Transfer Hydrogenation and Transfer Hydrogenolysis. II. Catalytic Activity of Some Soluble Complexes in Hydrogen Transfer from Alcohols to Olefins and the Mechanism of the Reaction Catalyzed by Hydridotetrakis(triphenylphosphine)rhodium(I)

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Hydrogen transfer from alcohols to olefins was studied to find effective homogeneous catalysts and convenient reaction conditions, and it was found that $RhH(PPh_3)_4$ had the highest catalytic activity among the complexes which were tried. Spectroscopic measurements (ir, uv, and gc–mass spectrum), hydrogenation by molecular hydrogen, and isotope effects were studied. Kinetic studies were carried out at 60–100° using the Rh(I) complex as a catalyst, 2-propanol as a hydrogen donor, cycloheptene as a hydrogen acceptor, and toluene as a solvent. The hydrogen transfer reaction is inferred to proceed in the following order: (1) the release of triphenylphosphine from $RhH(PPh_3)_4$, (2) coordination of 2-propanol to the metal, (3) hydrogen transfer from 2-propanol to the metal with the oxidative addition to form a trihydride complex, (4) coordination of cycloheptene to the metal, and (5) transfer of hydrogen of the trihydride complex to cycloheptene to form cycloheptane. These data are compatible with the expression rate = $K_1K_2k_5[D][Rh]_{total}/([P] + K_1)$, where [D], $[Rh]_{total}$, and [P] are donor, catalyst, and phosphine concentration, respectively. The rate-determining step of this reaction was considered as the transfer of hydogen from alcohol to a Rh(I) species.

Catalytic hydrogen transfer from organic compounds to olefins, which is called transfer hydrogenation,[1] has some advantages over the hydrogenation by molecular hydrogenation; for example, the reaction can be carried out in a closed and completely homogeneous system. However, the reaction requires rather drastic conditions and no detailed studies on its mechanism seem to have been reported. As for heterogeneous systems it has been reported that, in the presence of metallic nickel or palladium, primary and secondary alcohols donate hydrogen to olefins to give aldehydes and ketones, respectively.[2] For homogeneous systems, methyl linoleate or soybean oil have been reported to be hydrogenated to form monoenes selectively under the presence of nitrogen in the presence of $PtCl_2(PPh_3)_2$–$SnCl_2$,[3] $PtCl_2(AsPh_3)_2$–$SnCl_2$,[3] $PdCl_2(PPh_3)_2$,[4] or $NiX_2(PPh_3)_2$ (X = Cl, Br, and I)[5] in a benzene–methanol solution. In these cases, methanol is inferred as a hydrogen donor. The hydrogen transfer from benzyl alcohol to α,β-unsaturated carbonyl compounds catalyzed by $RuCl_2(PPH_3)_3$ has also been reported.[6] This study was undertaken to find more active catalysts and to elucidate the mechanism of transfer hydrogenation.

Experimental Section

Materials. Dichlorobis(triphenylphosphine)iron(II),[7] dichlorobis(triphenylphosphine)cobalt(II),[8] dihalogenobis(triphenylphosphine)nickel(II),[9] dichlorobis(tri-*n*-butylphosphine)nickel(II),[10] dichlorobis(triphenylphosphine)palladium(II),[11] dichlorobis(tri-*n*-butylphosphine)palladium(II),[12] dichlorobis(triphenylphosphine)platinum(II),[13] dichlorotris(triphenylphosphine)ruthenium(II),[14] hydridocarbonyltris(triphenylphosphine)rhodium(I),[15] chlorocarbonylbis(triphenylphosphine)rhodium(I),[16] and chlorotris(triphenylphopshine)rhodium(I)[16] were prepared by methods reported in the literature. Hydridotetrakis(triphenylphosphine)rhodium(I) was prepared by the method of Levison, *et al.*,[17] ν_{RhH} 2140 cm^{-1} (lit.[18] 2140 cm^{-1}), mp 160–162° (lit.[18] mp 162–163°). Olefins were purified by distillation over sodium. Alcohols were purified by distillation followed by dehydration with molecular sieves. Solvents were purified by distillation and degassed on a vacuum line with a liquid nitrogen bath before use.

An Example of the Transfer Hydrogenation. Cycloheptene (0.048 g, 0.5 mmol), $RhH(PPh_3)_4$ (0.0115 g, 0.01 mmol), and 2-propanol (0.060 g, 1.0 mmol) were put into a Pyrex glass tube which had been sealed at one end. Into the mixture, toluene 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. As the catalyst dissolved easily at room temperature, the reaction system was considered as a homogeneous system at reaction temperature. The sealed tube was heated in a silicone-oil bath kept at 90 ± 1°. To analyze the reaction mixture gas–liquid chromatography was performed at 70° with a Hitachi Perkin-Elmer instrument equipped with a flame ionization detector. A 2 m × 6 mm stainless steel column packed with 25% of 1,2,3-tris(2′-cyanoethoxy)propane on Celite 545 was used. The other transfer hydrogenations were carried out in a similar way.

An Example of Kinetic Measurements. Five sealed tubes, prepared by the method described above, were heated in a silicone-oil bath kept at 90 ± 1° for 5, 10, 15, 20, and 30 min, respectively. Each reaction mixture was submitted to the gas–liquid chromatographic analysis. The reaction rate was obtained by the gradiation of time against conversion plot.

Kinetic Isotope Effect. Cycloheptene (0.048 g, 0.5 mmol), $RhH(PPh_3)_4$ (0.0115 g, 0.01 mmol), and octadeuterio-2-propanol (0.068 g, 1.0 mmol) or 2-propanol (0.060 g, 1.0 mmol) were put into the Pyrex glass tubes. To the mixture, toluene was added and the total volume of this solution was made 1.0 ml. Several samples prepared by such a method were treated in the way described above and submitted to the gas–liquid chromatographic and gas–mass spectroscopic analysis.

An Example of Hydrogenation by Molecular Hydrogen. $RhH(PPh_3)_4$ (0.100 g, 0.0868 mmol) and toluene (10 ml) were placed in a 50-ml three-necked flask. The solution was saturated with hydrogen by flowing hydrogen over the solution, which was vigorously stirred. Then cyclohexene (0.41 g, 5 mmol) was added to the solution through the cerum cap which was attached to the one neck of the flask. To determine the reaction rate the reaction mixture was sampled and submitted to the gas–liquid chromatographic analysis. The reaction rate was obtained by the same method of transfer hydrogenation.

Measurement of Molecular Weight of $RhH(PPh_3)_4$. The molecular weight of $RhH(PPh_3)_4$ in benzene was measured by means of a vapor pressure osmometer with a Hitachi Perkin-Elmer 545 molecular weight apparatus. Benzene had been purified by shaking with sulfuric acid and distillation over sodium, and degassed by the method of three freeze–pump–thaw cycles at 10^{-3} Torr on a vacuum line and liquid nitrogen bath.

Infrared Spectroscopic Study. Ir spectra were recorded in a 0.1-mm liquid cell, which had been placed in a heating instrument, with a JASCO Model DS-402G grating infrared spectrophotometer. In the liquid cell $RhH(PPh_3)_4$ (0.04 *M*), octadeuterio-2-propanol (0.2 *M*), and toluene were placed and the heating instrument was heated to 70°. The ir spectra which covered the range of 4000–800 cm^{-1} were obtained.

Results

Catalytic Activity of Phosphine Complexes. The hydrogen transfer from alcohols to olefins has been reported to be catalyzed by $RuCl_2(PPh_3)_3$,[6] $PtCl_2(PPh_3)_2$–$SnCl_2$,[3]

Table I
Catalytic Activity of Phosphine Complexes[a]

Registry no.	Compd	Reaction time, hr	Reaction temp, °C	Conversion, %
	$FeCl_2(PPh_3)_2$	4	200	0
	$CoCl_2(PPh_3)_2$	4	200	0
	$NiCl_2(PPh_3)_2$	4	200	0
	$NiI_2(PPh_3)_2$	4	200	0
	$NiCl_2(PBu^n{}_3)_2$	4	200	0
	$PdCl_2(PPh_3)_2$	4	200	0[b]
	$PdCl_2(PPh_3)_2$–$SnCl_2$[c]	4	200	0[d]
	$PdCl_2(PBu^n{}_3)_2$	4	200	0
	$PtCl_2(PPh_3)_2$	4	200	8
	$PtCl_2(PPh_3)_2$–$SnCl_2$[c]	4	200	2[d]
34076-51-2	$RuCl_2(PPh_3)_3$	2	160	12
	$RhH(CO)(PPh_3)_3$	4	200	0[e]
13938-94-8	$RhCl(CO)(PPh_3)_2$	4	200	15
14694-95-2	$RhCl(PPh_3)_3$[f]	1	160	20
18284-36-1	$RhH(PPh_3)_4$[g]	0.25	100	43

[a] Unless otherwise noted, reaction system was 0.05 *M* catalyst and 0.5 *M* cyclopentene in 2-propanol. [b] Metallic mirror was formed. [c] 0.5 *M* $SnCl_2$. [d] Products with low boiling point were found. [e] Metallic precipitate was formed. [f] 0.02 *M* catalyst. [g] 0.01 *M* catalyst.

Table II
Effect of Reaction Solvents[a]

Solvent	Conversion, %	Solvent	Conversion, %
Dimethyl sulfoxide	2	Benzene	10
N,N-Dimethylacetamide	1.5	Toluene	11
N,N-Dimethylformamide	1	*m*-Xylene	5.5
Dioxane	2	Anisole	7
Tetrahydrofuran	3	Chlorobenzene	3
2-Propanol[b]	20	*o*-Dichlorobenzene	1

[a] Reaction system was 0.01 *M* $RhH(PPh_3)_4$, 0.5 *M* cycloheptene, and 1.0 *M* 2-propanol in toluene; reaction temperature 80°. [b] Catalyst was not soluble at the reaction temperature.

Table III
Effect of Hydrogen Donors[a]

Registry no.	Hydrogen donor	Rate, mol min^{-1}	Dehydrogenated product of donor
	Methanol	6.0×10^{-5}	*b*
64-17-5	Ethanol	4.6×10^{-4}	Acetaldehyde
17-23-8	1-Propanol	6.9×10^{-5}	Propanal
67-63-0	2-Propanol	1.1×10^{-3}	Acetone
78-92-2	2-Butanol	6.2×10^{-4}	Methyl ethyl ketone
6032-29-7	2-Pentanol	5.6×10^{-4}	Diethyl ketone
100-51-6	Benzyl alcohol	9.1×10^{-5}	Benzaldehyde

[a] Reaction system was 0.01 *M* $RhH(PPh_3)_4$, 0.5 *M* cycloheptene, and 1.0 *M* hydrogen donor in toluene; reaction temperature 80°. [b] Formaldehyde was not detected.

Table IV
Initial Rate of Hydrogenation of Cycloolefins[a]

Registry no.	Cycloolefin	Rate, mol min^{-1}
142-29-0	Cyclopentene	4.5×10^{-3}
110-83-8	Cyclohexene	4.4×10^{-3}
628-92-2	Cycloheptene	5.4×10^{-3}
931-88-4	Cyclooctene	4.8×10^{-3}
498-66-8	Norbornene	4.9×10^{-3}
	1,3-Cyclooctadiene	0.0
	1,5-Cyclooctadiene	0.0

[a] Reaction system was 0.01 *M* $RhH(PPh_3)_4$, 0.5 *M* olefin, and 1.0 *M* 2-propanol in toluene; reaction temperature 100°.

and $NiX_2(PPh_3)_2$ (X = Cl, Br, and I). To examine the catalytic activity of some representative phosphine complexes, the hydrogen transfer from 2-propanol to cyclopentene in the presence of the complexes was attempted and the results are summarized in Table I. The activity decreased in the order $RhH(PPh_3)_4 > RhCl(PPh_3)_3 > RuCl_2(PPh_3)_3 > RhCl(CO)(PPh_3)_2 > PtCl_2(PPh_3)_2 > PtCl_2(PPh_3)_2$-$SnCl_2$, and Fe(II), Ni(II), Co(II), Pd(II) complexes, and $RhH(CO)(PPh_3)_3$ had no catalytic activity.

$RhH(PPh_3)_4$, which has been reported to catalyze the reduction of olefin by molecular hydrogen only under relatively drastic conditions (at 80°),[19] was found to have the highest activity among complexes tried in the transfer hydrogenation.

Reaction Solvents. As the most active complex, $RhH(PPh_3)_4$, has a low solubility in alcohols at room temperature, several solvents were examined to find the ones of greater dissolving ability. The results of the transfer hydrogenation in some solvents are summarized in Table II. Some polar solvents, such as *N,N*-dimethylformamide and dimethyl sulfoxide, have high abilities to dissolve the catalyst, but the reduction in them did not proceed so fast. This may be understood by the fact that strong coordinating power of solvents makes the coordination ability of solvents exists in many reactions catalyzed by transition-metal complex.[16,20] In a few aromatic compounds, such as toluene and benzene, the reduction proceeded well and the catalyst dissolved in them easily even at room temperature; so toluene was used as a solvent in this study unless otherwise noted.

Hydrogen Donors. Several primary and secondary alcohols were investigated as hydrogen donors and found to form almost stoichiometric amounts of aldehydes and ketones, respectively. From the slope of the conversion *vs.* time plots, one of which is shown in Figure 1 as an example, initial rates of the reaction at 80° were derived. The results are summarized in Table III. This table shows that 2-propanol has the most excellent ability to supply hydrogen. It is also noteworthy that $RhH(PPh_3)_4$ formed no carbonyl complex by heating in primary alcohols even at elevated temperatures, in spite of the reports that $RhCl(PPh_3)_3$ abstracts the carbonyl group from primary alcohols[16] and aldehydes[21] to give $RhCl(CO)(PPh_3)_2$.

Hydrogenation of Cycloolefins. The initial rates of the transfer hydrogenation of some cycloolefins are shown in Table IV. It was found that the rates of cyclomonoenes show nearly the same value, 5×10^{-3} mol min^{-1}, and is independent of the kind of olefins. The result suggested that the coordination of olefins to the metal does not affect the rate of hydrogenation of olefins and occurs after the rate-determining step. However, chelating dienes such as 1,5-cyclooctadiene were not reduced. This may be understood for the reason that two double bonds of the diene coordinate to the metal and inhibit the formation of polyhydride complexes. In this study, cycloheptene was used as an accepter because of the ease in dealing with it.

An example of the quantitative relationship of transfer hydrogenation was as follows: when 0.5 mol of cycloheptene, 1.0 mol of 2-propanol, and 0.01 mol of $RhH(PPh_3)_4$ were heated in toluene at 100° for 4 hr, 0.19 mol of cycloheptane and 0.19 mol of acetone were detected in addition to the survival of 0.31 mol of the olefin. This shows the occurrence of the hydrogen transfer from 2-propanol to cycloheptene.

Reaction Time. It was found that the conversion of cy-

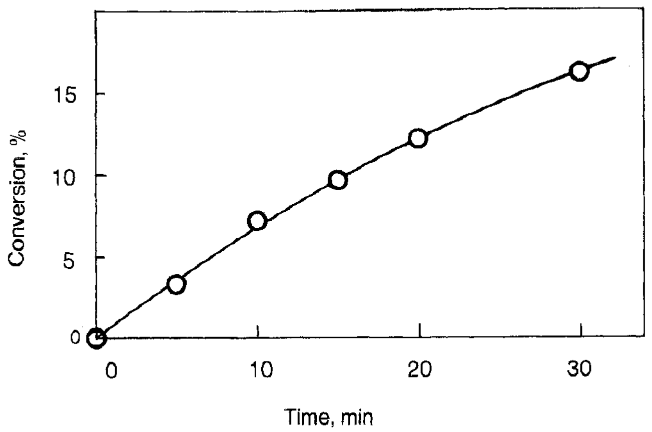


Figure 1. Plot of conversion *vs.* reaction time: 0.01 *M* $RhH(PPh_3)_4$, 0.5 *M* cycloheptene, and 1.0 *M* 2-propanol in toluene; reaction temperature 90°.

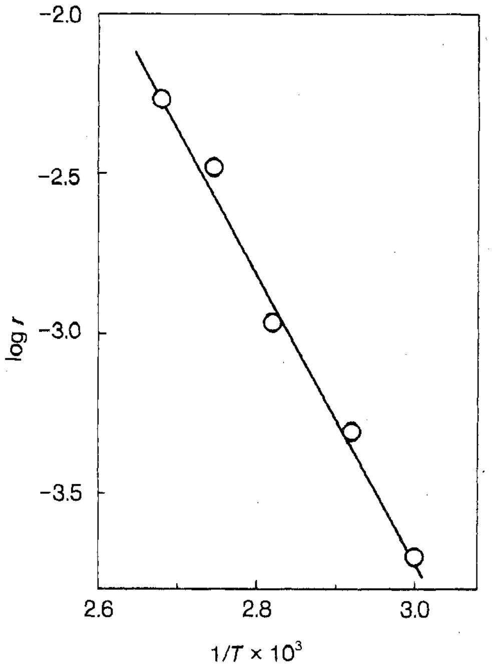


Figure 2. Plot of log *r vs.* $1/T$(°K) from data given in Table V.

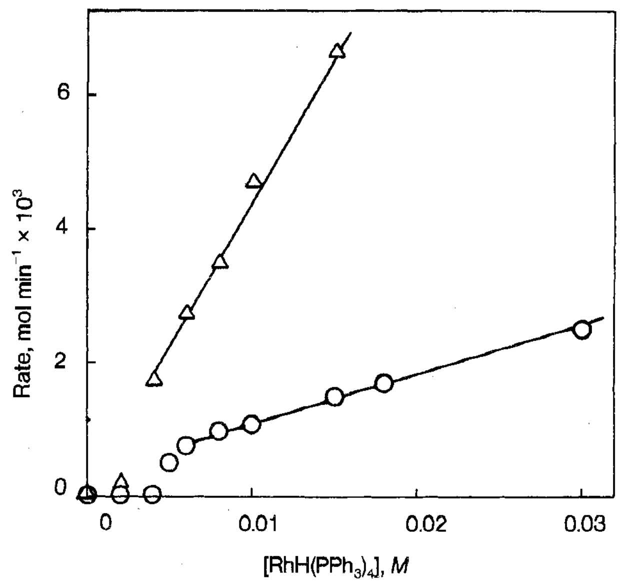


Figure 3. Dependence of rate of hydrogenation of cycloheptene on catalyst concentration in toluene at 80° (○) and at 100° (△), with 0.5 *M* cycloheptene and 1.0 *M* 2-propanol.

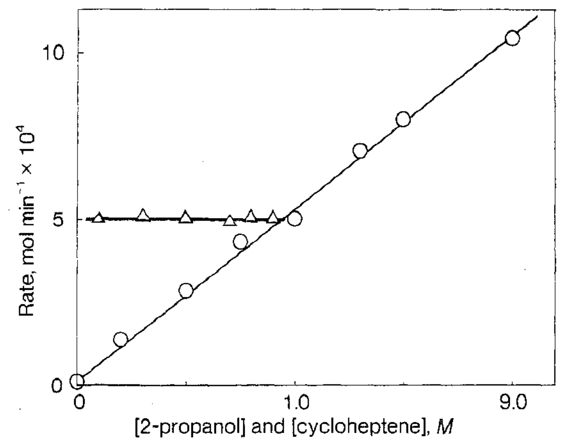


Figure 4. Dependence of rate of hydrogenation of cycloheptene on the concentration of the olefin (△) (1.0 *M* 2-propanol) and 2-propanol (○) (0.5 *M* cycloheptene) in toluene at 70°, with 0.01 *M* $RhH(PPh_3)_4$.

cloheptene to cycloheptane was linearly related with time up to 10%, as is shown in Figure 1. However, the conversion deviated from the linear relationship over 10%, notwithstanding the zero-order dependence of the concentration of the olefin on the rate as described later. Perhaps the deviation is caused by the retarding effect of acetone which is accumulated by the dehydrogenation of 2-propanol. The retarding effect of acetone will be discussed later. Initial rates of the reaction (r) were derived from the gradient of conversion *vs.* time curves in the linear region. Initial rates of the reduction (Table V) were measured at 60, 70, 80, 90, and 100°, and a plot of log r *vs.* $1/T \times 10^3$ is shown in Figure 2. The good linearity of the plot suggests that the kinetics of this system are not so complicated. From Figure 2 a value for the activation energy, E_a, of 21.4 kcal mol^{-1} is obtained; ΔH^* is 20.7 kcal mol^{-1} and ΔS^* is -10.8 eu (80°). As for activation energy, a comparable value of 21.6 kcal mol^{-1} has been reported in the hydrogen transfer from dioxane to cyclopentene.[22]

Dependence on the Concentration of $RhH(PPh_3)_4$. In more than 0.006 *M* at 80° or 0.004 *M* at 100°, the concentration of the catalyst had a linear relationship with the initial rate of the hydrogenation, as is shown in Figure 3. In this region, the poisoning of active species might not occur, and in the vicinity of the concentration of 0.01 *M*, at which this mechanistic study was carried out, the initial rate may be regarded as first order dependent on the concentration of the catalyst. However, in lower concentration than 0.006 *M* at 80° or 0.004 *M* at 100°, the linearity was not held. It is supposed that the reaction proceeds in a different mechanism in the region of these lower catalyst concentrations.

Dependence on the Concentration of Cycloheptene. The initial rate of the reaction was found to be zero-order dependence on the concentration of cycloheptene, as is shown in Figure 4. The interpretation of this phenomenon will be described later.

Dependence on the Concentration of 2-Propanol. As shown in Figures 4, the rate depends on the first order of the concentration of 2-propanol. This indicates that the coordination of the hydrogen donor takes place before the rate-determining step. Even in the absence of hydrogen donors, 2 mol of $RhH(PPh_3)_4$ could reduce about 1 mol of cycloheptene. For example, in the presence of 0.005 mol of $RhH(PPh_3)_4$, 0.0015 mol of cycloheptene was obtained in the reaction at 70° for 1 hr and prolonged heating did not increase the yield of cycloheptane. In this reaction, the hydride of $RhH(PPh_3)_4$ may be transferred to the olefin.

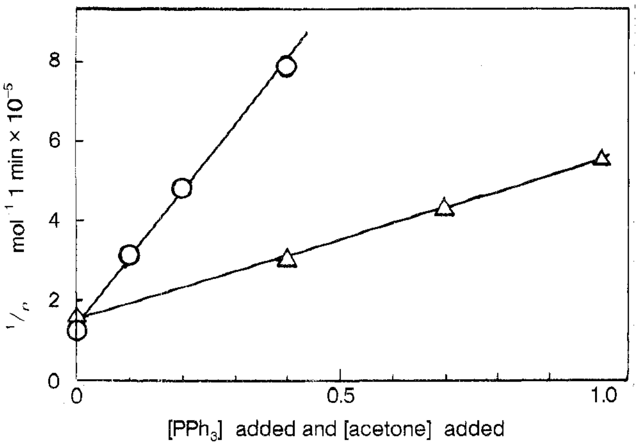


Figure 5. Plot of reciprocal of the rate of hydrogenation of cycloheptene *vs.* the concentration of added triphenylphosphine (○) (75°) and acetone (△) (70°) in toluene; 0.01 *M* RhH(PPh$_3$)$_4$, 0.5 *M* cycloheptene, and 1.0 *M* 2-propanol.

Table V
Dependence of the Rate of Hydrogenation on Reaction Temperature[a]

Temp, °K	$1/T \times 10^3$	Rate (r), mol min^{-1}	Log r
333 ± 1	3.00	2.0×10^{-4}	−3.70
343 ± 1	2.92	5.0×10^{-4}	−3.30
353 ± 1	2.82	1.1×10^{-3}	−2.97
363 ± 1	2.76	3.5×10^{-3}	−2.46
373 ± 1	2.67	5.4×10^{-3}	−2.27

[a] Reaction system was 0.01 *M* RhH(PPh$_3$)$_4$, 0.5 *M* cycloheptene, and 1.0 *M* 2-propanol in toluene.

Table VI
Molecular Weight Data for RhH(PPh$_3$)$_4$ in Benzene

Catalyst concn, mol l^{-1}	Mol wt	No. of released PPh$_3$
0.0027	482	1.4
0.0048	487	1.4
0.011	560	1.1
0.015	543	1.1

Effect of Added Triphenylphosphine. The addition of triphenylphosphine decreased the reaction rate. The reciprocal of the rate had a linear relationship with the concentration of added triphenylphosphine, as is shown in Figure 5, and the relation may be expressed in the form $1/r = a + b[\mathrm{PPh_3}]_{\mathrm{added}}$; here a and b are constants. The retarding effect of the added triphenylphosphine indicates that the reaction involves the dissociation of RhH(PPh$_3$)$_4$ to eliminate triphenylphosphine.

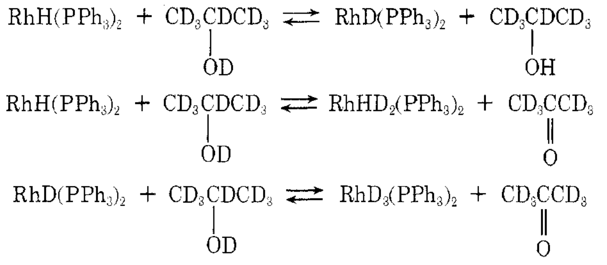
Effect of the Addition of Acetone. The addition of acetone to the reaction system also decreased the reaction rate. The relation between the rate and the concentration of added acetone is shown in Figure 5 and expressed by the formula $1/r = a' + b'[\mathrm{acetone}]_{\mathrm{added}}$, in which a' and b' are constants. This suggests that acetone competes for coordination sites of the metal complex with other reaction reagents.

Molecular Weight Measurement of RhH(PPh$_3$)$_4$. To investigate the behavior of RhH(PPh$_3$)$_4$ in the solution, the averaged molecular weight of RhH(PPh$_3$)$_4$ was measured in benzene at room temperature by a vapor pressure osmometer, and the results were summarized in Table VI. By comparison with the calculated value, 1153, the observed one, 550, seems to show that 1.1 molecules of triphenylphosphine are released from RhH(PPh$_3$)$_4$. The fact suggests the presence of a small amount of RhH(PPh$_3$)$_2$ or its solvated complexes. Perhaps the formation of the complex with two triphenylphosphines may be promoted at higher temperature, at which the transfer hydrogenation was carried out.

Isotope Effect. In order to determine the rate-limiting step, the isotopic study was carried out. As shown previously, the initial rate of the hydrogenation at 80° was 5.00×10^{-4} mol min^{-1}, while when 2-propanol-d_8 was used instead of 2-propanol the rate was 3.77×10^{-4} mol min^{-1}. The kinetic isotope effect, rate$_\mathrm{H}$/rate$_\mathrm{D}$ = 1.33, shows that a hydrogen transfer step is rate limiting. It has been reported that in the hydrogenation of 1-alkene by molecular hydrogen catalyzed by RhH(CO)(PPh$_3$)$_3$ the kinetic isotope effect, $k_\mathrm{H}/k_\mathrm{D}$, is equal to 1.47 and the transfer of hydrogen is the rate-determining step.[23] In the transfer hydrogenation, hydrogen transfer occurs twice. One is the transfer from 2-propanol to a metal complex and the other is that from a polyhydride complex to the coordinated olefin. The former is inferred to be rate determining as described later.

Hydrogenation by Molecular Hydrogen. Cyclohexene (0.5 mol) in toluene was completely hydrogenated by flowing hydrogen gas at 40° for 1 hr in the presence of RhH(PPh$_3$)$_4$ (0.01 mol). As the hydrogen transfer from alcohols to olefins was negligible at 40°, the steps involved in the hydrogenation by molecular hydrogen cannot be the rate-determining step of the transfer hydrogenation. Thus the hydrogen transfer from a polyhydride complex to the coordinated olefin cannot be rate limiting and the one from 2-propanol to a metal complex to form a trihydride complex is considered as the rate-determining step.

Infrared Spectroscopic Study. RhH(PPh$_3$)$_4$ (0.01 mol) and 2-propanol-d_8 in toluene were heated at 70° in a heating cell and submitted to an infrared analysis. Rapidly, two peaks appeared at 3600 and 1705 cm^{-1}. The strength of the former did not increase by prolonged heating. Thus the absorption may be due to the hydroxy group which resulted from the hydrogen–deuterium exchange between RhH(PPh$_3$)$_4$ and 2-propanol-d_8. That of the peak at 1705 cm^{-1} increased gradually and the absorption may be attributed to the carbonyl group of acetone which is produced by the dehydrogenation of 2-propanol. The reaction scheme might be as follows.



$$\mathrm{RhH(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{OD}}{\underset{|}{\mathrm{C}}}\mathrm{DCD_3} \rightleftarrows \mathrm{RhD(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{DCD_3}$$

$$\mathrm{RhH(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{OD}}{\underset{|}{\mathrm{C}}}\mathrm{DCD_3} \rightleftarrows \mathrm{RhHD_2(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CD_3}$$

$$\mathrm{RhD(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{OD}}{\underset{|}{\mathrm{C}}}\mathrm{DCD_3} \rightleftarrows \mathrm{RhD_3(PPh_3)_2} + \mathrm{CD_3}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CD_3}$$

Gc–Mass Spectrum. Gc–mass spectroscopic analysis of the reaction mixture, which had been heated at 100° for 4 hr in the presence of 2-propanol-d_8 (1.0 mol) instead of 2-propanol was carried out. The result showed that the percentages of d_0, d_1, d_2, d_3, and d_4 compound in the formed cycloheptenes were 27, 31, 23, 12, and 7%, respectively. The result shows clearly that hydrogen is transferred from 2-propanol to the olefin, and the formation of considerable amounts of d_0, d_1, d_3, and d_4 compounds indicates that the rapid isomerization of cycloheptene takes place.

Isomerization. In the reaction of 1-octene at 20° for 3 days, 5.4% of *n*-octane and 68.9% of the isomerized inner olefins were obtained. The result shows that the isomerization of the olefin took place faster than the hydrogenation, and it is compatible with the result of the reaction between cycloheptene and 2-propanol-d_8 described before. By the addition of acetone the hydrogenation was surpressed, while the isomerization was not. For example, the reaction of 1-octene at 100° for 15 min without the addition of acetone gave 56.5% of the isomerized inner octenes and 5.8% of *n*-octane, but the one with the addition of 1.0 mol of acetone gave 57.5% of the olefins and only 1.5% of the paraffin. The result suggests that the isomerization proceeds on a monohydride complex and the formation of the polyhydride complex, which may be an intermediate of the hydrogenation, is retarded by the presence of acetone. This is also supported by the fact that in the reaction at 60° for 30 min the isomerization was indifferent to the presence of the hydrogen donor; that is, 1-octane gave *ca.* 50% of the isomerized inner octene in the absence of 2-propanol and *ca.* 50% of the octenes and 1% of *n*-octane in the presence of the alcohol.

Discussion

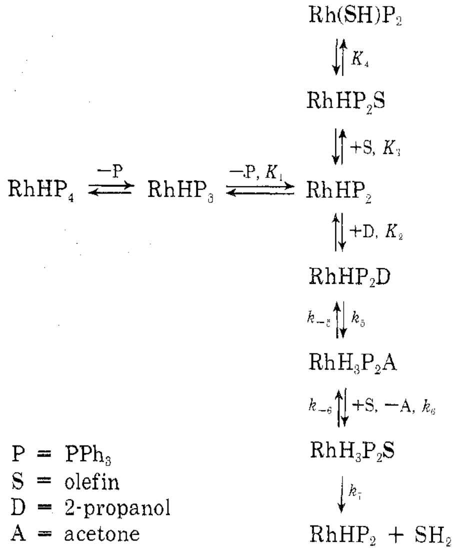
Rate-Determining Step. In the discussion of the mechanism of the transfer hydrogenation, the hydrogen transfer may be divided into three steps: (1) hydrogen transfer from the alcohol to the central Rh(I) metal to give a polyhydride Rh(III) species by the oxidative addition reaction; (2) transfer of a coordinated hydride to the coordinated olefin to form an alkyl complex; and (3) hydrogenolysis of the coordinated alkyl group by a coordinated hydride to yield the paraffin. As the existence of the kinetic isotope effect described previously showed that a hydrogen transfer step is rate limiting, one of the three steps must be rate limiting. The oxidative addition step 1 is inferred to be rate limiting for the following reasons: (a) the isomerization of olefins, which involves step 2, occurred much faster than the hydrogenation and also occurred even in the absence of hydrogen donors at room temperature; (b) the hydrogenation by molecular hydrogen, which involves step 2 and 3, took place under milder conditions than the transfer hydrogenation.

Kinetic Discussion. According to the kinetic data and the other results, the process of the transfer hydrogenation might be roughly divided into the following six steps: (1) the formation of coordinative unsaturated sites on the rhodium(I) metal by releasing triphenylphosphines from $RhH(PPh_3)_4$; (2) the coordination of 2-propanol; (3) the coordination of cycloheptene; (4) the hydrogen transfer from the hydrogen donor to the metal to form a polyhydride rhodium(III) complex; (5) the transfer of a hydrogen atom to the olefin to form an alkyl complex; and (6) the transfer of one more hydrogen atom to give cycloheptane and a rhodium(I) species. As plausible combinations of these steps, three reaction pathways may be considered: (a) 1-2-4-3-5-6; (b) 1-3-2-4-5-6; and (c) 1-3-5-2-4-6.

The assumption that step 2 occurs prior to step 3 in the transfer hydrogenation denies pathways b and c, and the assumption is supported by the following observations. (i) If step 3 proceeds prior to step 2, most of the rhodium complexes must exist in the form of olefin complexes or alkyl complexes which have no hydride ligand. However, neither olefin complexes nor alkyl complexes were detected by uv, ir, and nmr spectroscopic studies. In the uv spectroscopic study, $RhH(PPh_3)_4$ in dioxane showed several peaks at 265–280 nm, but the strength of the peaks did not change by the addition of cycloheptene. Also in the ir spectroscopic study, the strong peak of cycloheptene in benzene at 2900 cm^{-1}, which is attributable to ν_{CH}, did not change by the addition of $RhH(PPh_3)_4$. In the nmr spectrum, no peaks due to a coordinated olefin or alkyl groups were detected. (ii) The initial rate of the hydrogenation of some cycloolefins, which have different coordinating ability and steric effect, showed almost the same values. This suggests that olefins and alkyl groups, which are formed from cycloolefins, coordinated to a metal complex after the rate-determined step.

Based on the observations described previously and kinetic discussions described later, we should like to propose the following reaction (Scheme I).

Scheme I



Based on Scheme I and the assumption that the trihydride complexes are so active that steady-state treatment is applicable for trihydride species, the initial rate of the hydrogenation (r) is expressed by eq 1. The assumption described above may be reasonable, because hydrogenation by molecular hydrogen, which involves hydrogen transfer from polyhydride complex to the olefin, proceeded faster than the transfer hydrogenation. Though the complete dissociation of $RhH(PPh_3)_4$ to $RhH(PPh_3)_3$ is also assumed, the assumption may be rationalized by the result of the molecular weight measurement.

$$r = \frac{K_1K_2k_5k_6k_7[\mathrm{S}][\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}}{(k_{-5}k_7 + k_{-5}k_{-6}[\mathrm{A}] + k_6k_7[\mathrm{S}])[\mathrm{P}] + K_1 + K_1K_2[\mathrm{D}] + K_1K_3([\mathrm{S}] + K_4[\mathrm{S}])} \quad (1)$$

In the initial stage of the reaction, the concentration of acetone, formed in the reaction, is negligible. Thus the rate expression is simplified as follows (eq 2).

$$r = \frac{K_1K_2k_5k_6[\mathrm{S}][\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}}{(k_{-5} + k_6[\mathrm{S}])[[\mathrm{P}] + K_1(1 + K_2[\mathrm{D}] + (1 + K_4)K_3[\mathrm{S}])]} \quad (2)$$

As the rate has first-order dependence on the concentration of 2-propanol, the following relation should be satisfied in eq 2: $K_1K_2[\mathrm{D}] \ll [\mathrm{P}] + K_1 + K_1K_3(1 + K_4)[\mathrm{S}]$. The relation is rewritten as follows: $[RhHP_2D] \ll [RhHP_3] + [RhHP_2] + [RhHP_2S] + [Rh(SH)P_2]$. This may be reasonable in the reaction, because the spectra of $RhH(PPh_3)_4$ did not change by the addition of 2-propanol. Therefore, the rate expression becomes as follows (eq 3).

$$r = \frac{K_1K_2k_5k_6[\mathrm{S}][\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}}{(k_{-5} + k_6[\mathrm{S}])[[\mathrm{P}] + K_1(1 + K_3(1 + K_4)[\mathrm{S}])]} \quad (3)$$

Then, as the rate is the zero-order dependence on the concentration of the olefin, k_{-5} and K_1K_3 must be negligible. The former is reasonable because the step k_5, $RhHP_2D \rightarrow RhH_3P_2A$, is shown to be the rate-determining step. As K_1 is not negligible according to the result of the molecular weight measurement, the latter shows that K_3 is small; that is, the concentration of $RhHP_2S$ is far less than that of $RhHP_3$. This also agrees with the observed facts. Therefore, the rate is expressed in eq 4.

$$r = \frac{K_1K_2k_5[\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}}{[\mathrm{P}] + K_1} \qquad (4)$$

From eq 4, eq 5 is derived.

$$1/r = \frac{1}{K_2k_5[\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}} + \frac{[\mathrm{P}]}{K_1K_2k_5[\mathrm{D}][\mathrm{Rh}]_{\mathrm{total}}} \qquad (5)$$

The linear relationship between the reciprocal of the rate and the concentration of phosphine was also satisfied by the experiment shown in Figure 5.

By assuming that the concentrations of olefin, the alcohol, the catalyst, and phosphine may be regarded as almost constant at the initial stage of the transfer hydrogenation, eq 6 is derived from eq 1, where α and β are constants, and the assumption seems to be not so unreasonable. The linearity between the reciprocal of the rate and the concentration of acetone is shown in Figure 5.

$$1/r = \alpha[\text{acetone}] + \beta \qquad (6)$$

As described above, eq 1 or 4 is not contradictory to any observed fact and is able to explain all the experimental results. This supports the proposed reaction scheme.

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Catalytic Hydrogenolysis of Lumitestosterone Acetate

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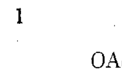
The hydrogenolysis of lumitestosterone acetate (**3**) over palladium in ethanol gave a mixture of products from which 17β-acetoxy-5α,10α-androstane (**7**), 5α-ethoxy-17β-acetoxy-10α-androstane (**9a**), and 17β-acetoxy,5α,10α-androstan-2α-ol (**12**) were isolated. These same products were also obtained from the Raney nickel catalyzed hydrogenolysis of **3**. In the later reaction a very small amount of 17β-acetoxy-5β,10α-androstan-2α-ol (**18**) was also obtained. The lack of stereoselectivity in this hydrogenolysis led to the proposal of a mechanistic rationale involving an initial catalytic isomerization of **3** to 17β-acetoxy-10α-androst-5-en-2-one (**17**) followed by the hydrogenation of **17** to give the 5α products.

While it appears that alkyl-substituted cyclopropane hydrogenolysis is nonstereoselective,[2] some reports have indicated that the hydrogenolysis of cyclopropyl ketones[3,4] or esters[5] is a stereoselective process. For instance, it has been shown[4] that the hydrogenolysis of a 10β-methyl-1α,5α-cyclo-2-keto steroid, **1**, gives only the 5α product, **2**, by what appears to be a stereospecific cleavage of the 1α,5α bond of the cyclopropane ring. In light of these reports it was felt that the hydrogenolysis of a 10α-methyl-1β,5β-cyclo-2-keto steroid such as lumitestosterone acetate (**3**) should provide a reasonable access route to the rather difficultly available 10α,5β steroids, **4**. This assumption was further supported by an examination of a molecular model of **3** which showed that the 1,5 bond was the most readily accessible to the catalyst surface of the three cyclopropane bonds in **3**.

It should be noted, though, that the ring cleavage in the 10α-methyl compounds (*e.g.*, **3**) is not as facile as it is in the 10β-methyl series (**1**). Hydrogenation of the Δ^3-10β-methyl-1α,5α-cyclo steroid, **5**, over palladium at room temperature and atmospheric pressure gave a 2:1 mixture of compounds **1** and **2**.[4a] Under comparable conditions hydrogenation of the Δ^3-10α-methyl-1β,5β-cyclo steroids, **6**, gave only the cyclopropyl ketones, such as **3**, with no ring-opened material formed.[6]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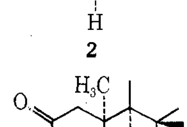
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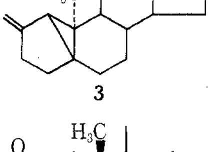
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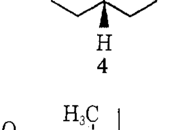
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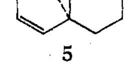
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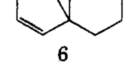
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