2562 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2562—2565 (1978) [Vol. 51, No. 9

Kinetics of the Oxidative Addition of Hydrogen to Chloro(acrylonitrile)bis(triphenylphosphine)rhodium(I) in Benzene

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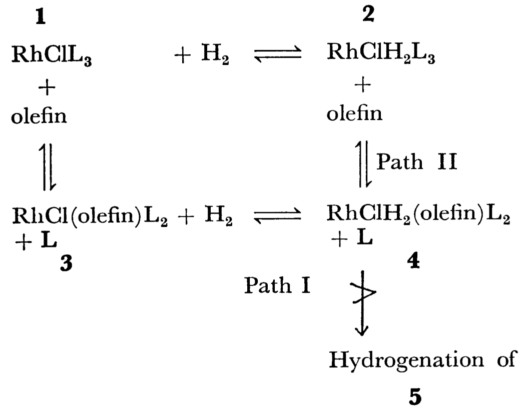
(Received January 6, 1978)

The reaction between chloro(acrylonitrile)bis(triphenylphosphine)rhodium(I) and hydrogen was studied by the stopped-flow method under an anaerobic condition. A solution of $RhCl(CH_2{=}CHCN)(PPh_3)_2$ was mixed with a benzene solution containing hydrogen under the condition of $[Rh]<[H_2]_0<[CH_2{=}CHCN]$. A fast decrease in the absorbance was followed by a slow increase in the absorbance, until finally the absorbance returned to the initial value. It was proved that the faster reaction was the oxidative addition of hydrogen to $RhCl(CH_2{=}CHCN)(PPh_3)_2$; $RhCl(CH_2{=}CHCN)(PPh_3)_2+H_2 \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} RhClH_2(CH_2{=}CHCN)(PPh_3)_2$. The slower reaction was the process in which hydrogen was consumed in the course of the hydrogenation of acrylonitrile and $RhCl(CH_2{=}CHCN)(PPh_3)_2$ was reproduced. The values of the rate constants were evaluated to be $k_{34}\geq 7.8\times 10^3$ mol^{-1} dm^3 s^{-1} and $k_{43}\leq 53$ s^{-1}.

Wilkinson's complex, $RhClL_3$ ($L{=}PPh_3$), is a useful catalyst for the hydrogenation of olefins.[1] Although many studies have been made to elucidate the reaction mechanism of the hydrogenation of olefins by means of Wilkinson's complex,[2–7] the mechanism has not yet been fully made clear. We previously proposed the following reaction mechanism, in which complex formation processes are assumed as a pre-equilibrium step,[7] though an intermediate species ($RhClH_2$(olefin)L_2) could not be detected spectrophotometrically:



The predominant species of the Rh complex is considered to be $RhClH_2L_3$ (**2**) or RhCl(olefin)L_2 (**3**). Whether the RhCl(olefin)L_2 species becomes a predominant species or not depends on the coordinating ability of the olefin. Thus, the hydrogenation of olefins with a weakly coordinating power may proceed mainly through a so-called "hydride route" (Path II) as proposed by Halpern *et al.*[6] However, the hydrogenation of olefins with a strongly coordinating power is expected to proceed predominantly through an "unsaturate route" (Path I). However, the latter has not so far been observed with the use of Wilkinson's complex.

We intend in the present study to detect the intermediate species, $RhClH_2$(olefin)L_2 (**4**), and also to obtain the kinetic data of the reaction $3\rightleftharpoons 4$. Acrylonitrile was chosen as an olefin since it strongly coordinates to Wilkinson's complex and is rapidly hydrogenated.[3] The concentration of $RhClH_2(CH_2{=}CHCN)L_2$ increases as the concentration of free PPh_3 decreases. Thus, a solution of $RhCl(CH_2{=}CHCN)L_2$ containing no free PPh_3 was prepared by dissolving $RhCl(C_2H_4)L_2$ in a benzene solution containing acrylonitrile. The coordinated ethylene was then replaced by an acrylonitrile molecule[7] and $RhCl(CH_2{=}CHCN)L_2$ was produced in the solution. As there was no free PPh_3 in the solution, only olefin complexes **3** and **4** can exist. The oxidative addition of hydrogen to $RhCl(CH_2{=}CHCN)L_2$ was observed by the addition of a solution containing hydrogen to a solution of $RhCl(CH_2{=}CHCN)L_2$.

Experimental

A solution of $RhCl(CH_2{=}CHCN)(PPh_3)_2$ was prepared by dissolving $RhCl(C_2H_4)(PPh_3)_2$ in oxygen-free benzene containing acrylonitrile and by removing the dissociated ethylene. The coordinated ethylene was easily replaced by acrylonitrile,[7] and $RhCl(CH_2{=}CHCN)(PPh_3)_2$ was produced in benzene. The value of the equilibrium constant $K{=}[RhCl(CH_2{=}CHCN)(PPh_3)_2][C_2H_4]/[RhCl(C_2H_4)(PPh_3)_2][CH_2{=}CHCN]$ was calculated to be 0.5 from the values of $K'{=}[RhCl(C_2H_4)(PPh_3)_2][PPh_3]/[RhCl(PPh_3)_3][C_2H_4]=0.4$[5] and $K''=[RhCl(CH_2{=}CHCN)(PPh_3)_2][PPh_3]/[RhCl(PPh_3)_3]\cdot[CH_2{=}CHCN]=0.2$.

Chloro(ethylene)bis(triphenynylphosphine)rhodium(I), $RhCl(C_2H_4)(PPh_3)_2$ was prepared from $RhCl(PPh_3)_3$.[2] Benzene was distilled. Acrylonitrile was distilled under reduced pressure. Commercial hydrogen was used without purification; the concentration was determined by gas-chromatography using a Molecular sieve 5A.

Kinetic measurements were made at 20 °C using a Union Giken RA-1300 stopped-flow apparatus. A solution of $RhCl(CH_2{=}CHCN)(PPh_3)_2$ containing an appropriate concentration of acrylonitrile (0.004—0.228 mol dm^{-3}) was mixed with a solution of hydrogen containing the same concentration of acrylonitrile as in the solution of $RhCl(CH_2{=}CHCN)(PPh_3)_2$ ($[H_2]=(0.8\text{—}2.8)\times 10^{-3}$ and $[CH_2{=}CHCN]=0.004\text{—}0.228$ mol dm^{-3}). The reaction was then carried out under a nitrogen or a hydrogen atmosphere. The change in the absorbance was observed at 458 nm (λ_{max} of $RhCl(CH_2{=}CHCN)(PPh_3)_2$).

The rate of hydrogen-gas uptake was measured as follows. A catalytic hydrogenation apparatus was evacuated and filled with 1 atm hydrogen. A benzene solution (10 ml) containing an appropriate concentration of acrylonitrile was introduced into the apparatus. The solution was vigorously stirred in order to saturate the apparatus with benzene vapor. The total pressure in the apparatus was 1 atm, and no attempt was made to compensate for the partial pressure of benzene. A benzene solution of the Rh complex (10 ml; the Rh complex existed in the form of $H_2[RhCl(PPh_3)_2]_2$), saturated with 1 atm of hydrogen beforehand, was dropped into the vessel while the solution was being vigorously stirred. The dimeric form of the Rh complex was rapidly decomposed to a monomeric olefin complex by the reaction with acrylonitrile.[8] The absorption rate of hydrogen was measured by means of a 10 ml gas buret. The limitation of the uptake rate due to the ability of the apparatus was not less than 0.25 ml s^{-1}. In the kinetic runs, the fastest uptake rate was 0.02 ml s^{-1}, so there was no hydrogen starvation in the solution.

Results and Discussion

When a solution containing $RhCl(CH_2{=}CHCN)L_2$ was mixed with a solution containing hydrogen, stepwise reactions took place. Figure 1 shows a typical example of the absorbance changes.

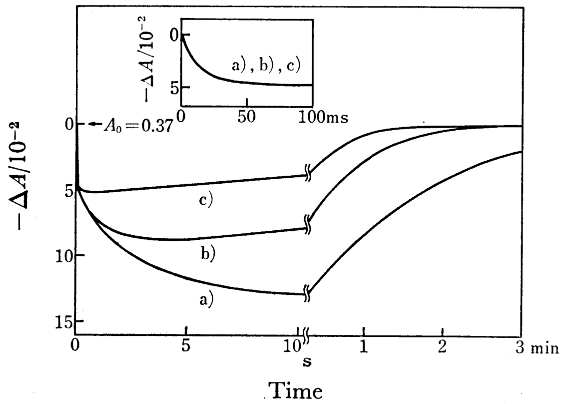


Fig. 1. Typical absorbance changes in the reaction between $RhCl(CH_2{=}CHCN)L_2$ and hydrogen in benzene. Inset shows an expanded signals for the first step of the reaction. $[RhCl(CH_2{=}CHCN)L_2]_0 = 3.2\times10^{-4}$ mol dm^{-3}, $[H_2]_0=1.4\times10^{-3}$ mol dm^{-3}, at 458 nm, and 20 °C. a) $[CH_2{=}CHCN]=0.004$, b) 0.076, and c) 0.228 mol dm^{-3}.

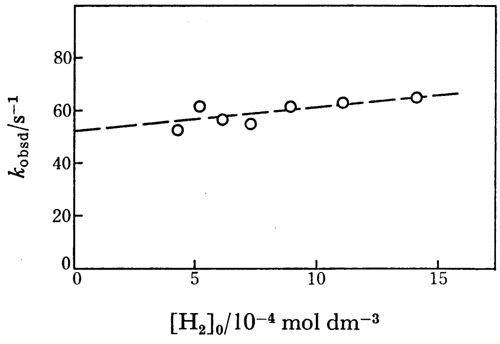


Fig. 2. Plot of k_{obsd} in the first step *vs.* $[H_2]_0$. $[Rh]=3.6\times10^{-4}$, $[CH_2{=}CHCN]=0.076$ mol dm^{-3}. Broken line is drawn assuming $K_{34}=k_{34}/k_{43}=1.5\times10^2$ $mol^{-1}\cdot dm^3$. As the concentration of $RhClH_2(CH_2{=}CHCN)L_2$ is small, the concentration of H_2, $[H_2]=[H_2]_0-[RhClH_2(CH_2{=}CHCN)L_2]$, is held nearly constant during the reaction.

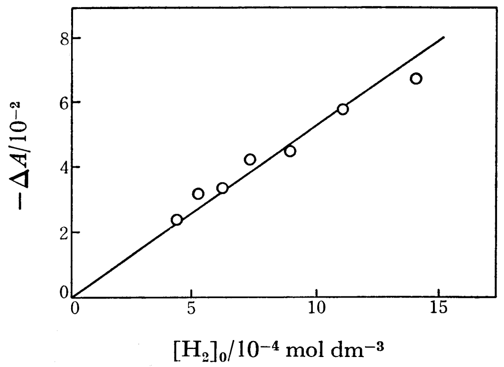


Fig. 3. Plot of the absorbance change, ΔA, in the first step *vs.* $[H_2]_0$. $[Rh]=3.6\times10^{-4}$, $[CH_2{=}CHCN]=0.076$ mol dm^{-3}.

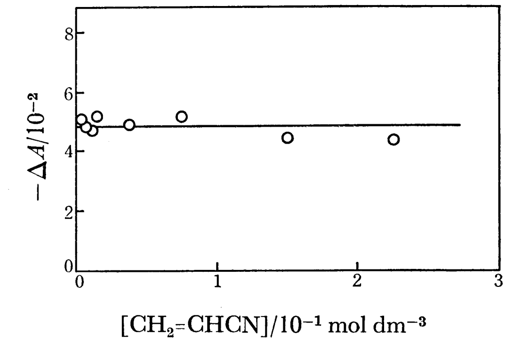
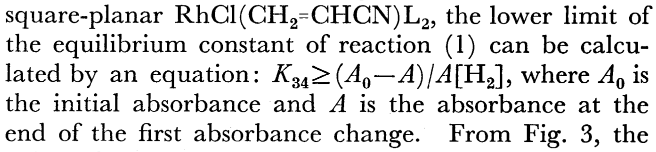


Fig. 4. Plot of the absorbance change, ΔA, in the first step *vs.* $[CH_2{=}CHCN]$. $[Rh]=3.2\times10^{-4}$ and $[H_2]_0=1.4\times10^{-3}$ mol dm^{-3}.

The first decrease in the absorbance shows an exponential curve. It terminates within 0.1 s. The rate does not depend on $[CH_2{=}CHCN]$, but depends somewhat on $[H_2]$ (Fig. 2). The change in the absorbance is nearly proportional to $[H_2]$ (Fig. 3), but does not depend on $[CH_2{=}CHCN]$ (Fig. 4). From these results it may be concluded that the coordination of hydrogen does not cause the dissociation of the previously coordinated acrylonitrile. The reaction in the first step is:



$$\begin{array}{c} Cl \\ | \\ L{-}Rh{-}L \\ | \\ CH_2{=}CHCN \end{array} + H_2 \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \begin{array}{c} H \\ Cl\diagdown\,|\,\diagup L \\ Rh \\ L\diagup\,|\,\diagdown H \\ CH_2{=}CHCN \end{array} \cdot \qquad (1)$$

Figure 3 suggests that the equilibrium lies far to the reactant side even when $[H_2]=1.4\times10^{-3}$ mol dm^{-3}. If the molar absorption coefficient of the octahedral $RhClH_2(CH_2{=}CHCN)L_2$ at 458 nm is very small (as in the case of $RhClH_2L_3$) compared with that of the square-planar $RhCl(CH_2{=}CHCN)L_2$, the lower limit of the equilibrium constant of reaction (1) can be calculated by an equation: $K_{34}\geq(A_0-A)/A[H_2]$, where A_0 is the initial absorbance and A is the absorbance at the end of the first absorbance change. From Fig. 3, the value of K_{34} was evaluated to be $K_{34}\geq1.5\times10^2$ $mol^{-1}\cdot dm^3$. The broken line in Fig. 2 is drawn assuming that $K_{34}=k_{34}/k_{43}=1.5\times10^2$ mol^{-1} dm^3. The observed rate constant, $k_{obsd}=k_{34}[H_2]+k_{43}$, was mainly attributed to the rate constant of the reverse reaction. The rate constants were $k_{43}\leq53$ s^{-1} and $k_{34}\geq7.8\times10^3$ $mol^{-1}\cdot dm^3$ s^{-1}.

The addition and the dissociation rate constants, k_{34} and k_{43}, for several Rh(I) complexes are listed in

TABLE 1. ADDITION AND DISSOCIATION RATE CONSTANTS FOR THE HYDROGENATION OF SEVERAL Rh(I) COMPLEXES

Rh complex	k_1/mol^{-1} dm^3 s^{-1}	k_{-1}/s^{-1}	K_1/mol^{-1} dm^3
$RhCl(PPh_3)_3$[a]	4.8	2.3×10^{-4}[d]	2.1×10^4
$RhCl(NCCH_3)(PPh_3)_2$[b]	1.4×10^2	5.6×10^{-3}[d]	2.5×10^4
$RhCl(CH_2{=}CHCN)(PPh_3)_2$[c]	$\geq7.8\times10^3$	≤53	$\geq1.5\times10^2$
$RhCl(PPh_3)_2$[a]	$>7\times10^4$	—	

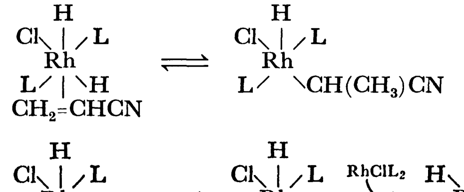
a) At 25 °C, from Ref. 4. b) At 20 °C, from Ref. 9. c) At 20 °C, the present study. d) Calculated from $k_{-1}=k_1/K_1$.

Table 1. The values of k_{34} increased in the sequence: $RhClL_3$ < $RhCl(NCCH_3)L_2$ < $RhCl(CH_2{=}CHCN)L_2$< $RhClL_2$. The larger rate constant for $RhClL_2$ indicates that $RhClL_2$ has a labile site to which the benzene molecule coordinates. That the rate constant for $RhCl(CH_2{=}CHCN)L_2$ is larger than that for $RhClL_3$ suggests that $CH_2{=}CHCN$ is sterically less hindered than the PPh_3 attached to $RhClL_3$. A larger rate constant for $RhCl(CH_2{=}CHCN)L_2$ than that for $RhCl(NCCH_3)L_2$ may be predicted from the fact that the coordination of olefin stabilizes the lower valency state of the central metal more than the coordination of acetonitrile does.

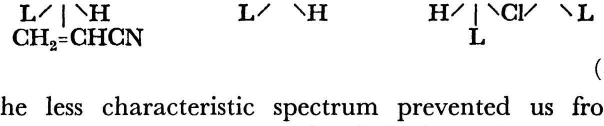
The values of k_{43} increased in the sequence: $RhClL_3$< $RhCl(NCCH_3)L_2 \ll RhCl(CH_2{=}CHCN)L_2$. $RhCl(CH_2{=}CHCN)L_2$ had an especially large rate constant. $CH_2{=}CHCN$ has the largest *trans*-effect among $CH_2{=}CHCN$, CH_3CN, and PPh_3. The Rh–H bond may be most weakened through the coordination of $CH_2{=}CHCN$. Thus, the dissociation of hydrogen from $RhClH_2(CH_2{=}CHCN)L_2$ is accelerated.

When $[CH_2{=}CHCN]$ is small, a second, slower decrease in the absorbance is observed (Fig. 1). The absorbance change gradually decreased with the increase in $[CH_2{=}CHCN]$ and finally disappeared. The accurate value of the rate constant cannot be obtained since the signal overlaps with that of the third step. The observed rate constant was about 0.35±0.15 s^{-1} when $[H_2]_0=(1.41-0.56)\times10^{-3}$ and $[CH_2{=}CHCN]=7.6\times10^{-3}$ mol dm^{-3}.

Alternative explanations of the results will be presented below. One is an interpretation by the formation of a reaction intermediate alkyl complex (2), and another is an interpretation by the formation of a dimeric dihydrido species (3) which is inactive for the hydrogenation of olefin.



(2)



(3)

The less characteristic spectrum prevented us from distinguishing between $RhClH(-CH(CH_3)CN)L_2$ and $H_2(RhClL_2)_2$.

In the third step, the absorbance returned to that of the initial stage (Fig. 1). This step involves the consumption of hydrogen for the hydrogenation of acrylonitrile. The rate is dependent on $[CH_2{=}CHCN]$ when it is small, but gradually approaches the constant value as $[CH_2{=}CHCN]$ increases. The measurements of the hydrogen-gas uptake also showed that the hydrogenation rate depended on $[CH_2{=}CHCN]$ when it was small (Fig. 5). From Fig. 5, the value of k_{45}, the rate constant of the hydrogenation of $CH_2{=}CHCN$ in $RhClH_2(CH_2{=}CHCN)L_2$, can be estimated by means of the following equation

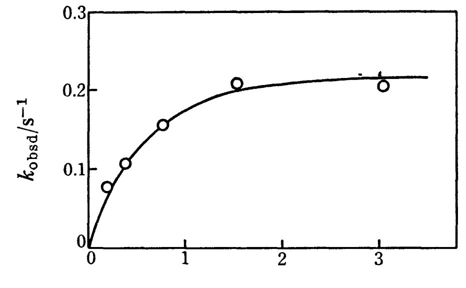


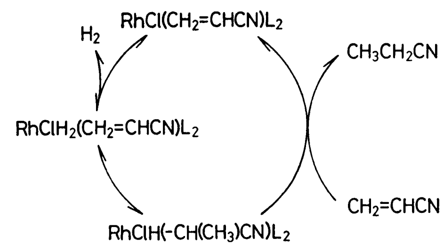
Fig. 5. Plot of the number of H_2 molecules taken up per Rh per s *vs.* $[CH_2{=}CHCN]$. $[Rh]=1.4\times10^{-4}$ mol·dm^{-3} (2.8×10^{-6} mol), and $[H_2]=2.8\times10^{-3}$ mol·dm^{-3} ($P(H_2)=1$ atm).

$$k_{45}=\frac{[RhCl(CH_2{=}CHCN)L_2]+[RhClH_2(CH_2{=}CHCN)L_2]}{[RhClH_2(CH_2{=}CHCN)L_2]}\times k_{\mathrm{obsd}} \tag{4}$$
$$=\left(1+\frac{1}{K_{34}[H_2]}\right)\times0.22\ \mathrm{s}^{-1}$$
$$\leq0.74\ \mathrm{s}^{-1}.$$

If an alkyl complex is formed in the second step, this result can be interpreted as follows: the addition of acrylonitrile to the vacant site of the alkyl complex weakens the *trans* Rh–H bond, and the insertion of the alkyl group to the second hydride is accelerated. At a high $[CH_2{=}CHCN]$ value, the formation of the alkyl complex becomes rate-determining for the hydrogenation of acrylonitrile.

If a dimeric dihydrido species is formed in the second step, the rate of hydrogenation depends on $[CH_2{=}CHCN]$ as the concentration of the active species decreases.

The total mechanism proposed is shown in Scheme 1. Because of the absence of the free PPh_3 molecule and the strong coordinating power of acrylonitrile, the hydrogenation of acrylonitrile proceeds through a so-called "unsaturate route." The existence of an intermediate species, $RhClH_2(CH_2{=}CHCN)L_2$, is indicated by the absorbance change, but no certain evidence of another reaction intermediate, $RhClH(-CH(CH_3)CN)L_2$, is



Scheme 1.

obtained in the present study.

Since the coordinating power of CH_3CH_2CN would be much smaller than that of $CH_2{=}CHCN$,[10] and since its concentration is small ($[CH_3CH_2CN] \leq [H_2]_0$), the formation of a propionitrile complex is very unlikely during the course of the hydrogenation.

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10) The small value of $K = [RhCl(NCCH_3)L_2][L]/[RhClL_3][CH_3CN] = 1.1 \times 10^{-3}$ suggests that CH_3CH_2CN may also have a low complexation constant.