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The Effect of Halo Ligand on the Rate of Hydrogenation of Coordinated Olefin in Dihydrido-olefin Complexes $RhXH_2(ol)(PPh_3)_2$ (X=Cl, Br, I)

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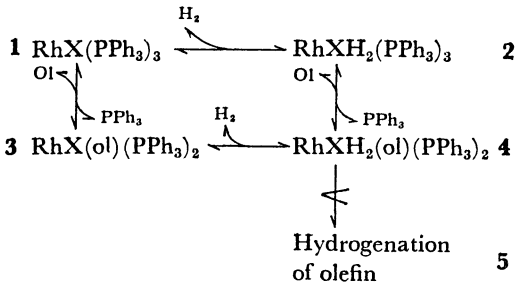
Synopsis. The formation constant of $RhXH_2(ol)(PPh_3)_2$ (ol=acrylonitrile or styrene, X=Cl, Br, or I) and the rate of hydrogenation of coordinated olefin in $RhXH_2(ol)(PPh_3)_2$ were determined. The effects of halo ligand on the equilibrium and rate constants showed a different trend for the two olefin complexes.

Knowledge of the effect of halo ligand on the catalytic activity of Wilkinson's complex is necessary for understanding electronic factors of individual steps in the catalytic hydrogenation reaction (Scheme 1).



Scheme 1.

The effects of halo ligand and other tertiary phosphine ligand analogs were studied,[1-3] but in most investigations only the overall rate of catalytic reactions were reported. Since both the complex formation constants and hydrogenation rate of coordinated olefin may vary with change of ligand, discussions based only on the observed rate constants of the overall reaction sometimes leave ambiguities. Thus, it is necessary to know the effects of ligands on the complex formation and on the rate of the hydrogenation of coordinated olefin, separately. In particular, information concerning a catalytically active intermediate (**4**) is required to elucidate the nature of Wilkinson's complex as a catalyst.

Recently, we detected a catalytically active intermediate, $RhClH_2(ol)(PPh_3)_2$ (ol=acrylonitrile or styrene), in benzene under anaerobic conditions.[4,5] Detection of the intermediate made it possible to determine accurately the equilibrium and/or rate constants of the individual steps in Scheme 1. We have studied a bromo and an iodo complex in a manner similar to that for the chloro complex to elucidate the effects of halo ligand on each step composing the catalytic reaction.

The results are summarized in Table 1. The effects of halo ligand on equilibrium and rate constants differ largely for acrylonitrile and styrene. The values of K_{34} (and also K_{24}), stability constants of dihydrido-olefin complex, increase in the order Cl<Br<I for acrylonitrile, and decrease in the order Cl>Br>I for styrene. The difference might be attributed to that in the coordinating properties of the two olefins. The coordination of acrylonitrile, which has an electron-withdrawing cyano group, would decrease the electron density of rhodium atom. On the other hand, the coordination of styrene, which has an electron-releasing phenyl group, would increase the electron density of rhodium. In the case of acrylonitrile, the iodo complex with the least electronegative ligand gives the largest stability of $RhXH_2(ac)(PPh_3)_2$. In the case of styrene, the chloro complex with the most electronegative ligand gives the largest stability of $RhXH_2(st)(PPh_3)_2$. The most stable dihydrido-olefin complex would be formed by the halo ligand, which offsets the change in electron density of central rhodium atom induced by the coordination of olefin.

As regards the effect of halo ligand on k_{45}, it is concluded that the complex which has a larger value of K_{34} gives the smaller value of k_{45}, a less stable dihydrido-olefin complex having a larger rate constant for the hydrogenation of coordinated olefin. The rate of the migratory insertion of olefin into Rh–H bond would be slowed down as the Rh–H bond becomes strong.

The effects of coordinated halo ligand on the stability constants of dihydrido-olefin complex may also be interpreted by the Dewar-Chatt-Duncanson model.[6] Figure 1 shows tentative schematic diagrams of energy levels. The energy level of rhodium atom is taken to be consistent with the present experimental results. In the case of acrylonitrile complex, back-donation from rhodium atom to acrylonitrile would be predominant for the coordination of acrylonitrile, as the π^* energy level of acrylonitrile lies near the highest occupied

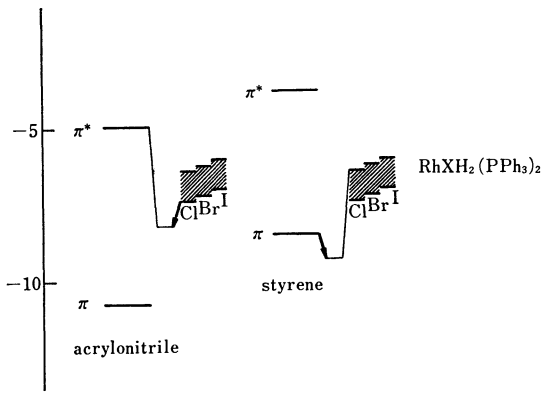


Fig. 1. A tentative energy level diagram. The energy levels of of rhodium are taken arbitarily so as to be consistent with the experimental results.

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Table 1. Equilibrium and rate constants observed

X	ol	K_{12} / $mol^{-1}\,dm^3$	K_{13}	K_{24} [a]	K_{34} / $mol^{-1}\,dm^3$	k_{34} / $mol^{-1}\,dm^3\,s^{-1}$	k_{43} / s^{-1}	k_{45} / s^{-1}
Cl	ac	2.1×10^4	0.22	3.7×10^{-3}	3.5×10^2	1.5×10^4	43	0.50
Cl	st	2.1×10^4	2.4×10^{-4}	3.7×10^{-5}	3.2×10^3	—	—	2.7
Br	ac	3.3×10^4	0.20	1.2×10^{-2}	1.9×10^3	3.9×10^4	21	0.15
Br	st	3.3×10^4	3.3×10^{-4}	$\approx1.7\times10^{-5}$	$\approx1.9\times10^3$	—	—	$\approx$9.7
I	ac	6.3×10^4	0.19	2.1×10^{-2}	7.0×10^3	3.2×10^4	4.6	0.050
I	st	6.3×10^4	7.6×10^{-4}	$\approx1.1\times10^{-5}$	$\approx9.0\times10^2$	—	—	$\approx$35

ac=acrylonitrile and st=styrene. K_{ij} and k_{ij} denote the equilibrium and rate constants of the reactions from species i to species j, respectively, shown in Scheme 1. a) Calculated from $K_{24}=K_{13}K_{34}/K_{12}$.

energy level of rhodium. Since the electron density of central rhodium atom increases in the order chloro< bromo<iodo complex, the highest occupied energy level of rhodium atom would be the highest for iodo complex. The distance between π^* energy level of acrylonitrile and the highest occupied energy level of rhodium would be the shortest for the iodo complex, $RhXH_2(ac)(PPh_3)_2$ thus being the most stable for iodo complex. In contrast, donation from styrene to rhodium would be predominant for the coordination of styrene. $RhXH_2(st)(PPh_3)_2$ is the most stable when X=Cl.

In the case of acrylonitrile, the value of k_{45} was found to be 100 times as small as that of k_{43} for all three halo complexes. It should be noted that both k_{43} and k_{45} decrease in the same order Cl>Br>I. k_{43} corresponds to the dissociation rate of hydrogen from the $RhXH_2(ac)(PPh_3)_2$ complex, while k_{45} corresponds to the migratory insertion rate of coordinated olefin into Rh–H bond in the same complex. It is suggested that both reactions proceed through a similar activated state, where Rh–H bond becomes weak.

Experimental

All measurements were carried out at 20±1 °C in oxygen-free benzene. Solutions of $RhCl(ol)(PPh_3)_2$ and $RhBr(ol)(PPh_3)_2$ were prepared as described.[4] A solution of $RhI(ol)(PPh_3)_2$ was prepared by dissolving $RhI(PPh_3)_3$ in benzene containing acrylonitrile or styrene. A small amount of free PPh_3 dissociated from $RhI(PPh_3)_3$ was neglected for the stopped-flow measurements. For the measurements of hydrogen gas uptake, the total concentration of PPh_3 was taken as the sum of the concentration of added PPh_3 and $RhI(PPh_3)_3$. The procedure of measurements is described in previous papers.[4,5]

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