

Transfer-Hydrogenation and Transfer-Hydrogenolysis. III. Hydrogen Transfer from Dioxane to Olefins Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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Abstract: Hydrogen transfer from 1,4-dioxane to olefins catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ occurred. Stoichiometric amounts of paraffins and dioxene were formed from olefins and dioxane. After the reaction, the dioxane complex, $\text{RhCl}(\text{PPh}_3)_2(\text{C}_4\text{H}_8\text{O}_2)$, was isolated. The large value of the kinetic isotope effect, $R^H/R^D = 3.1$, in the use of octa-deuteriodioxane and the kinetic result showed that the rate-determining step of the reaction is the dehydrogenation, that is, the formation of the monohydride complex, $\text{RhClH}(\text{C}_4\text{H}_7\text{O}_2)(\text{PPh}_3)_2$, by the oxidative addition of dioxane by the cleavage of a C-H bond.

In catalytic transfer-hydrogenation,¹ the donation of hydrogen to olefins by alcohols² and six-membered cyclic olefins³ has clearly been shown. However, with the exception of alcohols there seems to have been no report of double hydrogen abstraction from saturated compounds by soluble complexes.⁴

We have reported previously that a saturated cyclic ether, 1,4-dioxane, donated hydrogen to an olefin to give stoichiometric amounts of dioxene and a paraffin in the presence of $\text{RhCl}(\text{PPh}_3)_3$.⁵ This complex not only has high catalytic activity in the hydrogen transfer reaction but also has been thoroughly studied in the hydrogenation of olefins by molecular hydrogen by Wilkinson and other researchers.^{4,6} It was expected that the information on the properties of this complex in the latter reaction would help to clarify the mechanism of the transfer-hydrogenation easier.

Experimental Section

Materials. $\text{RhCl}(\text{PPh}_3)_3$ was prepared by the method of Wilkinson, *et al.*⁷ Olefins were purified prior to use by passage through a silica gel and neutral alumina column, followed by distillation over sodium. Dioxane and toluene were distilled over sodium. Octa-deuteriodioxane (Deutration grade; min 99%, E. Merk) was dehydrated by molecular sieves. Pyrocatechol was purified by recrystallization from benzene. Dioxene was synthesized by the method of Summerbell and Umhoefer.⁸

An Example of Transfer-Hydrogenation. Cyclopentene (0.034 g, 0.5 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (0.0185 g, 0.02 mmol) were put into a Pyrex glass tube which had been sealed at one side. Into the mixture, dioxane 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 with liquid

nitrogen. The sealed tube was heated for 1 hr in a silicone-oil bath kept at $170 \pm 1^\circ$. The catalyst dissolved slowly at room temperature, but quickly at the elevated temperature. Gas-liquid chromatographic analysis was performed at 80° with a Hitachi-Perkin-Elmer instrument equipped with a flame ionization detector, using $10 \mu\text{l}$ of *n*-propylbenzene as an internal standard. A $2 \text{ m} \times 6 \text{ mm}$ stainless steel column packed with 25% 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 Runs. Five samples, prepared by the method described above, were heated in a silicone oil bath kept at $170 \pm 1^\circ$ for 6, 8, 10, 12, and 14 min, respectively. The reaction mixtures were submitted to the gas-liquid chromatographic analysis.

From the reaction mixtures in the sealed tubes, red crystals separated on standing overnight at room temperature. The crystals were collected on a filter, washed with a small amount of ether, dried *in vacuo*, and submitted to elemental, nmr, and ir analysis.

Preparation of $\text{RhCl}(\text{PPh}_3)_2(\text{C}_4\text{H}_8\text{O}_2)$. $\text{RhCl}(\text{PPh}_3)_3$ (0.074 g) and dioxane (4 ml) were sealed in a Pyrex glass tube under vacuum and heated at 120° for 30 min. The red needles formed upon cooling were separated by filtration, washed with ether, dried, and shown to be identical with the ones isolated in the transfer-hydrogenation.

$[\text{RhCl}(\text{PPh}_3)_2]_2$ was prepared in toluene or ethyl methyl ketone by the method of Osborn, *et al.*⁷

Kinetic Isotope Effect. Cyclopentene (0.017 g, 0.25 mmol), $\text{RhCl}(\text{PPh}_3)_3$ (0.0185 g, 0.02 mmol), and octa-deuteriodioxane (0.192 g, 2.0 mmol) or dioxane (0.176 g) were placed in the Pyrex glass tube. Into the mixture, toluene was added and the total volume of the 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 chromatographic and gas-mass spectroscopic analysis.

Results

Outline of Transfer-Hydrogenation. To determine favorable reaction conditions, cyclopentene and $\text{RhCl}(\text{PPh}_3)_3$ were heated in dioxane with or without additives under various conditions. The results are summarized in Table I. Under appropriate conditions the hydrogenation proceeds almost completely. The reduction of the olefin was retarded by the addition of 2-propanol which has strong ability to donate hydrogen in some other cases.⁹ The reaction was not retarded at all by the addition of pyrocatechol which is an inhibitor of radical reactions. Consequently, the reaction may not proceed *via* radical species.¹⁰

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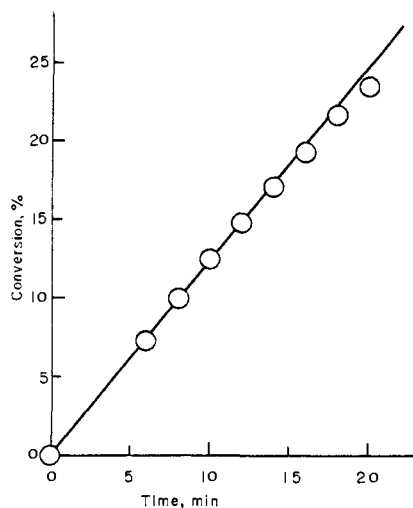


Figure 1. The conversion of cyclopentene vs. time curve.

Table I. Summary of the Transfer-Hydrogenation^a

Temp, °C	Time, hr	Additive (0.5 M)	Conversion, %
120	15	None	6
130	14	None	14
140	7	None	40
150	1	None	22
150	1	2-Propanol	13
150	1	Pyrocatechol	23
150	6	Pyrocatechol	82
170	10	None	100
200	1	Pyrocatechol	94 ^b

^a Cyclopentene (0.5 M) and RhCl(PPh₃)₃ (0.02 M) were heated in dioxane. ^b The concentration of the catalyst was 0.01 M.

Unless otherwise noted, the transfer-hydrogenation was carried out in any instance under the condition that a dioxane solution of 0.5 M cyclopentene and 0.02 M RhCl(PPh₃)₃ was heated at 170° in a degassed Pyrex glass tube.

Dependence of Conversion on Time. Figure 1 shows an example of the conversion of cyclopentene to cyclopentane against reaction time plots. At the initial state of the reaction, the conversion was proportional to the time, partly because the initial rate of the reaction is independent on the concentration of the olefin as described later. However, the linearity did not hold in the conversion more than 20%, perhaps because the formed dioxene competes with cyclopentene for a vacant coordination site of the catalyst. The initial rate of the reaction was derived from the linear part.

Source of Hydrogen. When 0.5 M cyclopentene was heated in dioxane at 180° for 1 hr along with the catalyst, the formation of 0.43 M dioxene and 0.42 M cyclopentane in addition to the survival of 0.08 M cyclopentene was shown by gas-liquid chromatographic analysis of the reaction mixture.¹¹ Dioxene was identified by comparison with authentic samples.⁸ This result and other observations are summarized as follows: (1) the amount of the dioxene was equal to that of cyclopentane within experimental error; (2) the total amount of the cyclopentane and cyclopentene was equal to the amount of the charged cyclopentene; (3) only a negligible

(11) This result was offered by K. Tachi and will be published separately along with other results.

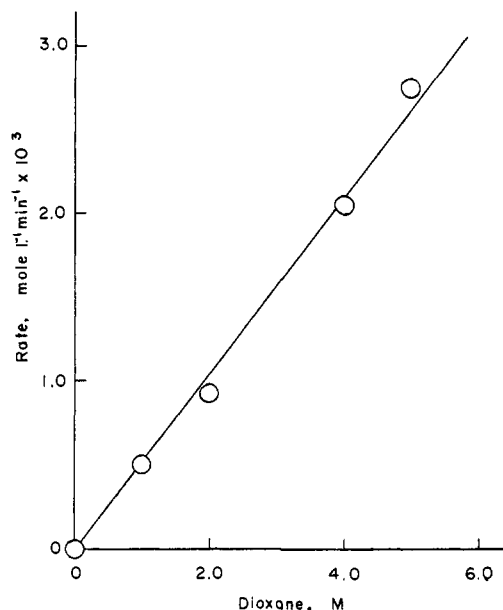
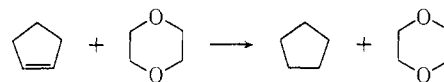


Figure 2. The dependence of the initial rate on the concentration of dioxane in toluene. Cyclopentene (0.5 M), the catalyst (0.02 M), and dioxane in toluene were heated at 170°, and the dimer, [RhCl(PPh₃)₂]₂, was the only complex obtained after the reaction.

amount of cyclopentadiene or the products of Diels-Alder reactions involving the diene was detected; (4) the reduction did not proceed without dioxane in toluene and the initial rate was proportional to the amount of dioxane in toluene as shown in Figure 2; (5) when cyclopentene and RhCl(PPh₃)₃ were heated in dioxane-*d*₈, the main product was found to be cyclopentane-*d*₂ by gas-mass spectroscopic study. The percentage of cyclopentane-*d*₂ in cyclopentanes was more than 90% in most cases, though it was varied by the reaction condition and the conversion. Some isomerization of cyclopentene was inferred, because small amounts of -*d*₃, -*d*₁ and cyclopentane-*d*₀ were formed in addition to cyclopentane-*d*₂. These results indicate that the reduction is not caused by the disproportionation of the olefin but by the hydrogen transfer such as the following.



Isolation of a Reaction Intermediate. After the reactions in dioxane, orange-red needles (A) were isolated by leaving the reaction mixtures at room temperature. The structure of A was inferred as RhCl(PPh₃)₂(C₄H₈O₂), formed by replacing a triphenylphosphine of RhCl(PPh₃)₃ by a dioxane molecule. The identification of the structure of A was based on the following grounds: (1) the value of the elemental analysis of A fitted the calculated value (Anal. Calcd for C₄₀H₃₈ClO₂P₂Rh: C, 66.72; H, 5.32. Found: C, 66.88; H, 5.16). (2) The ¹H nmr spectrum in CDCl₃ has a peak assignable to dioxane (singlet, τ 6.3) and peaks attributable to the aromatic hydrogens of triphenylphosphines (multiplet centered at τ 2.7). The ratio of the area of the former to that of the latter was about 1:4 and nearly equal to the calculated value. (3) A was obtained also by dissolving RhCl(PPh₃)₃ in dioxane on warming and then cooling the solution. (4) Though

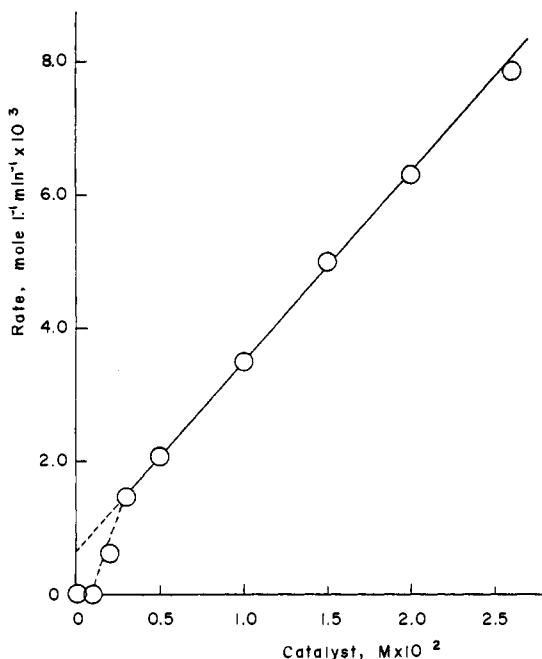


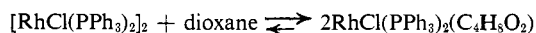
Figure 3. The dependence of the initial rate on the catalyst concentration.

$\text{RhCl}(\text{PPh}_3)_3$ has been reported to give the dimer, $[\text{RhCl}(\text{PPh}_3)_2]_2$, on heating in solvents such as toluene and ethanol,⁷ the infrared spectrum of A is different from the dimer and has peaks attributable to coordinated dioxane at 870 and 890 cm^{-1} .

Notwithstanding the report that $\text{RhCl}(\text{PPh}_3)_3$ gave $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ on warming in dioxane with excess triphenylphosphine and $[\text{RhCl}(\text{PPh}_3)_2]_2$ without the excess phosphine,⁷ we observed neither the formation of the carbonyl complex nor the dimer in the transfer-hydrogenation in dioxane.

Moreover, the dimer gave $\text{RhCl}(\text{PPh}_3)_2(\text{C}_4\text{H}_8\text{O}_2)$ on warming in dioxane. Perhaps the complexing ability of dioxane is strong enough to cleave the chloro bridges of the dimer.

In spite of the report that the dimer has no catalytic activity in the reduction by molecular hydrogen,⁷ it had nearly twice as strong activity as $\text{RhCl}(\text{PPh}_3)_3$ in the transfer-hydrogenation in dioxane. From these facts, it is inferred that the following equilibrium is almost completely to the right side in dioxane. The inference



is also supported by the relation between the reaction rate and the concentration of $\text{RhCl}(\text{PPh}_3)_3$ described later.

Dependence on Kinds of Olefins. Table II shows the initial rate of the transfer-hydrogenation of cycloolefins. There is little difference among the rates of the reaction of cyclomonoenes except for cyclohexene. This suggests that the coordination of monoenes occurs after the rate-determining step. A smaller rate of reaction of cyclohexene might be caused by the retarding effect of a trace of benzene, which was formed by the disproportionation of cyclohexene. This reasoning may be supported by the fact that the rate of reduction of cyclopentene was depressed to about one-eighth by the addition of 0.5 M benzene. The reactivity of 1,3-cyclooctadiene was much smaller than that of

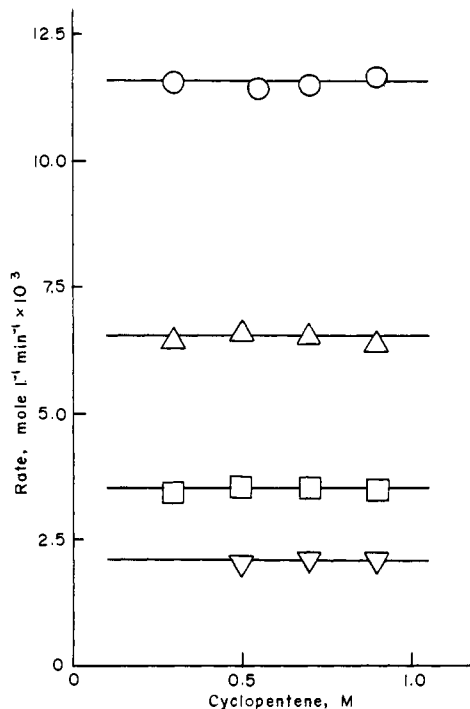


Figure 4. The dependence of the initial rate upon the concentration of cyclopentene: (O) at 180°, (Δ) at 170°, (\square) at 160°, and (∇) at 150°.

Table II. The Transfer-Hydrogenation of Cycloolefins

Cycloolefin (0.5 M)	Initial rate, mol $\text{l}^{-1} \text{min}^{-1} \times 10^3$
Cyclopentene	6.2
Cyclopentene	0.8 ^a
Cyclohexene	4.0
Cycloheptene	5.9
Cyclooctene	6.1
1,3-Cyclooctadiene	1.2 ^b
1,5-Cyclooctadiene	0 ^b

^a 0.5 M of benzene was added. ^b Calculated from the rate of the formation of dioxene.

monoenes, and 1,5-cyclooctadiene was not reduced. The inactivity of the latter diene may be rationalized either by the assumption that the strong coordinating power of the chelating diene takes the coordinative unsaturation away from the catalyst or by the assumption that the double bonds of the diene as ligands make the formation of a dihydride complex difficult. The rationalization is based on the report⁷ that (1) chelating dienes form stable complexes with Rh(I) species, (2) a double bond as a ligand is strongly π acidic and resembles carbon monoxide, and (3) the oxidative addition of molecular hydrogen to the complexes with ligands of stronger π acidity is harder.

Dependence on the Catalyst Concentration. It has been reported that the dimerization of $\text{RhCl}(\text{PPh}_3)_3$ to the inactive species, $[\text{RhCl}(\text{PPh}_3)_2]_2$, takes place in the reduction by molecular hydrogen in benzene and that the rate is expressed in the form: $R = \alpha'[\text{RhCl}(\text{PPh}_3)_3] - \beta'[\text{RhCl}(\text{PPh}_3)_3]^2 + \gamma'$, in which α' , β' , and γ' are constants.⁷ However, the rate of the transfer-hydrogenation was expressed in the form $R = \alpha[\text{RhCl}(\text{PPh}_3)_3] + \gamma$ (α and γ are constants.), as seen from Figure 3. In the region where the catalyst con-

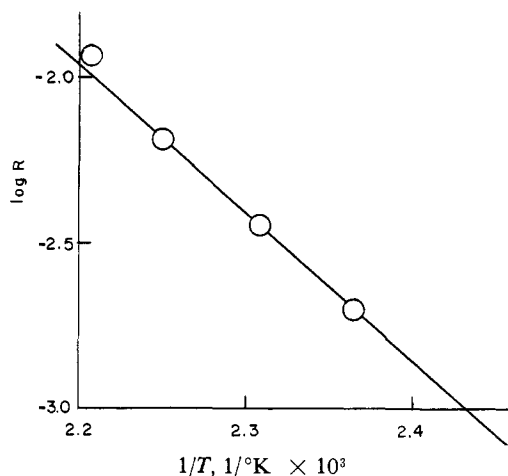


Figure 5. Arrhenius plot of the transfer-hydrogenation at 180°, 170°, 160°, and 150°.

centration was higher than 0.003 *M*, the rate might be regarded as having pseudo-first-order dependence on the catalyst concentration. The observation suggests that the poisoning of the catalyst by the dimerization, which occurs more easily at higher catalyst concentration, does not take place in this reaction. It is supposed that the reaction proceeds by a different mechanism in the region of the catalyst concentration lower than 0.003 *M*.

Dependence of the Olefin Concentration. In contrast to the reduction by molecular hydrogen in which the coordination of an olefin to the dihydride complex, $\text{RhClH}_2(\text{PPh}_3)_2(\text{solvent})$, by replacing a solvent molecule, is the rate-determining step and the influence of the olefin concentration on the rate is rather complicated,⁷ the initial rate of the transfer-hydrogenation was independent of the concentration of cyclopentene, as seen from Figure 4. The zero-order dependence may be explained either by the assumption that the coordination of the olefin 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 as to cause a leveling effect. The former assumption seems to be more plausible, because (1) the complexing ability of inner olefins to $\text{RhCl}(\text{PPh}_3)_3$ is not so strong,⁷ and (2) the ultraviolet and the visible spectra of a solution of $\text{RhCl}(\text{PPh}_3)_3$ in dioxane were hardly changed by the addition of cyclopentene. Furthermore, it may be assumed that a hydrido Rh(III) complex, which is formed by an oxidative addition to the Rh(I) species having cyclopentene as a ligand, exists in only small amounts in the reaction mixture, because (1) there was no retarding effect of cyclopentene, (2) the rate-limiting step of the reaction is the formation of a hydride complex by an oxidative addition (see later), and (3) an olefin as a ligand seems to make the formation of a hydride complex more difficult as described earlier.

Dependence on Temperature. Initial rates were measured at 180, 170, 160, and 150° for various cyclopentene concentrations as shown in Figure 4, and a plot of $\log R$ against $1/T$ was shown in Figure 5. A rather good linear plot is obtained, indicating that the kinetics of the system are not complicated. A small deviation from the linear relation was observed at 180°. Perhaps this is caused by the partial irreversible decomposition of the catalyst, for the yield of the recovered

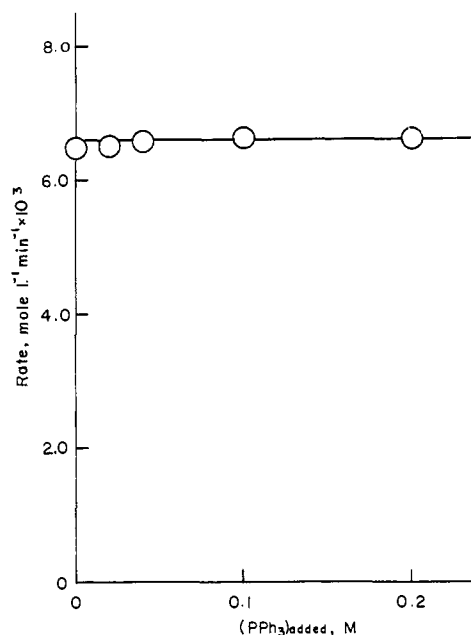


Figure 6. The dependence of the initial rate upon the added triphenylphosphine.

complex, $\text{RhCl}(\text{PPh}_3)_2(\text{C}_4\text{H}_8\text{O}_2)$, was lower in the reaction at that temperature. The value for the activation energy, E_a , of 21.6 kcal mol⁻¹ is obtained from the gradient from the linear line in Figure 5.

Effect of Added Phosphine. It has been reported that the addition of an excess of triphenylphosphine inhibits the reduction by molecular hydrogen⁷ and the reaction rate reaches the maximum when the ratio of triphenylphosphine to Rh is equal to 2.¹² In contrast, the rate of the transfer-hydrogenation was not decreased at all by the addition of the phosphine as shown in Figure 6. This may be interpreted by the assumption that the complexing ability of dioxane is so strong as to replace a triphenylphosphine of $\text{RhCl}(\text{PPh}_3)_3$ almost completely even in the presence of an excess of the phosphine.

Kinetic Isotope Effect. The initial rate of the reduction in which cyclopentene (0.25 *M*), dioxane (2.0 *M*) and the catalyst (0.02 *M*) in toluene were heated at 180° was 2.1×10^{-3} mol l. min, while that of the one in which octadeuteriodioxane was used instead of dioxane was 6.9×10^{-4} . The value of the isotope effect, $R^{\text{H}}/R^{\text{D}} = 3.1$, shows that a hydrogen transfer step is rate determining¹³ and exhibits a clear contrast to the reduction by molecular hydrogen in which the isotope effect is 0.78–1.0^{7,14} or 1.10–1.17¹⁵ and the replacement of a solvent molecule from $\text{RhClH}_2(\text{PPh}_3)_2(\text{solvent})$ by an olefin is rate limiting.

Discussion

The reduction of olefins by molecular hydrogen has been studied thoroughly by many researchers,^{4,5} and the mechanism shown in Scheme I proposed.⁷ As the

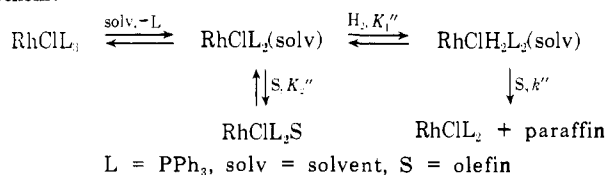
(12) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1059 (1968).

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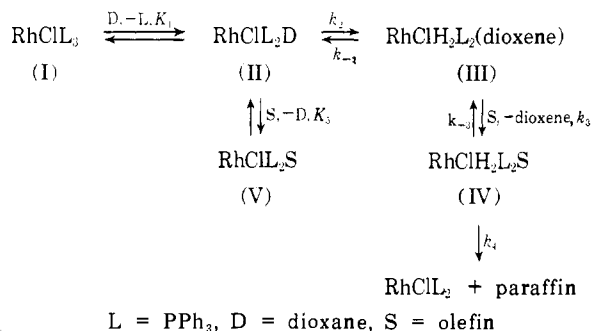
Scheme I



hydrogenation, the isomerization,¹⁶ and the hydrogen-deuterium exchange¹⁷ of olefins under molecular hydrogen in the presence of $\text{RhCl}(\text{PPh}_3)_3$ proceed easily even at room temperature, any step involved in these reactions may be faster at the elevated temperatures at which the transfer-hydrogenation proceeded.

Based on the studies on these reactions and the facts described in the Results, we should like to propose Scheme II for the transfer-hydrogenation. From

Scheme II



Scheme II and the assumptions described below, the rate is expressed as eq 1, where [S], [D], [L], and [C] are the concentration of cyclopentene, dioxane, triphenylphosphine, and the catalyst, respectively. The assumptions which seem reasonable are: (1) the inter-

$$R = \frac{k_2 k_3 K_1 [S][D][C]}{(k_{-2} + k_3[S])([L] + K_1[D] + K_1 K_5'[S])} \quad (1)$$

mediates, III and IV, are in steady state and the concentration of them is small, because the transfer of the hydrides to olefins in the complexes is faster, (2) the amount of the formed dioxane is negligible at the initial stage of the reaction,¹⁸ and (3) the change of the concentration of dioxane which is a hydrogen donor and solvent is negligible.

By introducing the expression, $K_1' = K_1[D]$ and $K_5' = K_5/[D]$, based on the last assumption, we rearranged eq 1 as

$$\begin{aligned}
 1/R &= \frac{k_{-2}([L] + K_1')}{k_2 k_3 K_1 [C]} \frac{1}{[S]} + \\
 &\quad \frac{k_3([L] + K_1') + k_{-2} K_1' K_5'}{k_2 k_3 K_1 [C]} + \frac{K_5'}{k_2 [C]} [S] \quad (2)
 \end{aligned}$$

As the rate of the reduction was independent of the concentration of the olefin, the coefficients which are divided or multiplied by the concentration of the olefin

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(17) (a) A. I. Odell, J. B. Richardson, and W. R. Roper, *J. Catal.*, **8**, 393 (1967); (b) A. S. Hussey and Y. Takeuchi, *J. Org. Chem.*, **35**, 643 (1970); (c) G. V. Smith and R. Shuford, *Tetrahedron Lett.*, 525 (1970).

(18) $R = k_4[\text{IV}] = k_3[\text{S}][\text{III}]$ is derived from this assumption, so k_4 does not appear in eq 1.

must be so small as to be negligible. By assuming that the coefficient of the first term in eq 2 is zero, k_{-2} is supposed negligible at the initial stage of the reaction. Further assumption that the third term is negligible suggests $K_5' = 0$. This means that the concentration of the Rh(I)-olefin complex is negligibly small because $[V] = K_5'[\text{II}][\text{S}]$, and the inference is compatible with the experimental results mentioned earlier. Then, the rate expression can be reduced to

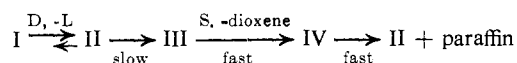
$$R = \frac{k_2 K_1 [C]}{[L] + K_1'} \quad (3)$$

As described earlier, the addition of excess triphenylphosphine did not retard the transfer-hydrogenation at all. In eq 3, this fact appears to mean $K_1 \gg [L]$, i.e., $\text{RhCl}(\text{PPh}_3)_3 + \text{dioxane} \rightleftharpoons \text{RhCl}(\text{PPh}_3)_2(\text{dioxane}) + \text{PPh}_3$. Then, the rate expression becomes

$$R = k_2 [C] \quad (4)$$

Though k_2 is the function of the concentration of dioxane, it is shown that the dehydrogenation from dioxane is rate limiting and the conclusion is compatible with the experimental results.

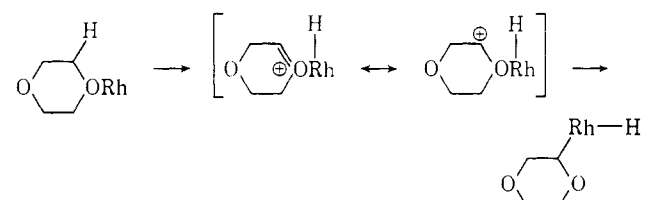
In summary, the reaction in an early stage appears to proceed in the following way.



Though the dehydrogenation step involves the formation of the monohydrido complex, $\text{RhClH}(\text{C}_4\text{H}_7\text{O}_2)(\text{PPh}_3)_2$ or $\text{RhClH}(\text{C}_4\text{H}_7\text{O}_2)(\text{PPh}_3)_2\text{S}'$ ($\text{S}' = \text{dioxane}$ or olefin), and that of the dihydrido complex, $\text{RhClH}_2(\text{PPh}_3)_2$ or $\text{RhClH}_2(\text{PPh}_3)_2\text{S}'$, the rate-determining step is inferred to be the formation of the monohydrido alkyl complex by the oxidative addition of dioxane by cleavage of a C-H bond,¹⁹ on the following grounds: (1) a large kinetic effect, $R^H/R^D = 3.0$, was observed. (2) as the reduction,^{4,6} the isomerization,¹⁶ and the hydrogen-deuterium exchange¹⁷ of olefins under hydrogen gas take place under milder conditions than the transfer-hydrogenation, the steps which can correspond to the steps in the former reactions may not be rate determining in the latter. All the hydrogen transfer steps in the latter other than the oxidative addition step have the corresponding ones in the former which involve the steps, $\text{RhClH}_2(\text{PPh}_3)_2(\text{olefin}) \rightleftharpoons \text{RhClH}(\text{alkyl})(\text{PPh}_3)_2 + \text{solvent} \rightarrow \text{RhCl}(\text{PPh}_3)_2(\text{solvent}) + \text{paraffin}$.

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(19) By analogy to hydride removal from alcohols, a referee suggested the following scheme for the dehydrogenation step from dioxane or



the insertion of a Rh(I) species to the C-H bond might be a concerted one-step reaction.