June, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (6), 1453—1459 (1977) 1453

# Kinetic Study of Oxidative Addition and Replacement Reactions of Chlorotris(triphenylphosphine)rhodium(I) in Benzene

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(Received August 7, 1976)

Chlorotris(triphenylphosphine)rhodium(I) exists in benzene as $RhCl(PPh_3)_3$, a dimeric species $[RhCl(PPh_3)_2]_2$ and a reaction intermediate $RhCl(PPh_3)_2$. The rates of oxidative addition and replacement reactions were examined in benzene. For the oxidative addition reaction, $RhCl(PPh_3)_3$, $RhCl(PPh_3)_2$, or $[RhCl(PPh_3)_2]_2+X_1 \overset{k_{add}}{\rightleftharpoons}$ Products ($X_1=H_2$, $O_2$, $C_2H_4$, $CHCl{=}CCl_2$, $CH_3I$), it was found that the reaction intermediate $RhCl(PPh_3)_2$ is most reactive, the degree of its reactivity depending largely on the reactants ($X_1$). A significant enhancement of the rate ($k_{sub}>k_{add}$) was observed for the ligand substitution reaction, $RhClX_1(PPh_3)_m+X_2 \overset{k_{sub}}{\rightleftharpoons} RhClX_2(PPh_3)_n+X_1$ ($m, n=3$ or 2), where $X_1=H_2$ and $X_2=$olefin and *vice versa*. The results are discussed in relation to the mechanism of hydrogenation.

In recent years homogeneous reactions catalyzed by metal complexes have attracted attention and have been studied extensively.[1] Wilkinson's complex, chlorotris(triphenylphosphine)rhodium(I), is well known owing to its high reactivity in hydrogenation reactions.[2-6] A number of works have appeared on the mechanisms of the hydrogenation reactions catalyzed by this complex. In most works the overall rate of the reactions was determined by following the rate of $H_2$ gas absorption[3,4] or the change in concentration of the reactant and the product by gas-liquid chromatography.[7,8] The mechanisms of the hydrogenation of olefins were assumed by the dependence of the overall rate on the reactant concentrations. However, this sometimes leads to erroneous conclusions. There is another method in which the concentration change of the identified species of metal complexes or metal-reactant complexes is followed in solution. From the transient change of the species, it would be possible to establish the sequence of the reaction steps leading to the final hydrogenation products. Halpern and Wong studied the $H_2$ addition on Wilkinson's complex in benzene with a stopped-flow apparatus.[9] They determined the rate constant for several elementary steps with little ambiguity. We applied a similar method to study monomer⇄dimer reactions of Wilkinson's complex, $2RhCl(PPh_3)_3 \rightleftharpoons [RhCl(PPh_3)_2]_2+2PPh_3$, in benzene,[10] and identified the total mechanisms of the above reaction taking the intermediate species $RhCl(PPh_3)_2$ into consideration.

As an extension of the above work we report on the results of kinetic studies on the reactivities of the three species for the addition and the replacement reactions,

$$RhCl(PPh_3)_3,\ RhCl(PPh_3)_2,\ [RhCl(PPh_3)_2]_2 + X_1 \rightleftharpoons \text{Products} \quad \text{(addition)}$$

$$RhClX_1(PPh_3)_m + X_2 \rightleftharpoons RhClX_2(PPh_3)_n + X_1, \quad \text{(replacement)},$$

where X denotes a substrate and $m, n=3$ or 2. The intermediate structure of Wilkinson's complex during the course of hydrogenation is also discussed.

## Experimental

Chlorotris(triphenylphosphine)rhodium(I) was prepared by the method described by Osborn *et al.*[3] Di-$\mu$-chloro-tetrakis(triphenylphosphine)dirhodium(I) $[RhCl(PPh_3)_2]_2$ was obtained by dissolving Wilkinson's complex in benzene *in vacuo* and heating at *ca.* 60 °C. The precipitate was rapidly filtered and stored *in vacuo*. For the kinetic measurements it was solubilized in benzene by warming at 60 °C *in vacuo*. Triphenylphosphine was recrystallized from ethanol. Benzene, trichloroethylene, and acrylonitrile were distilled. Hydrogen, oxygen, ethylene, and methyl iodide were used without purification. The concentrations of $H_2$, $O_2$, and $C_2H_4$ at 1 atm were calculated from the solubility data.[11] The concentrations of $H_2$ and $C_2H_4$ were obtained by the gas-chromatography with a Molecular sieve 5A.

All the reactions were studied at 20 °C in oxygen-free benzene. The addition reactions of $CHCl{=}CCl_2$ and $CH_3I$ were slow enough to measure with a Hitachi recording spectrophotometer model EPS-3T *in vacuo*. The progress of the reaction was followed by the absorbance change at 400 nm for $CHCl{=}CCl_2$ and 430 nm for $CH_3I$. The experiments of the addition and the replacement reactions involving $C_2H_4$, $CH_2{=}CHCN$, $H_2$, and $O_2$ were carried out with a Union Giken RA-1300 stopped-flow apparatus. The addition and the replacement reactions of $C_2H_4$ and $CH_2{=}CHCN$ were followed by the absorbance change at 422 nm and 400 nm, respectively. The addition reaction of $O_2$ was followed at 400 nm or 440 nm. The replacement reactions, $RhClX_1(PPh_3)_m+X_2 \rightleftharpoons RhClX_2(PPh_3)_n+X_1$ ($m, n=3$ or 2), were observed by mixing an $X_2$ solution with an $RhClX_1(PPh_3)_m$ solution, where $X_1=H_2$ and $X_2=$olefin and *vice versa*. Above reactions were followed either by the decrease of $RhClX_1(PPh_3)_m$ or by the increase of $RhClX_2(PPh_3)_n$.

## Results and Discussion

*Oxidative Addition Reactions.* Figure 1 shows the visible spectra of the addition products between $RhCl(PPh_3)_3$ ($5.0\times10^{-4}$ M) and $H_2$ ($1.4\times10^{-3}$ M), $O_2$($4.6\times10^{-3}$ M), $C_2H_4$ ($7.5\times10^{-2}$ M), $CH_2{=}CHCN$($1.5\times10^{-1}$ M), $CHCl{=}CCl_2$ (0.56 M), and $CH_3I$ ($2.5\times10^{-2}$ M). The values in parentheses are the initial concentrations of the reactants.

*Addition of Ethylene*: Ethylene reacts reversibly with Wilkinson's complex to produce $RhCl(C_2H_4)L_2$, where $L=PPh_3$.[3,12] The stoichiometry of the reaction is

$$RhClL_3 + C_2H_4 \rightleftharpoons RhCl(C_2H_4)L_2 + L. \tag{1}$$

The equilibrium constant of Eq. 1 is calculated to be $K=0.4$, which agrees with the value obtained by Tolman and co-workers.[12] The pseudo-first-order rate constant

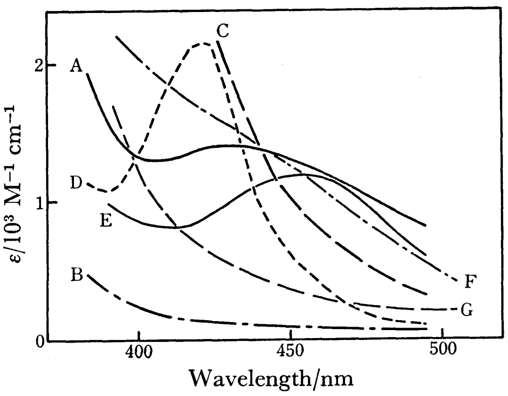


Fig. 1. Visible spectra of the equilibrium addition products on $RhClL_3$. $[RhClL_3]=5.0\times10^{-4}$ M, and $[PPh_3]=3\times10^{-3}$ M was added to exclude dimer formation. (A) none, (B) $H_2$ ($1.4\times10^{-3}$ M), (C) $O_2$ ($4.6\times10^{-3}$ M), (D) $C_2H_4$ ($7.5\times10^{-2}$ M), (E) $CH_2$=CHCN ($1.5\times10^{-1}$ M), (F) $CHCl$=$CCl_2$ ($5.6\times10^{-1}$ M), (G) $CH_3I$ ($2.5\times10^{-2}$ M). The values in the parentheses are the initial concentrations of the reactants.

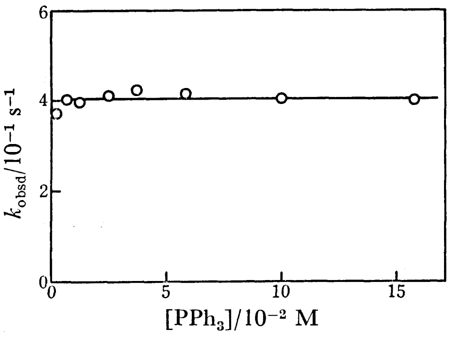


Fig. 2. Dependence of the observed rate constant of the ethylene addition reaction on the concentration of $PPh_3$. $[RhCl(PPh_3)_3]_0=5.0\times10^{-4}$ M, $[C_2H_4]=7.5\times10^{-2}$ M, and at 422 nm.

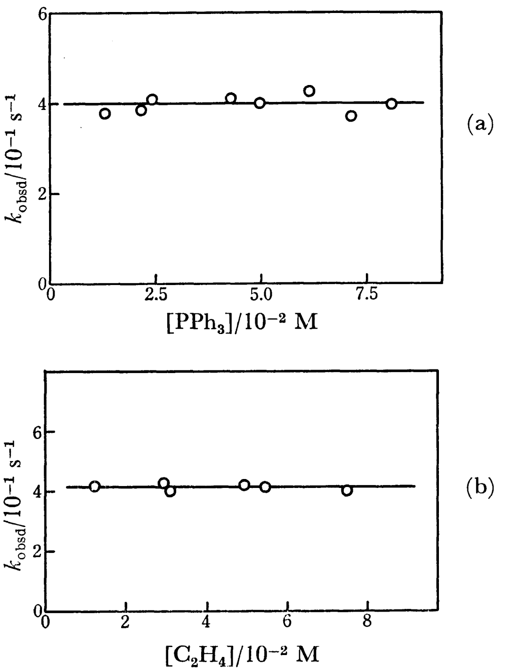


Fig. 3. Dissociation rate of ethylene from $RhCl(C_2H_4)(PPh_3)_2$. (a) Plot of $k_{obsd}$ *vs.* $[PPh_3]$. $[RhCl(C_2H_4)(PPh_3)_2]_0=5\times10^{-4}$ M, $[C_2H_4]=7.5\times10^{-2}$ M, and at 422 nm. (b) Plot of $k_{obsd}$ *vs.* $[C_2H_4]$. $[RhCl(C_2H_4)(PPh_3)_2]_0=5\times10^{-4}$ M, $[PPh_3]=5.2\times10^{-2}$ M, and at 422 nm.

of the ethylene addition, $k_{obsd}$, is dependent neither on the concentration of L (0.002—0.16 M) (Fig. 2) nor on that of ethylene (0.025—0.075 M) added. The rate of the dissociation of ethylene from $RhCl(C_2H_4)L_2$ was measured by mixing the solution of L with the solution of the ethylene complex, $RhCl(C_2H_4)L_2$. The dissociation rate constant is also independent of the concentrations of L (0.012—0.081 M) (Fig. 3a) and ethylene (0.012—0.075 M) (Fig. 3b). The results are consistent with the following mechanism:

$$\mathrm{RhClL_3 + C_2H_4} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RhClL_2 + L + C_2H_4}$$
$$\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{RhCl(C_2H_4)L_2 + L.} \tag{2}$$

The value of $k_{obsd}$ is expressed in terms of $k_1$, $k_{-1}$, $k_2$, and $k_{-2}$ as

$$k_{obsd}=\frac{k_1k_2[C_2H_4]+k_{-1}k_{-2}[L]}{k_2[C_2H_4]+k_{-1}[L]}. \tag{3}$$

Since the rate of addition and dissociation show no dependence on the concentration of either $C_2H_4$ or L, we have $k_1=k_{-2}$; that is, $k_{obsd}=k_1=k_{-2}=0.4\ s^{-1}$ from Figs. 2 and 3. The value of the ratio $k_1k_2/k_{-1}=0.16\ s^{-1}$ since $K=k_1k_2/k_{-1}k_{-2}=0.4$. It is found that $C_2H_4$ reacts with only $RhClL_2$, whereas $RhClL_3$ is inactive for $C_2H_4$ addition.

*Addition of Oxygen.* Molecular oxygen adds to the Wilkinson's complex,[3,13] followed by the oxidation of the ligand $PPh_3$ in the Wilkinson's complex with coordinated active oxygen. In the present work, the fast addition reactions were studied:

$$\begin{aligned}&\mathrm{RhClL_{3,2} + O_2 \longrightarrow RhCl(O_2)L_n}\quad (n=3\text{ or }2)\\&\mathrm{(RhClL_2)_2 + O_2 \longrightarrow Product.}\end{aligned} \tag{4}$$

When a solution of Wilkinson's complex ($5.0\times10^{-4}$ M) was mixed with a solution of $O_2$ ($9.1\times10^{-3}$ M) under the conditions where the concentration of L is lower than $3\times10^{-3}$ M, a two-step increase in absorbance was observed at 400 nm, the faster process terminating within 2 s and the slower one within 20 s. At 440 nm, the isosbestic point for $RhClL_3$ and $RhCl(O_2)L_n$ in equilibrium,[14] only the faster increase of the absorbance was observed. When the concentration of L exceeded $3\times10^{-3}$ M, the faster process disappeared. This indicates that the slower step consists of the reaction between monomeric species $RhClL_3$ ($RhClL_2$ partly participates) and molecular oxygen. The faster one consists of the reaction between the dimer $(RhClL_2)_2$ and $O_2$. This was confirmed by a study of the solution containing only di-$\mu$-chloro-terakis(triphenylphosphine)dirhodium (I) and oxygen.

The rate of the slower step is proportional to the concentration of $O_2$ ($(0.9$—$4.1)\times10^{-3}$ M). Figure 4 shows the dependence of the observed rate constant, $k_{obsd}$, on the concentration of L added. The value of $k_{obsd}$ decreases until the concentration of L becomes *ca.* $1\times10^{-2}$ M, attaining a constant value beyond this value. This trend is similar to that of the addition reaction of $H_2$ to the same complex reported by Halpern and Wong.[9] As in the case of the $H_2$ addition, the decrease of $k_{obsd}$ with the addition of L may arise from the decrease of an active intermediate, $RhClL_2$, which is produced from $RhClL_3$ according to

$$RhClL_3 \rightleftarrows RhClL_2 + L. \quad (5)$$

The mechanism for the $O_2$ addition to the monomeric species $RhClL_3$ is thus expressed by

$$\begin{tikzcd} RhClL_3 + O_2 \arrow[r, "k_M"] \arrow[d, shift right, "k_1"'] & RhCl(O_2)L \arrow[d, shift right] \\ RhClL_2 + O_2 \arrow[r, "k_I"] \arrow[u, shift right, "k_{-1}"'] & RhCl(O_2)L \arrow[u, shift right, "fast"'] \\ + & + \\ L & L \end{tikzcd} \quad (6)$$

Application of the steady state approximation to $RhClL_2$ gives the following rate law:

$$-\frac{d[RhClL_3]}{dt} = \left\{k_M + \frac{k_1k_I}{k_{-1}[L]+k_I[O_2]}\right\}[O_2][RhClL_3]. \quad (7)$$

The ratio $k_1/k_{-1}$ is less than $1\times10^{-5}$ M.[9] $k_1$ was found to be 0.4 $s^{-1}$ from the experiments of ethylene.[15] Thus $k_{-1}>4\times10^4\ M^{-1}\ s^{-1}$. The value of $k_M$ is found to be 26 $M^{-1}\,s^{-1}$ by means of Eq. 7 from the constant value in Fig. 4. Introducing the above values of $k_{-1}$ and $k_M$ into Eq. 7 and applying the curve-fitting method to the results given in Fig. 4, we get the following rate constants: $k_1k_I/k_{-1}=1.7\times10^{-2}\ s^{-1}$, $k_I>1.7\times10^3\ M^{-1}\ s^{-1}$.

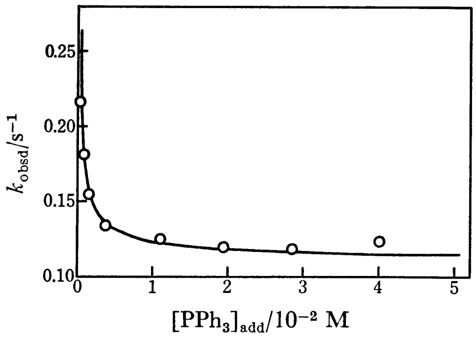


Fig. 4. Plot of the observed rate constant of the addition of $O_2$ *vs.* $[PPh_3]$. A solid curve is calculated from Eq. 7. $[RhCl(PPh_3)_3]_0=2.5\times10^{-4}$ M, $[O_2]=4.6\times10^{-3}$ M, and at 400 nm.

The rate of the following dimerization is negligibly small as compared to the rates of the $O_2$ addition (4).[10]

$$2RhClL_3 \rightleftarrows (RhClL_2)_2 + 2L \quad (8)$$

The rate constant of the $O_2$ addition on the dimer which initially exists in Eq. 8 can thus be obtained by observing the decrease of the initial concentration of the dimer estimated from Eq. 8. The result is given in Fig. 5: $k_D=7.5\times10^2\ M^{-1}\,s^{-1}$, where $k_D$ is the addition rate constant on the dimer. The figure also contains the result involving only the dimer and $O_2$. It is seen that the faster process mentioned above corresponds to the $O_2$ addition on the dimer. Ethylene does not react with the monomer, while oxygen reacts with the monomer. The order of the rate constants is $k_I>k_D>k_M$ for the $O_2$ addition. The order corresponds to that for the $H_2$ addition reported by Halpern and Wong.[9]

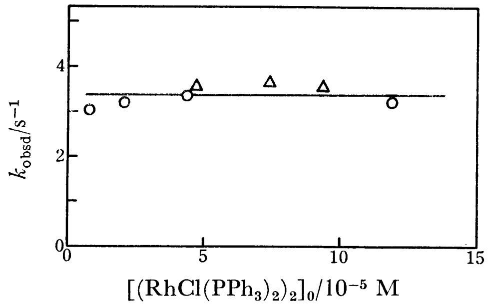


Fig. 5. Addition rate constant of $O_2$ on the dimer. ○; using Wilkinson's complex, △: using a pure dimer solution. $[O_2]=4.6\times10^{-3}$ M, at 440 nm.

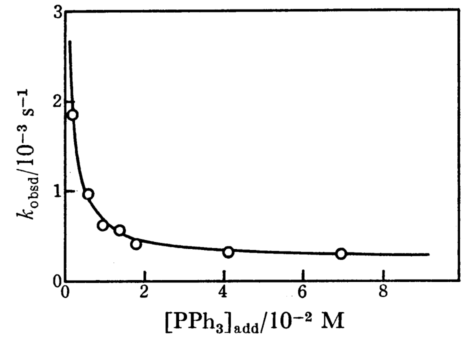


Fig. 6. Addition rate of $CHCl{=}CCl_2$. Plot of $k_{obsd}$ *vs.* $[PPh_3]$. $[RhCl(PPh_3)_3]_0=5.0\times10^{-4}$ M, $[CHCl{=}CCl_2]=5.4\times10^{-2}$ M, and at 400 nm.

*Addition of Trichloroethylene.* The observed rate constant for the addition of $CHCl{=}CCl_2$ on Wilkinson's complex depends on the concentration of L as shown in Fig. 6. The trends of $k_{obsd}$ are similar to those for the $O_2$ addition (Fig. 4), analysis thus being carried out in a similar way to that for oxygen. The results $k_M=4.6\times10^{-3}\ M^{-1}\ s^{-1}$, $k_1k_I/k_{-1}=6.5\times10^{-5}\ s^{-1}$ and $k_I>6.5\ M^{-1}\cdot s^{-1}$ were obtained.

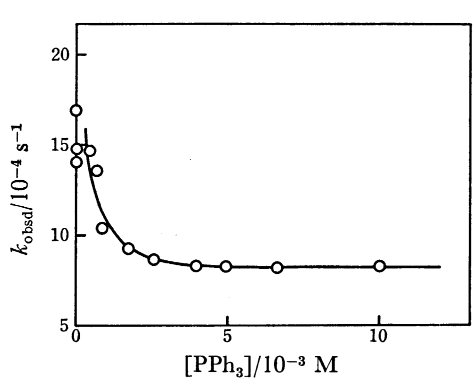
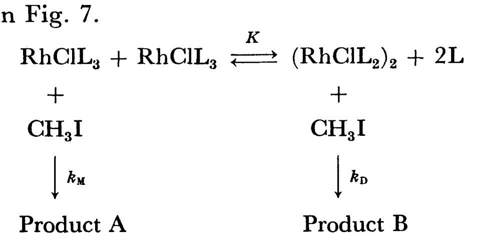


Fig. 7. Addition rate of $CH_3I$. Plot of $k_{obsd}$ *vs.* concentration of $PPh_3$. The curve is calculated from Eq. 9. $[RhCl(PPh_3)_3]_0=5.1\times10^{-4}$ M, $[CH_3I]=2.5\times10^{-2}$ M, anda at 400 nm.

*Addition of Methyl Iodide.* Figure 7 shows the dependence of $k_\mathrm{obsd}$ for the addition of $\mathrm{CH_3I}$ on the concentration of L. When $[\mathrm{L}] > 1\times10^{-2}$ M, phosphonium salt precipitates during the course of measurement. However the $\mathrm{CH_3I}$ addition rate is not affected.[16] The value of $k_\mathrm{obsd}$ decreases with the addition of L as in the case of $\mathrm{O_2}$ and $\mathrm{CHCl{=}CCl_2}$.

By assuming the following mechanism involving the fast monomer-dimer equilibrium we obtained the curve given in Fig. 7.



$$\begin{array}{ccc} \mathrm{RhClL_3} + \mathrm{RhClL_3} & \overset{K}{\rightleftarrows} & (\mathrm{RhClL_2})_2 + 2\mathrm{L} \\ + & & + \\ \mathrm{CH_3I} & & \mathrm{CH_3I} \\ \downarrow k_\mathrm{M} & & \downarrow k_\mathrm{D} \\ \text{Product A} & & \text{Product B} \end{array} \tag{9}$$

$$-\frac{\mathrm{d}[\mathrm{RhClL_3}]}{\mathrm{d}t} = k_\mathrm{M}[\mathrm{RhClL_3}][\mathrm{CH_3I}] + k_\mathrm{D}[(\mathrm{RhClL_2})_2][\mathrm{CH_3I}], \tag{10}$$

$$= k_\mathrm{M}[\mathrm{RhClL_3}][\mathrm{CH_3I}] + k_\mathrm{D}K\frac{[\mathrm{RhClL_3}]^2}{[\mathrm{L}]^2}[\mathrm{CH_3I}], \tag{10'}$$

$$k_\mathrm{obsd} = \left\{k_\mathrm{M} + k_\mathrm{D}K\frac{[\mathrm{RhClL_3}]}{[\mathrm{L}]^2}\right\}[\mathrm{CH_3I}], \tag{11}$$

where $k_\mathrm{M}$ is the rate constant under the higher L concentration ($>3\times10^{-3}$ M) and $k_\mathrm{D}$ the rate constant obtained for the solution of di-$\mu$-chloro-tetrakis(triphenylphosphine)dirhodium(I) and $\mathrm{CH_3I}$. The curve shows that the decrease of $k_\mathrm{obsd}$ is interpreted by the monomer-dimer equilibrium species alone. No contribution of the reaction intermediate, $\mathrm{RhClL_2}$, is observed. This is confirmed by the dependence of $k_\mathrm{obsd}$ on the concentration of $\mathrm{RhClL_3}$ ($(2\text{—}15)\times10^{-4}$ M) observed without L added ($[\mathrm{CH_3I}]=0.025$ M=const.) (Fig. 8). The fact that $k_\mathrm{obsd}$ increases with the increase in the total concentration of Rh complex even under the conditions of $[\mathrm{CH_3I}] \gg [\text{Rh complex}]$ indicates that the aggregated form of Rh complex (dimer) is more active than a monomer for the addition of $\mathrm{CH_3I}$.

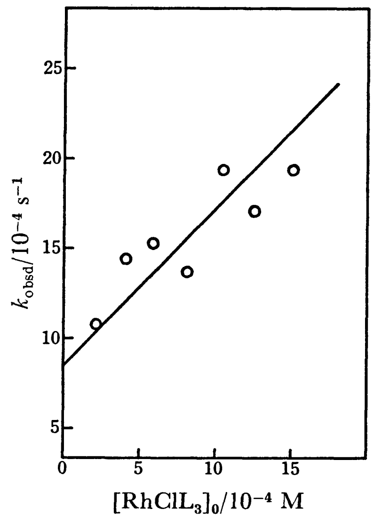
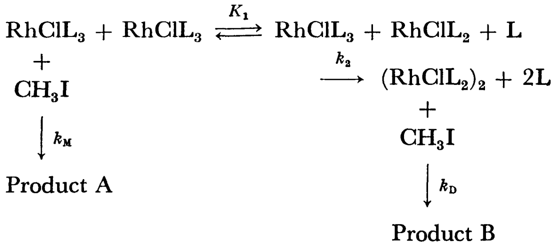


Fig. 8. Addition rate of $\mathrm{CH_3I}$. Plot of $k_\mathrm{obsd}$ *vs.* $[\mathrm{RhCl(PPh_3)_3}]_0$. $[\mathrm{CH_3I}]=2.5\times10^{-2}$ M, $[\mathrm{PPh_3}]_\mathrm{add}=0$ M, and at 400 nm.

If the dimerization process is rate-determining in the reaction path of product B, Eq. 10 is modified as Eq. 13:



$$\begin{array}{ccc} \mathrm{RhClL_3} + \mathrm{RhClL_3} & \overset{K_1}{\rightleftarrows} & \mathrm{RhClL_3} + \mathrm{RhClL_2} + \mathrm{L} \\ + & & \xrightarrow{k_2} (\mathrm{RhClL_2})_2 + 2\mathrm{L} \\ \mathrm{CH_3I} & & + \\ \downarrow k_\mathrm{M} & & \mathrm{CH_3I} \\ \text{Product A} & & \downarrow k_\mathrm{D} \\ & & \text{Product B} \end{array} \tag{12}$$

$$-\frac{\mathrm{d}[\mathrm{RhClL_3}]}{\mathrm{d}t} = k_\mathrm{M}[\mathrm{RhClL_3}][\mathrm{CH_3I}] + K_1k_2\frac{[\mathrm{RhClL_3}]^2}{[\mathrm{L}]}, \tag{13}$$

$$k_\mathrm{obsd} = k_\mathrm{M}[\mathrm{CH_3I}] + K_1k_2\frac{[\mathrm{RhClL_3}]}{[\mathrm{L}]},$$

where $K_1k_2 = 1.1\times10^{-3}\ \mathrm{s^{-1}}$.[10] The intercept of the curve in Fig. 8 gives $8\times10^{-4}\ \mathrm{s^{-1}}$ which is equal to the value in the higher concentration of L in Fig. 7. Thus the value $8\times10^{-4}\ \mathrm{s^{-1}}$ corresponds to the observed rate constant of the reaction of $\mathrm{CH_3I}$ with the monomer.

*Conclusion of the Addition Reactions*: The results are summarized in Table 1. The main findings are as follows.

(i) Except for $\mathrm{CH_3I}$, an intermediate complex ($\mathrm{RhClL_2}$) is the most reactive among the three species, $\mathrm{RhClL_3}$, $\mathrm{RhClL_2}$, and $(\mathrm{RhClL_2})_2$.

(ii) The values of $k_\mathrm{M}$ and $k_\mathrm{D}$ increase in the sequence of $\mathrm{CHCl{=}CCl_2} < \mathrm{CH_3I} < \mathrm{H_2} < \mathrm{O_2}$ and $k_\mathrm{I}$ in the sequence of $\mathrm{CHCl{=}CCl_2} < \mathrm{O_2} < \mathrm{C_2H_4} < \mathrm{H_2}$.

$\mathrm{RhClL_2}$ might be a solvated species obtained by replacing one L of $\mathrm{RhClL_3}$ with a solvent molecule. Thus the first finding implies that the main factor in determining the reactivity of the metal complex for oxidative addition is the presence of the labile site occupied by a solvent molecule. If the addition rate were determined by the dissociation of L from $\mathrm{RhClL_3}$ (Eq. 5), $k_\mathrm{I}$ would be constant irrespective of the kind of substrate. However, as stated in (ii), $k_\mathrm{I}$ varies over several orders of magnitude for the substrates studied. $k_\mathrm{I}$ is remarkably large for $\mathrm{C_2H_4}$ and $\mathrm{H_2}$ but not for $\mathrm{O_2}$. Therefore the addition reaction on $\mathrm{RhClL_2}$ may be of an

TABLE 1. RATE CONSTANTS OF OXIDATIVE ADDITION

| | $\frac{k_\mathrm{M}}{\mathrm{M^{-1}\,s^{-1}}}$ | $\frac{k_\mathrm{D}}{\mathrm{M^{-1}\,s^{-1}}}$ | $\frac{k_1k_\mathrm{I}/k_{-1}}{\mathrm{s^{-1}}}$ | $\frac{k_\mathrm{I}}{\mathrm{M^{-1}\,s^{-1}}}$ | $k_\mathrm{I}/k_\mathrm{M}$ |
|---|---|---|---|---|---|
| $\mathrm{C_2H_4}$ | small[b] | — | $1.6\times10^{-1}$ | $>1.6\times10^{4}$ | very large |
| $\mathrm{H_2}$[a] | 4.8 | 5.4 | $4.8\times10^{-1}$ | $>4.8\times10^{4}$ | $>1\times10^{4}$ |
| $\mathrm{O_2}$ | $2.6\times10$ | $7.5\times10^{2}$ | $1.7\times10^{-2}$ | $>1.7\times10^{3}$ | $>6.3\times10$ |
| $\mathrm{CHCl{=}CCl_2}$ | $4.6\times10^{-3}$ | $1.0\times10^{-2}$ | $6.5\times10^{-5}$ | $>6.5$ | $>1.4\times10^{3}$ |
| $\mathrm{CH_3I}$ | $3.3\times10^{-2}$ | $2.5\times10^{-1}$ | small[b] | small[b] | small[b] |

a) From Ref. 9, at 25 °C. b) The exact values could not be estimated.

associative character proceeding through a five coordinated complex, $RhClL_2SYZ$, where S and YZ are the solvent molecule and the reactant, respectively.

The kinetic nature of Wilkinson's complex becomes more evident when the present results are compared with those for Vaska's complex, $IrCl(CO)L_2$. Vaska's complex undergoes the oxidative addition reaction as follows.

$$IrCl(CO)L_2 + X \rightleftharpoons IrClX(CO)L_2.$$

For Vaska's complex, the rates of the addition of various substrates follow the order $C_2H_4 < O_2 < H_2$ in chlorobenzene at 30 °C.[17)] Probably because of the presence of a labile site in Wilkinson's complex, the magnitude of $k_I$ is generally much higher than for Vaska's complex.[18)] Comparing the reactivities with $C_2H_4$ and $O_2$ of Wilkinson's complex with those of Vaska's complex we find that their reactivities are reversed. The difference in the reactivities for both complexes may also be related to the bond nature of metal-substrate, but not entirely to the electronic property intrinsic to the substrate such as electron affinity.

Chock and Halpern[18)] suggested that for the addition reaction of $CH_3I$ to the $IrCl(CO)L_2$ complex the transition-state configuration would be

$$L_2(CO)ClIr^{\delta+}\cdots CH_3\cdots I^{\delta-}.$$

The present reaction for $CH_3I$ may proceed through a similar transition-state configuration. Thus the change in the polarity both in a central metal and $CH_3I$ plays a more important role than the substitution lability in $RhClL_2$. The labile site is not highly effective also in the case of the addition reaction of $CH_3I$ on Pt complex. The rate constants are reported to be $3.5\times10^{-3}\ M^{-1}s^{-1}$ and $2.0\times10^{-2}\ M^{-1}\,s^{-1}$ for $Pt(PPh_3)_3$ and $Pt(PPh_3)_2$, respectively.[16)]

*Replacement Reactions.* *$RhCl(C_2H_4)L_2+H_2+L$ and $RhClH_2L_3+C_2H_4$*: When a solution of $RhCl(C_2H_4)L_2$ ($[C_2H_4]=7.5\times10^{-2}$ M) is mixed with a solution of $H_2$ ($[H_2]=1.4\times10^{-3}$ M), a rapid decrease of $RhCl(C_2H_4)L_2$ occurs. No hydrogenation of $C_2H_4$ takes place within the time range[3)] studied. There is no free Rh complex present under the given $H_2$ and $C_2H_4$ concentrations. The reaction of $RhCl(C_2H_4)L_2$ and $H_2$ thus seems to proceed as follows:

$$RhCl(C_2H_4)L_2 + H_2 + L \rightleftharpoons RhClH_2L_3 + C_2H_4. \quad (14)$$

The equilibration is confirmed by the same spectra of $RhCl(C_2H_4)L_2+H_2+L$ and of $RhClH_2L_3+C_2H_4$, irrespective of the mode of mixing. Figures 9(a) and (b) give the dependence of $k_{obsd}$ on [L] for the reaction of $RhCl(C_2H_4)L_2+H_2+L$ and $RhClH_2L_3+C_2H_4$, respectively. Increase of $k_{obsd}$ with decreasing [L] suggests that in the replacement reaction $RhClH_2L_3$ is activated by dissociation of an L molecule. Thus the mechanism of the replacement reaction is

$$\begin{aligned}&RhCl(C_2H_4)L_2 + H_2 + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\\ &\quad RhClH_2L_2 + C_2H_4 + L \underset{K}{\rightleftharpoons}\\ &\qquad\qquad RhClH_2L_3 + C_2H_4, \quad (15)\end{aligned}$$

$$k_{obsd} = k_1[H_2] + k_{-1}\frac{[C_2H_4]}{1+[L]/K}, \quad (16)$$

where $K$ is the equilibrium constant for the dissociation of L from $RhClH_2L_3$. It is assumed in the derivation of the equation that the dissociation of L from $RhClH_2L_3$ is much faster than the replacement reaction of $RhCl(C_2H_4)L_2$ with $H_2$.[19)] Equation 16 shows that the value of $k_{obsd}$ in the plateau region of Figs. 9 (a) and (b) ($20\ s^{-1}$) corresponds to the forward reaction rate of Eq. 14 (when $[L]>5\times10^{-3}$ M, $k_{obsd}=k_1[H_2]$). Figures 10(a) and (b) show the dependence of $k_{obsd}$ on the concentration of $H_2$ and $C_2H_4$ for the reactions $RhCl(C_2H_4)L_2+H_2+L$ and $RhClH_2L_3+C_2H_4$, respectively ($[L]=7.0\times10^{-3}$ M). The fact that $k_{obsd}$ is independent of $[C_2H_4]$ is in line with the conclusion that $k_{obsd}$ corresponds to the forward reaction rate. It will be expected from Eq. 16 that $k_{obsd}$ is proportional to $[H_2]$. The dependence of $k_{obsd}$ on the $H_2$ concentration, however, does not follow the relation $k_{obsd}=k_1[H_2]$. The results in Fig. 10(a) imply that the forward rate consists of at least two terms, one independent of $[H_2]$ and the other proportional to $[H_2]$. Thus we assume two parallel paths for the replacement of $RhCl(C_2H_4)L_2$ with $H_2$.

$$\begin{array}{lll} & \xrightarrow[A]{L} & RhClH_2L_3 + C_2H_4 \text{ (path 1)} \\ RhCl(C_2H_4)L_2 + H_2 & & \\ & \xrightarrow[B]{} & Rh^{*}Cl(C_2H_4)L_2 + H_2 \\ & & \quad \downarrow L \\ & & RhClH_2L_3 + C_2H_4 \text{ (path 2)} \end{array} \quad (17)$$

Path 1 is the direct exchange between $H_2$ and the coordinated $C_2H_4$ ($k=7.8\times10^3\ M^{-1}\,s^{-1}$). Path 2 involves the uni-molecular step (B) in which $RhCl(C_2H_4)L_2$ is

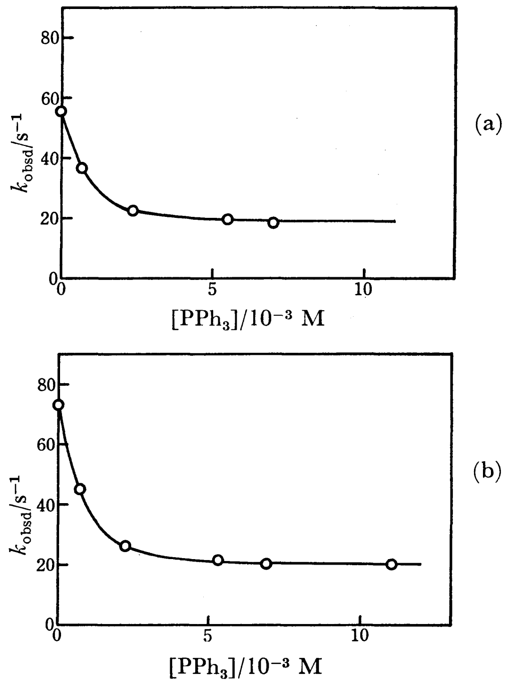


Fig. 9. Replacement reactions. Plot of $k_{obsd}$ *vs.* $[PPh_3]$. (a) $RhCl(C_2H_4)(PPh_3)_2+H_2+PPh_3$; $[RhCl(C_2H_4)(PPh_3)_2]=2.5\times10^{-4}$ M, $[C_2H_4]=7.5\times10^{-2}$ M, $[H_2]=1.4\times10^{-3}$ M, and at 422 nm. (b) $RhClH_2(PPh_3)_3+C_2H_4$; $[RhClH_2(PPh_3)_3]_0=2.5\times10^{-4}$ M, $[H_2]=1.4\times10^{-3}$ M, $[C_2H_4]=7.5\times10^{-2}$ M, and at 422 nm.

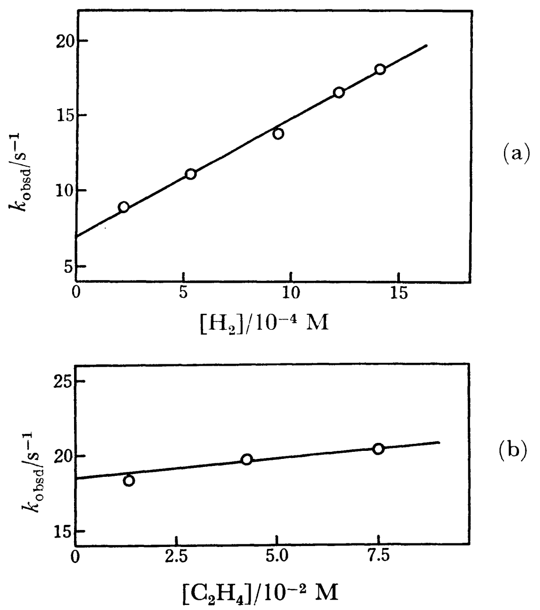


Fig. 10. Replacement reactions. Plots of $k_{obsd}$ *vs.* concentration of the reactants. (a) $RhCl(C_2H_4)(PPh_3)_2+H_2+PPh_3$; dependence of $k_{obsd}$ on the concentration of $H_2$. $[RhCl(C_2H_4)(PPh_3)_2]_0=1.6\times10^{-4}$ M, $[C_2H_4]=7.5\times10^{-2}$ M, $[PPh_3]=7.0\times10^{-3}$ M, and at 422 nm. (b) $RhClH_2(PPh_3)_3+C_2H_4$; dependence of $k_{obsd}$ on the concentration of $C_2H_4$. $[RhClH_2(PPh_3)_3]_0=2.5\times10^{-4}$ M, $[H_2]_0=1.4\times10^{-3}$ M, $[PPh_3]=7.0\times10^{-3}$ M, and at 422 nm.

activated ($k=7$ s$^{-1}$). Process B does not involve the dissociation of $C_2H_4$. The rate constant of the dissociation of $C_2H_4$, $k_{diss}$, is 0.4 s$^{-1}$ as determined previously. On the other hand the intercept in Fig. 10(a) gives 7 s$^{-1}$ to the rate constant of the uni-molecular process in path 2, which is much greater than $k_{diss}$. The uni-molecular process seems to be the dissociation process of a solvent molecule which is loosely coordinated to the central metal above or below the plane of $RhCl(C_2H_4)L_2$ complex.

*$RhCl(CH_2{=}CHCN)L_2+H_2+L$ and $RhClH_2L_3+CH_2{=}CHCN$*: The results of kinetic studies on this system are very similar to those obtained for $RhCl(C_2H_4)L_2+H_2+L$ and $RhClH_2L_3+C_2H_4$. The results are summarized in Table 2.

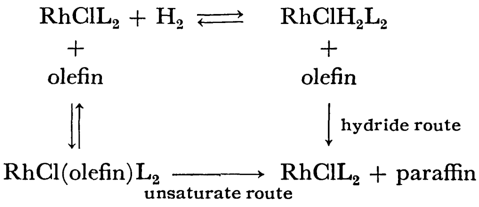
TABLE 2. OBSERVED RATE CONSTANTS OF THE REPLACEMENT REACTIONS ($RhClX_1L_m+X_2\rightleftarrows RhClX_2L_n+X_1$; $m$, $n$=3 or 2)

$k_{obsd}/s^{-1}$

| $RhClX_1L_m$ | X$_2$ | | |
|---|---|---|---|
| | $H_2$ | $C_2H_4$ | $CH_2{=}CHCN$ |
| $H_2$ | — | 20 | 32 |
| $C_2H_4$ | 18 | — | 310 |
| $CH_2{=}CHCN$ | 20 | 250 | — |
| None[a)] | 0.071 | 0.4 | 0.5 |

a) Observed rate constants of the addition reactions under comparable conditions. $[RhCl(PPh_3)_3]_0=2.5\times10^{-4}$ M, $[PPh_3]=7\times10^{-3}$ M, $[H_2]_0=1.4\times10^{-3}$ M, and $[C_2H_4]=[CH_2{=}CHCN]=7.5\times10^{-2}$ M.

*Conclusion on the Replacement Reactions*: In the replacement reaction the rate of replacement of the coordinated olefin by $H_2$ is greater by about two orders of magnitude than the rate of the oxidative addition of $H_2$ on Rh complex under comparable conditions. The acceleration effect observed implies that the approach of $H_2$ to Rh(olefin) complex makes the coordinated olefin labile. In other words, a strong interaction exists through the central metal between $H_2$ and the coordinated olefin. It strongly supports the presence of an associative intermediate $RhClH_2(olefin)L_2$. The hydrogenation of the olefins proceeds much more slowly than the replacement reaction.[3)] However, it is probable that on hydrogenation of the olefins the same associative intermediate exists, on which 2H migrate on olefin to produce paraffin. If that is the case the complex formation step is considered to be a pre-equilibrium in the hydrogenation of olefins. If this conclusion is correct, there is no question as to whether $H_2$ or olefin adds first on the Rh complex during the course of hydrogenation, that is the hydride route or the unsaturate route.[3,4,6,7)]



We consider that the high activity of Wilkinson's complex may arise from the existence of both the intermediates $RhClL_2$ and $RhClH_2(olefin)L_2$ through which hydrogenation of the olefin proceeds.

We wish to express our thanks to Dr. Tokio Iizuka of this department for the supply of ethylene. The present work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education.

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