value of $K_{34}=3.2\times10^3$ mol^{-1} dm^3 evaluated from the measurements of the hydrogen-gas uptake, showing a good agreement with the results of the stopped-flow measurements.

The value of K_{12} was estimated to be 2.1×10^4 mol^{-1} dm^3.[13] Thus, from the relationship $K_{24}=K_{13}K_{34}/K_{12}$ the value of K_{24} was calculated to be 3.7×10^{-5}.

Hydrogen-gas Uptake:[11] The rate of the hydrogenation of styrene was directly measured by the hydrogen-gas uptake at 1 atm hydrogen. Figure 3 shows the rate constants observed at various concentrations of added PPh_3. From the results, the values of K_{34} and k_{45} can be estimated by the curve-fitting method.

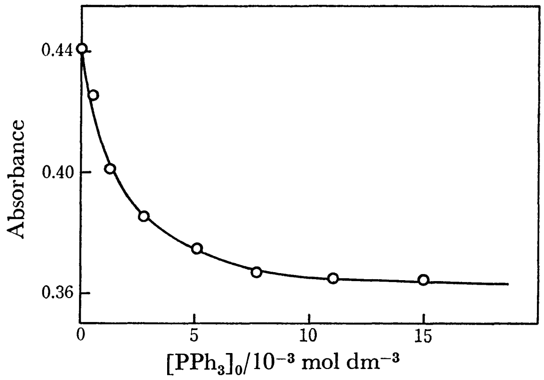


Fig. 1. The dependence of the absorbance of the $RhCl(st)(PPh_3)_2$ solution on the concentration of PPh_3 added. $[RhCl(st)(PPh_3)_2]_0=2.6\times10^{-4}$ mol dm^{-3}, at 450 nm, and 20 °C. The solid curve in the figure is reproduced with the value $K_{13}=2.4\times10^{-4}$.

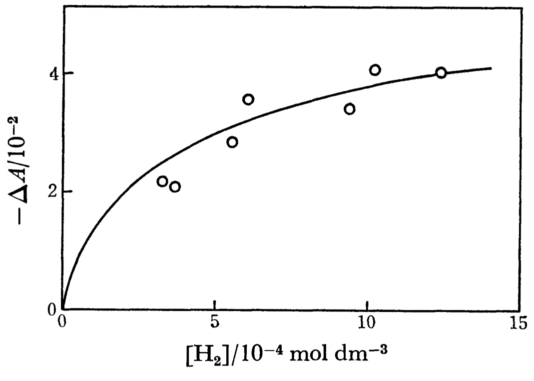


Fig. 2. The dependence of the absorbance decrease on the concentration of hydrogen in the reaction of $RhCl(st)(PPh_3)_2$ with hydrogen. The solid line in the figure is reproduced using the value $K_{34}=3.2\times10^3$ mol^{-1} dm^3, which is obtained from the measurements of hydrogen-gas uptake.

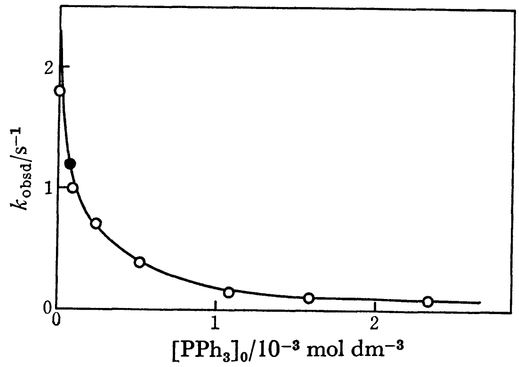


Fig. 3. The plot of the observed rate constant k_{obsd} for the hydrogenation of styrene *vs.* the concentration of PPh_3 added. The initial rates of the hydrogen-gas uptake were measured. $[Rh]_0=6.4\times10^{-5}$ (1.3×10^{-6} mol), [St]=2.6, and $[H_2]=2.8\times10^{-3}$ mol dm^{-3}. ●; $RhCl(PPh_3)_3$ without adding PPh_3. The solid line in the figure is reproduced using $K_{34}=3.2\times10^3$ mol^{-1} dm^3 and $k_{45}=2.7$ s^{-1}.

According to Scheme 1, the observed overall rate constant is expressed by

$$k_{obsd}=k_{45}\frac{[RhClH_2(st)L_2]}{[Rh]_t},\tag{1}$$

where $[Rh]_t$ denotes the total concentration of rhodium species. Since the value of $[RhClL_3]$ is about 1/60 of $[RhClH_2L_3]$ at 1 atm hydrogen, as calculated from the value $K_{12}=[RhClH_2L_3]/[RhClL_3][H_2]=2.1\times10^4$ mol^{-1} dm^3, the contribution of $RhClL_3$ can be neglected. Therefore, $[Rh]_t$ and the total concentration of added PPh_3, $[L]_0$, are approximated as follows:

$$[Rh]_t\simeq[RhClH_2L_3]+[RhCl(st)L_2]+[RhClH_2(st)L_2]\tag{2}$$

$$[L]\simeq[L]_0-[RhClH_2L_3]\tag{3}$$

The value of equilibrium constant K_{23} is calculated by

$$\begin{aligned} K_{23} = K_{13}/K_{12} &= \frac{[RhCl(st)L_2][H_2][L]}{[RhClH_2L_3][St]} \\ &= \frac{[RhCl(st)L_2][H_2]\{[L]_0-[RhClH_2L_3]\}}{[RhClH_2L_3][St]} \qquad (4) \\ &= 1.2 \times 10^{-8}\ \text{mol dm}^{-3}. \end{aligned}$$

The concentrations of $RhClH_2(st)L_2$ are calculated from Eqs. 2 and 4 by estimating an adequate value for $K_{34}=[RhClH_2(st)L_2]/[RhCl(st)L_2][H_2]$. The value of k_{45} can be determined by introducing the calculated value of $[RhClH_2(st)L_2]$ into Eq. 1. A set of K_{34} and k_{45} used for the calculations, which fit well with the experimental values, is evaluated to be $K_{34}=3.2\times10^3\ \text{mol}^{-1}\ \text{dm}^3$ and $k_{45}=2.7\ \text{s}^{-1}$, giving the solid line depicted in Fig. 3. Disagreement of the values obtained under the condition without PPh_3 added may be caused by the partial decomposition of the bis(triphenylphosphine) complex.

The experiments at varying concentrations of styrene were not possible, since at lower concentrations the formation of the dimeric species could not be neglected, and at higher concentrations other unidentified species were formed.

The equilibrium constant K_6 in Eq. 6 was determined to be $5.5\times10^{-4}\ \text{mol}^{-1}\ \text{dm}^3$ from the measurements of the reaction varying amounts of styrene with the dimer.

$$(RhClL_2)_2 + 2St \overset{K_6}{\rightleftharpoons} 2RhCl(st)L_2 \qquad (6)$$

$$2RhClL_3 \overset{K_7}{\rightleftharpoons} (RhClL_2)_2 + 2L \qquad (7)$$

The value of K_{13} was determined also from K_6 and K_7[14] to be 2.2×10^{-4} based on the relationship $K_{13}=K_6^{1/2}K_7^{1/2}$. The value agrees well with that obtained above.

Acrylonitrile. *Hydrogen-gas Uptake*:[8] In the previous paper we reported the values, $K_{34}\geq150\ \text{mol}^{-1}\ \text{dm}^3$ and $k_{45}\leq0.74\ \text{s}^{-1}$. In the present study, the rate of the hydrogen-gas uptake was directly measured at various concentrations of acrylonitrile and added PPh_3 (Fig. 4). The values of K_{34} and k_{45} were calculated in a similar manner to the case of styrene, to be $350\ \text{mol}^{-1}\ \text{dm}^3$ and $0.50\ \text{s}^{-1}$, respectively, the value $K_{23}=K_{13}/K_{12}=0.22/(2.1\times10^4)=1.0\times10^{-5}$ being used. The solid line in Fig. 4 are reproduced using these values of K_{34} and k_{45}.

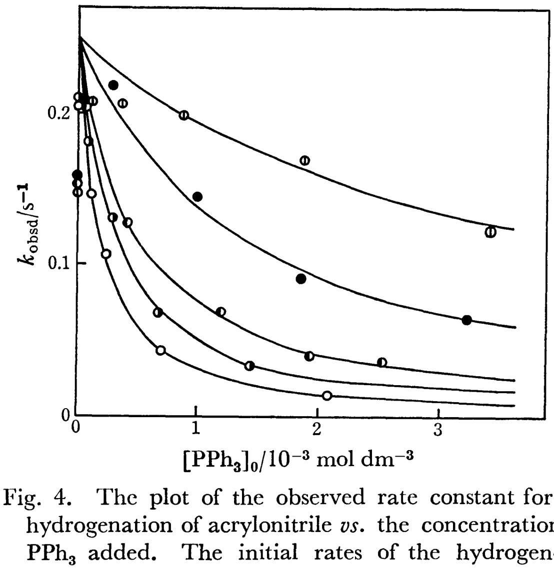


Fig. 4. The plot of the observed rate constant for the hydrogenation of acrylonitrile *vs*. the concentration of PPh_3 added. The initial rates of the hydrogen-gas uptake were measured. $[Rh]_0=1.5\times10^{-4}$ (2.9×10^{-6} mol), $[H_2]=2.8\times10^{-3}$, and [Ac]=○; 0.015, ◑; 0.031, ◐; 0.046, ●; 0.15, ⦶; 0.46 mol dm^{-3}. The solid curves in the figure are reproduced using the values of $K_{34}=3.5\times10^2\ \text{mol}^{-1}\ \text{dm}^3$ and $k_{45}=0.50\ \text{s}^{-1}$.

Discrepancies in the data observed without PPh_3 added may be due to the dissociation of the coordinated ligand PPh_3, which causes the formation of some catalytically inactive species.

The distinct differences observed in the behavior of acrylonitrile and styrene are summarized as follows: Whereas the value of K_{13} for acrylonitrile is about 10^3 times as large as that for styrene, the values of K_{34} and k_{45} for styrene are by several times larger than those for acrylonitrile. These differences may be attributed to the difference in the coordinating properties of the two olefins having a cyano and a phenyl group as substituents. Acrylonitrile having a strong electron-withdrawal cyano group shows a large K_{13} because of the strong back-donation from the central rhodium atom. Therefore, the addition of hydrogen molecule to $RhCl(ac)L_2$ would become difficult, since the electron density on the central rhodium atom is decreased owing to the strong back-donation. The electron-releasing phenyl group in styrene would act oppositely.

Recently Halpern *et al.* reported the value of k_{45} for cyclohexene $0.20\pm0.04\ \text{s}^{-1}$ at 25 °C in the presence of a large excess of PPh_3. Although we intended also to obtain the value of k_{45} for cyclohexene without PPh_3 added, the measurements were not possible owing to the unfavorable precipitation of the dimeric species under the given conditions. The value of K_{13} for cyclohexene may be much smaller than that for styrene, suggesting a much lower concentration of the resultant intermediate dihydrido-olefin complex, $RhClH_2(ol)L_2$, than that for styrene. When tris(triphenylphosphine) complex, $RhClL_3$, is used as the catalyst, the observed overall rate constant for the catalytic hydrogenation of cyclohexene is about 1/3 as small as that of styrene.[7] Thus, the value of k_{45} for cyclohexene is expected not to be much smaller than that for styrene. It may be estimated to be at least larger than $0.20\ \text{s}^{-1}$.

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