Transfer Hydrogenation and Transfer Hydrogenolysis VII. The Mechanism of Hydrogen Transfer from 2-Propanol to Olefins Catalyzed by Dihydridotetrakis-(triphenylphosphine)ruthenium(II)

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The dihydride complex, $RuH_2(PPh_3)_4$, has been found to be an excellent catalyst for the hydrogen transfer from 2-propanol to olefins. For cyclohexene in toluene solution, the rate law at 80°C was:

$$\text{Rate} = \frac{0.04[C]_o[D]}{1+24[P]}$$

where $[C]_o$, [D] and [P] are the concentration of the catalyst, 2-propanol and triphenylphosphine, respectively. It is pressumed that active intermediates of the reaction are not Ru(IV)-species but Ru(0)-species. The rate-determining step of the reaction is inferred to be the dehydrogenation of 2-propanol, that is, the hydrogen transfer from the alcohol to Ru(0)-complex to form a hydride complex by oxidative addition.

We have reported previously that cyclic ethers,[1] amines[2] and 2-propanol[3] donate hydrogen to olefins in the presence of $RhCl(PPh_3)_3$ or $RhH(PPh_3)_4$. In these transfer hydrogenations or in other homogeneous catalytic hydrogenations with molecular hydrogen, hydride complexes of transition metals have been considered as active intermediate.[4] Thus, hydride complexes may be expected to have high catalytic activity. Moreover, they seem to have good solubilities in organic solvent.

We have studied the catalytic nature of the monohydride complex, $RhH(PPh_3)_4$,[3] for the hydrogen transfer from alcohol to olefins, and now have undertaken to study that of the dihydride complex, $RuH_2(PPh_3)_4$. It has been reported that $RuH_2(PPh_3)_4$[5] and $RuH_4(PPh_3)_3$[6] have activity for hydrogenation of olefins and $RuH_2(PPh_3)_4$ gives $RuH_4(PPh_3)_3$ in the reaction with hydrogen.[7] Further, $RuClH(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ are thought to catalyze the hydrogenation of olefins *via* Ru(IV)-species.[4] So, which of the Ru(0)-, Ru(II)- and/or Ru(IV)-complex is a reaction intermediate in the transfer hydrogenation is of interest.

Results and Discussion

Measurement of Initial Rates. Unless otherwise noted, the transfer hydrogenation was carried out in any instance under the standard condition that $RuH_2(PPh_3)_4$ (0.01 mol·l^{-1}), cyclohexene (0.5 mol·l^{-1}) and 2-propanol (1.0 mol·l^{-1}) were heated in toluene at 80°. The reaction proceeded stoichiometrically without side reactions, for the amount of the dehydrogenation product, acetone, was equal to that of the formed cyclohexane and the total amounts of the cyclohexene and cyclohexane were equal to the amount of the charged cyclohexene within experimental error. The conversion of the olefin to paraffin was proportional to reaction time until 30% conversion. However, the linearity did not hold at higher conversion, perhaps because the formed acetone competes with the olefin for a vacant coordination site of the catalyst though the initial rate of the reaction, which was derived from the linear part, is independent of the olefin concentration as described later.

Table 1. Effect of solvents on the initial rate[a]

Solvent	Rate×10^4 (mol·l^{-1} min^{-1})
Dimethylsulfoxide	0.0
Acetic acid	0.1
Chlorobenzene	0.1
N,N-Dimethylacetamide	1.0
Anisole	3.6
Toluene	4.0
Benzene	4.1

a) Cyclohexene (0.5 mol·l^{-1}), 2-propanol (1.0 mol·l^{-1}) and $RuH_2(PPh_3)_4$ (0.01 mol·l^{-1}) were heated at 80°C in the solvent.

Initial rates of the transfer hydrogenation in several solvents were measured and the results are summarized in Table 1. Some solvents, which have high polarity and strong coordinating power, dissolved the catalyst easily but the reaction in those solvents was slow. This may be explainable by the fact that highly polar solvents make the coordination of other reagents difficult. In a few aromatic solvents, such as toluene and benzene, the catalyst dissolved well at room temperature and the reaction proceeded rapidly. Toluene was used as a solvent in this kinetic study.

The rate of the hydrogenation of several cycloolefins is given in Table 2. The rate was not so varied by the

Table 2. Effect of olefine on the initial rate[a]

Olefin	Rate×10^4 (mol·l^{-1}·min^{-1})	Product
Cyclopentene	3.1	Cyclopentane
Cyclohexene	4.0	Cyclohexane
Cycloheptene	3.5	Cycloheptane
Cyclooctene	3.4	Cyclooctane
Norboranadiene	0.5	Norbornene
1,3-Cyclooctadiene	0.0	
1,5-Cyclooctadiene	0.0	

a) Olefin(0.5 mol·l^{-1}), 2-propanol (1.0 mol·l^{-1}) and $RuH_2(PPh_3)_4$ (0.01 mol·l^{-1}) were heated at 80°C in toluene.

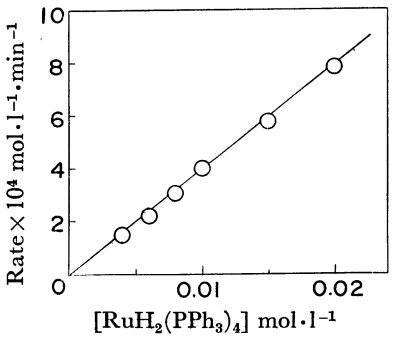


Fig. 1. Dependence of the rate of hydrogenation of cyclohexene on catalyst concentration in toluene at 80 °C, with 0.5 mol·l^{-1} cyclohexene and 1.0 mol·l^{-1} 2-propanol.

kinds of cyclomonoenes. As for dienes, norbornadiene was slowly hydrogenated to norbornene and cyclooctadienes were not reduced. Perhaps the difficulty in reduction of these dienes may be understandable by the fact that they are bidentate ligands and have strong coordinating power.

Figure 1 shows the dependence of the rate on the catalyst concentration. In the region of the catalyst concentration higher than 0.004 mol·l^{-1}, the rate was first-order in the catalyst concentration. Extrapolation of the line to lower catalyst concentration passes through the origin.

The initial rate of the hydrogenation was independent of the cyclohexene concentration in the range, examined. The zero-order dependence may be interpreted either by the assumption that the coordination of olefins to the metal occurs after the rate-determining step or by the assumption that though the olefin coordinates before the rate-determining step, the coordination occurs so completely that the intermediate olefin complex concentration is not greately changed over the range of 0.05 to 1.30 mol·l^{-1}. The former assumption seems to be more plausible on the basis of spectroscopic data described later.

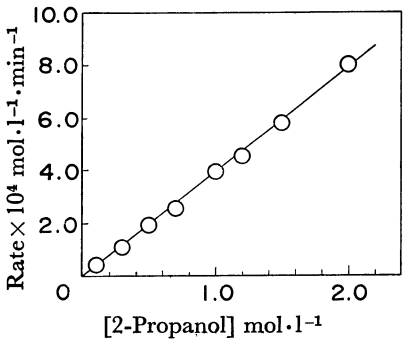
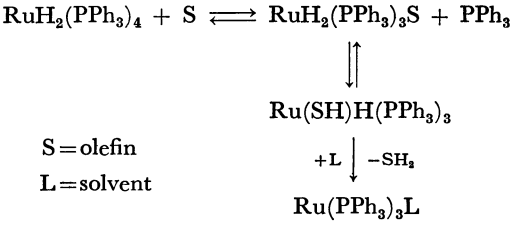


Fig. 2. Dependence of the rate of hydrogenation of cyclohexene on 2-propanol concentration in toluene at 80 °C, with 0.01 mol·l^{-1} $RuH_2(PPh_3)_4$ and 0.5 mol·l^{-1} cyclohexene.

As shown in Fig. 2, the rate of the reduction showed a good linear dependence on the concentration of 2-propanol.

Initial rates were measured at 70, 80, 90 and 100°C and a good linear plot of $\log_{10}$ (Rate) against $1/T$ was obtained, from which a value for activation energy, E_a of 31.4 kcal mol^{-1} is obtained; ΔH^* being 30.7 kcal mol^{-1}. The obserbed rate constant provides a value of 20 e.u. for ΔS^*.[8]

Reaction between $RuH_2(PPh_3)_4$ and Olefins. When cyclohexene (0.5 mol·l^{-1}) and $RuH_2(PPh_3)_4$ (0.03 mol·l^{-1}) in toluene were kept at 20°C for 1 day in the absence and in the presence of 2-propanol (1.0 mol·l^{-1}), 0.01 mol·l^{-1} of cyclohexane was formed. In the reaction of 1-hexene and $RuH_2(PPh_3)_4$ (0.01 mol·l^{-1}) under the same condition, 0.33 mol·l^{-1} of internal hexenes was obtained in addition to 0.007 mol·l^{-1} of *n*-hexane. The hydrogen transfer from $RuH_2(PPh_3)_4$ to olefins at room temperature has also been reported by Komiya *et al.*[5] The transfer hydrogenation did not take place at room temperature. This fact suggests that the first step of the overall transfer hydrogenation is the transfer of hydride ligands of the metal complex to olefins. The hydrogen transfer from the catalyst to olefins is considered as Scheme 1.



Scheme 1.

Isotopic Study. When octadeutero-2-propanol was used instead of 2-propanol at 80°C, the initial rate was 1.5×10^{-4} mol·l^{-1} min^{-1}, while in the case of 2-propanol the rate was 4.0×10^{-4} mol·l^{-1} min^{-1}. Moreover, in the reaction of octadeutero-2-propanol GC-MS spectroscopic study revealed that cyclohexane-d_1 and -d_2 were major product and cyclohexane-d_0, -d_3 and -d_4 were minor. The result proved clearly that hydrogen atoms transferred from the alcohol to cyclohexene and double bond migration of the olefin scarcely take place during the hydrogenation.

The value of the kinetic isotope effect, $R_H/R_D=2.7$, shows that a hydrogen transfer step is rate limiting.

The IR spectrum of the ether solution of $RuH_2(PPh_3)_4$ (0.03 mol·l^{-1}) and octadeutero-2-propanol (1.0 mol·l^{-1}), which had been heated at 100°C for 2 hr, showed no peaks assignable to –OH and C=O, and that of the recovered complex was identical with that of the original complex, $RuH_2(PPh_3)_4$, having no absorption attributable to Ru–D bond. As no hydrogen exchange occurred between 2-propanol and $RuH_2(PPh_3)_4$, tetrahydride species are not the reaction intermediate in this transfer hydrogenation.

Effect of Added Acetone. By the addition of 1.0 mol·l^{-1} acetone to the reaction system, the rate was decreased to one-eighth. The retarding effect is explained by the fact that acetone was hydrogenated to 2-propanol in tetralin, so it competes for the coordination sites of the metal complex with other reagents. From this point of view, when the total concentration of acetone and cyclohexene was kept constant (2.0 mol·l^{-1}) and the ratio of acetone against cyclohexene was changed, the reciprocal of the rate against [acetone]/

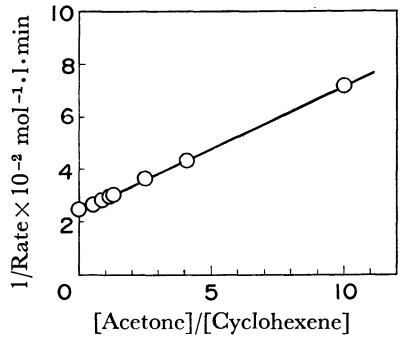


Fig. 3. Plot of the reciprocal of the rate of hydrogenation of cyclohexene *vs.* the ratio of [acetone]/[cyclohexene] in toluene at 80 °C, with 0.01 mol·l^{-1} $RuH_2(PPh_3)_4$, 0.5 mol·l^{-1} cyclohexene and 1.0 mol·l^{-1} 1-propanol.

[cyclohexene] was linear with a positive intercept on y-axis, as shown in Fig. 3.

Effect of Added Triphenylphosphine. The rate was decreased by the addition of excess triphenylphosphine to the reaction system, as in cases of the hydrogenation by molecular hydrogen catalyzed by transition metal complexes.[9-11] The plots of the reciprocal of the rate against the added triphenylphosphine concentration was linear with a positive intercept on y-axis, as shown in Fig. 4.

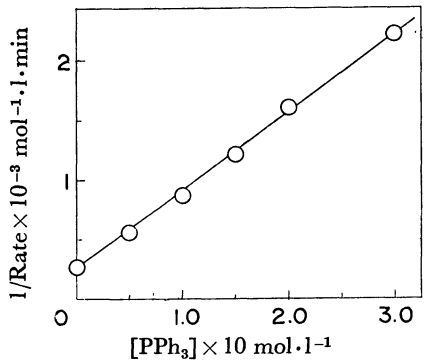


Fig. 4. Plot of the reciprocal of the rate of hydrogenation of cyclohexene *vs.* the concentration of added triphenylphosphine in toluene at 80 °C, with 0.01 mol·l^{-1} $RuH_2(PPh_3)_4$, 0.5 mol·l^{-1} cyclohexene and 1.0 mol·l^{-1} 2-propanol.

Reaction Intermediate. The infrared spectrum of a toluene solution of 0.03 mol·l^{-1} catalyst, 1.0 mol·l^{-1} 2-propanol and 0.5 mol·l^{-1} cyclohexene, which had been heated at 100 °C for 1 hr, showed no peaks assignable to the hydride ligands. The residual solid obtained from the solution had peaks at 1380 cm^{-1} and 3250 cm^{-1} (broad) in infrared spectrum (KBr). These absorption bands are attributable to 2-propanol and the ones assignable to cyclohexene or acetone were not detected. To evaluate the numbers of coordinated triphenylphosphine, diethylene glycol dimethyl ether (0.0134 g) was added as an internal standard into $CDCl_3$ solution of the residual solid (0.200 g). The NMR spectrum showed three multiplets centered at τ 2.7, τ 8.8 and τ 6.4 and a singlet at τ 6.7, with 50: 1: 38: 29 area. The peak at τ 2.7 are assignable to phenyl protons, the peaks at τ 6.4 and τ 6.7 are due to diethylene glycol dimethyl ether and the peak at τ 8.8 is due to 2-propanol, respectively. The peaks which are assignable to cyclohexene and acetone were not obserbed. Though methyl groups of free 2-propanol show a doublet, the doublet might be changed to the multiplet by the hindrance of the rotation of the methyl groups on account of the coordination on the metal. As the number of coordinated triphenylphosphine molecules, the value of 3.1 was obtained from the ratio of the area of peak at τ 2.7 to the one at τ 6.4 or at τ 6.7. This value is not contradictory to the result of elemental analysis of the residual solid. (Found: C, 73.12; H, 5.08%. Calcd for $Ru(PPh_3)_4$ C, 75.05; H, 5.21%; for $Ru(PPh_3)_3$ C, 72.89; H, 5.06%; for Ru(2-propanol)-$(PPh_3)_4$ C, 74.28; H, 5.65%; and for Ru(2-propanol)-$(PPh_3)_3$ C, 74.44; H, 5.62%;)

These result shows that $Ru(PPh_3)_3$ is the major species and $Ru(PPh_3)_4$, Ru(2-propanol)$(PPh_3)_4$ and Ru(2-propanol)$(PPh_3)_3$ are minor. When this recovered complex was used as a catalyst, the initial rate of the reaction was 3.5×10^{-4} mol·l^{-1} min^{-1}, which is roughly equal to that of the reaction in which $RuH_2(PPh_3)_4$ was used. The fact that Ru(0)-species were isolated and they had catalytic activity suggests that the Ru(0)-complex existed in the reaction process as a major intermediate and the first step of this reaction is the hydrogen transfer from catalyst to olefin to give Ru(0)-species.

Rate-determining Step. The observed kinetic isotope effect, $R_H/R_D=2.7$, distinctly shows that a hydrogen transfer step is rate limiting. There may be three hydrogen transfer steps in this transfer hydrogenation, that is; (1) hydrogen transfer from the coordinated alcohol to the Ru(0)-complex to give the Ru(II) species, (2) hydride transfer to the coordinated olefin to give the Ru(II)-alkyl complex and (3) hydrogenolysis of the Ru(II)-alkyl complex by a coordinated hydride to yield the paraffin.

The isomerization of the terminal olefin (involving step (2)) and the hydrogenation of olefins by molecular hydrogen (involving steps (2) and (3)) occurred at room temperature in the absence of 2-propanol. As the steps (2) and (3) are inferred to occur fast at the reaction temperatures of the transfer hydrogenation, these steps may not be rate limiting. Therefore, the dehydrogenation of 2-propanol to give acetone, that is step (1), is inferred be rate limiting.

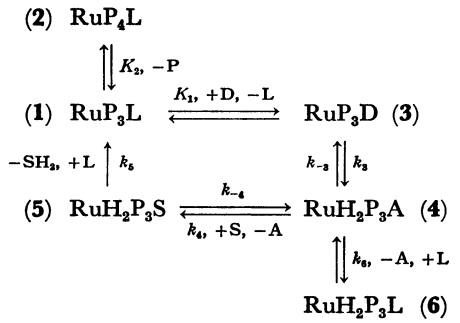
Kinetic Discussion

The first step of this transfer hydrogenation was as shown in Scheme 1. So upon the results described earlier and the facts described in the literature,[1-9] we should like to propose the following reaction scheme for the catalytic cycle of transfer hydrogenation.

Based on the proposed scheme and the assumption described later, the rate (R) is expressed as follows;

$$R=\frac{k_3k_4k_5K_1[D][S][C]_0}{(k_{-3}k_{-4}[A]+k_4k_5[S])(1+K_1[D]+K_2[P])} \quad (1)$$

where K_1 and K_2 are equilibrium constants and k_3, k_{-3}, k_4, k_{-4} and k_5 are rate constants, and [D], [S], $[C]_0$, [A]



where,

P=PPh_3 S=olefin D=2-propanol
A=acetone L=solvent, PPh_3 or 2-propanol

and [P] are the concentrations of the hydrogen donor, the olefin, the added catalyst, acetone and triphenylphosphine, respectively. The assumption is that the dihydride species, **4**, **5** and **6** are so active as steady state treatment to be applied. This assumption seems not so unreasonable, because the spectroscopic study of this reaction system showed no sign of the existence of hydride species as described before.

Equation (1) accommodates the effect of the added acetone. At initial stage of the hydrogenation, the concentration of the added acetone may approximately be regarded as the total acetone concentration in the reaction system. So the dependence of the rate on [A]/[S] is derived from Eq. (1);

$$\frac{1}{R}=\frac{k_{-3}k_{-4}(1+K_1[D]+K_2[P])}{k_3k_4k_5K_1[D][C]_0}\cdot\frac{[A]}{[S]}+\frac{1+K_1[D]+K_2[P]}{k_3K_1[D][C]_0} \quad (2)$$

As free phosphine concentration is negligible compared with acetone and olefin concentration, Eq. (2) is identical in form to that obtained from Fig. 3. When acetone was not added, the initial rate was independent on the olefin concentration. Therefore, the numerator of the first term of Eq. (2) must be zero. This may be realized by the fact that at the initial stage of the reaction the amount of the formed acetone is negligible. This reasoning is supported by the fact that in the presence of added acetone the initial rate depended on the olefin concentration. Then the rate expression is reduced to;

$$R=\frac{k_3K_1[C]_0[D]}{1+K_1[D]+K_2[P]} \quad (3)$$

As described earlier, the rate had the first order dependence on the concentration of 2-propanol. This fact requires $1+K_2[P]\gg K_1[D]$, that is, $[1]+[2]\gg[3]$. This assumption seems to be not so unreasonable from the results of the isolation of reaction intermediate described previously. Therefore, Eq. (3) is reduce to;

$$R=\frac{k_3K_1[C]_0[D]}{1+K_2[P]} \quad (4)$$

This expression is found to accommodate most of the other experimental observations; (a) The dependence of the rate on the catalyst concentration should be linear, and this agrees with the experimental result shown in Fig. 1. From this figure, 4.0×10^{-4} min^{-1} was obtained as the value of $k_3K_1/(1+K_2[P])$. (b) The dependence of the rate on the donor concentration should be linear, and this agrees with Fig. 2. From this figure, 4.0×10^{-4} min^{-1} was obtained as the value of $k_3K_1/(1+K_2[P])$. (c) When triphenylphosphine was added to the reaction system, the concentration of the added triphenylphosphine may approximately equal to the total phosphine concentration in the reaction system. The dependence of the rate on the phosphine concentration is;

$$\frac{1}{R}=\frac{K_2}{k_3K_1[C]_0[D]}[P]+\frac{1}{k_3K_1[C]_0[D]} \quad (5)$$

which is in agreement with experimental observation. From Fig. 4, the value for gradient, 6.0×10^4 $mol^{-2}\cdot l$ min and the value for the intercept, 2.5×10^3 $mol^{-2}\cdot l$ min were obtained, respectively. By using these values $K_2=24$ $mol^{-1}\cdot l$ and $k_3K_1=0.04$ $mol\cdot l^{-1}\cdot min^{-1}$ were obtained, as the values at 80 °C. Then the overall rate expression at 80 °C may be formulated as;

$$R=\frac{0.04[C]_0[D]}{1+24[P]} \quad (6)$$

The intercept of Fig. 3, $(1+K_1[D]+K_2[P])/k_3K_1[D][C]_0=2.5\times10^{-3}$ $mol^{-1}\cdot l$ min, is in good agreement with the intercept of Fig. 4, $(1+K_2[P])/k_3K_1[D][C]_0=2.5\times10^{-3}$ $mol^{-1}\cdot l$ min. This suggests that the reduction of Eq. (3) to Eq. (4) is feasible. Moreover, both Figs. 1 and 2 gave 2.5×10^{-3} $mol^{-1}\cdot l$ min as the value of $(1+K_2[P])/k_3K_1[D][C]_0$. This value also agrees well with the one obtained from Fig. 4. (d) In Eq. (4), k_3 is the only rate constant and the most important step, so the dehydrogenation step, **3**—**4**, may be rate limiting in the transfer hydrogenation. This supposition is supported by the results of the kinetic isotope effect which has a value of 2.7 and the experimental observations described earlier.

Experimental

Materials. The experimental techniques, together with the methods of purification of the materials have been given previously.[3] Dihydridotetrakis(triphenylphosphine)-ruthenium(II) was prepared by a method given in the literature.[12] The complex was identified as follows; ν_{Ru-H} 2080 cm^{-1} (lit,[13] 2080 cm^{-1}), mp 180 °C (lit,[13] 180 °C).

An Example of Kinetic Runs. Hydrogenation were carried out in a Pyrex glass tube. The sealed tube was prepared by the following procedure. Catalysts, alcohols and olefins were put into Pyrex glass tubes which had been sealed an one end. Into the mixture, solvent was added and the total volume of the solution was made 1.0 ml. The tube was sealed under vacuum after two freeze-pump-thaw cycles at 10^{-3} Torr on a vacuum line and liquid nitrogen bath. Five samples, prepared by the method described above, were heated in the polyethylene glycol-bath kept at 80±1 °C for 15, 30, 45, 60, and 90 min. The reaction mixture were submitted to glc analysis.

Isolation of a Reaction Intermediate. Toluene was added to the mixture of $RuH_2(PPh_3)_4$ (0.0345 g, 0.03 mmol), 2-propanol (0.0600 g, 1.00 mmol) and cyclohexene (0.0410 g, 0.50 mmol), and the total volume of the solution was made 1.0 ml. This sample was heated at 100 °C for 1 hr. After cooling the solution, the volatile compounds were evaporated

from this solution *in vacuo* and the residual solid was washed with ether twice and dried *in vacuo* for 48 hr. This residual solid was submitted to IR, NMR and elemental analysis.

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