Hydrogenation of Tris(triphenylphosphine)chlororhodium(I)

By Jack Halpern* and Chun Sing Wong

(*Department of Chemistry, The University of Chicago, Chicago, Illinois* 60637)

Summary The reactivities of $\mathrm{RhCl(PPh_3)_3}$, $\mathrm{RhCl(PPh_3)_2}$, and $\mathrm{Rh_2Cl_2(PPh_3)_4}$ toward $\mathrm{H_2}$, and the contributions of each of these species to the overall rate of hydrogenation of $\mathrm{RhCl(PPh_3)_3}$ in solution, have been determined; $\mathrm{RhCl(PPh_3)_2}$ is at least 10^4 times as reactive as the other two species.

The hydrogenation of olefins catalysed by Wilkinson's complex $\mathrm{RhCl(PPh_3)_3}$ has generally been interpreted[1,2] in terms of mechanisms, a component step of which is equation (1), *i.e.*, the reaction of $\mathrm{RhCl(PPh_3)_3}$ [or, alternatively, the corresponding reaction of its dissociation product $\mathrm{RhCl(PPh_3)_2}$] with $\mathrm{H_2}$ to form a dihydrido-complex.

$$\mathrm{RhCl(PPh_3)_3} + \mathrm{H_2} \xrightarrow{k_1} \mathrm{RhClH_2(PPh_3)_3} \qquad (1)$$

In view of the considerable interest in this catalytic system it is remarkable that the kinetics and mechanisms of reaction (1) do not appear to have been thus far directly examined. One possible explanation is that, unless inhibited by the addition of excess of $\mathrm{PPh_3}$, reaction (1) is too fast for conventional rate measurements. We have, however, been able to determine its kinetics by means of the stopped-flow technique. The results of such measurements which we report here, establish the mechanistic features of this reaction and define the hitherto controversial roles of the dissociated species $\mathrm{RhCl(PPh_3)_2}$ and $\mathrm{Rh_2Cl_2(PPh_3)_4}$.[1-4]

Our kinetic measurements were performed in benzene solution at 25·0°. The rates of reaction of $\mathrm{RhCl(PPh_3)_3}$ with $\mathrm{H_2}$ were determined spectrophotometrically by monitoring the absorbance change at 390 nm. The rates of reactions with half-lives shorter than 3 s were measured with a Durrum–Gibson stopped-flow spectrophotometer and those of slower reactions (*i.e.*, in the presence of added excess of $\mathrm{PPh_3}$) with a Cary 14 spectrophotometer. The kinetic measurements encompassed the initial concentration ranges, $6{\cdot}0 \times 10^{-5}$ to $4{\cdot}2 \times 10^{-4}$ M $\mathrm{RhCl(PPh_3)_3}$, $7{\cdot}1 \times 10^{-4}$ M to $2{\cdot}8 \times 10^{-3}$ M $\mathrm{H_2}$, and $1{\cdot}8 \times 10^{-3}$ to $1{\cdot}5 \times 10^{-1}$ M added $\mathrm{PPh_3}$.

The results of these kinetic measurements are quantitatively accommodated by a mechanistic scheme which includes, in addition to the direct hydrogenation (1) a contribution from the dissociative reaction pathway described by equations (2)—(4).

$$\mathrm{RhCl(PPh_3)_3} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{RhCl(PPh_3)_2} + \mathrm{PPh_3} \qquad (2)$$

$$\mathrm{RhCl(PPh_3)_2} + \mathrm{H_2} \xrightarrow{k_3} \mathrm{RhClH_2(PPh_3)_2} \qquad (3)$$

$$\mathrm{RhClH_2(PPh_3)_2} + \mathrm{PPh_3} \overset{\text{fast}}{\rightleftharpoons} \mathrm{RhClH_2(PPh_3)_3} \qquad (4)$$

Under the conditions of most of the kinetic measurements, *i.e.*, in the presence of added excess of $\mathrm{PPh_3}$, dissociation of $\mathrm{RhCl(PPh_3)_3}$ [into $\mathrm{RhCl(PPh_3)_2}$ and/or $\mathrm{Rh_2Cl_2(PPh_3)_4}$] is slight,[3,4] so that $[\mathrm{RhCl(PPh_3)_3}] = ca.\ [\mathrm{Rh^I}]_{\mathrm{total}}$, and the equilibrium (4) lies far to the left, *i.e.*, in favour of the undissociated hydride, $\mathrm{RhClH_2(PPh_3)_3}$.[4] Application of the steady state approximation to $\mathrm{RhCl(PPh_3)_2}$, accordingly, yields the rate-law described by equation (5) which was found to fit our kinetic data accurately for the values, $k_1 = 4{\cdot}8\ \mathrm{l\ mol^{-1}\ s^{-1}}$, $k_2 = 0{\cdot}71\ \mathrm{s^{-1}}$, and $k_{-2}/k_3 = 1{\cdot}1$.

$$\frac{-d[\mathrm{RhCl(PPh_3)_3}]}{dt} = \left[k_1 + \frac{k_2k_3}{k_{-2}[\mathrm{PPh_3}] + k_3[\mathrm{H_2}]}\right] \times [\mathrm{H_2}][\mathrm{RhCl(PPh_3)_3}] \qquad (5)$$

Extension of our earlier spectral measurements[3] on the dissociation of $RhCl(PPh_3)_3$ over a sufficiently wide concentration range to establish this point serves to support the conclusion, also reached by Meakin *et al.*[4] on the basis of n.m.r. measurements, that the equilibrium of equation (6) lies far to the right and that the principal species in equilibrium with $RhCl(PPh_3)_3$ in solution through dissociation of PPh_3 is thus the Cl-bridged dimer $Rh_2Cl_2(PPh_3)_4$. However, under the reaction conditions described above, *i.e.*, starting with $RhCl(PPh_3)_3$, the interception of $RhCl(PPh_3)_2$ by reaction with H_2 according to equation (3) apparently is sufficiently fast compared with reaction (6) to preclude the formation of $Rh_2Cl_2(PPh_3)_4$ so that the latter does not contribute significantly to the overall reaction with H_2.

$$2RhCl(PPh_3)_2 \rightleftharpoons Rh_2Cl_2(PPh_3)_4 \qquad (6)$$

Examination of equation (5) reveals that at sufficiently low PPh_3 concentrations, such that $k_{-2}[PPh_3] << k_3[H_2]$, the pseudo-first-order rate constant for reaction with H_2, *i.e.*, rate/$[RhCl(PPh_3)_3]$, approaches the value $(k_1[H_2] + k_2)$ which approximates to k_2 since $k_1[H_2]$ (= *ca.* 0·01 s^{-1} at 1 atm H_2) $<< k_2$ (0·71 s^{-1}). Under these conditions, the dissociative reaction pathway [equations (2)—(4)] is the principal one so that the rate of reaction with H_2 becomes limited by the rate of dissociation (k_2) of $RhCl(PPh_3)_3$ and is thus independent of $[H_2]$. We have confirmed this point experimentally.

In the absence of added PPh_3 the preformed dimer $Rh_2Cl_2(PPh_3)_4$ was found to react directly with H_2, apparently in accord with equation (7), to form $Rh_2H_2Cl_2(PPh_3)_4$ in which H_2 has added to only one of the Rh atoms.[5] Kinetic measurements, similar to those described above for $RhCl(PPh_3)_3$, yielded the rate law (8), with a value of k_8 = 5·4 l mol^{-1} s^{-1}, *i.e.*, close to that of k_1. The intrinsic reactivities toward H_2 of the two four-co-ordinate Rh^I complexes, $RhCl(PPh_3)_3$ and $Rh_2Cl_2(PPh_3)_4$ are thus very similar.

$$Rh_2Cl_2(PPh_3)_4 + H_2 \rightarrow Rh_2Cl_2H_2(PPh_3)_4 \qquad (7)$$

$$-d[Rh_2Cl_2(PPh_3)_4]/dt = 2k_8[H_2][Rh_2Cl_2(PPh_3)_4] \qquad (8)$$

From the combination of the spectrally determined[3] equilibrium constant (*ca.* 1×10^{-4} M) for the dissociation reaction $2RhCl(PPh_3)_3 \rightleftharpoons Rh_2Cl_2(PPh_3)_4 + 2PPh_3$, and the lower limit of *ca.* 10^6 M^{-1} that can be assigned to the equilibrium constant of reaction (6) [based on the absence of detectable dissociation of $Rh_2Cl_2(PPh_3)_4$ in *ca.* 10^{-5} M solutions of the latter], the value of the equilibrium constant of equation (2) (*i.e.*, k_2/k_{-2}) can be deduced to be $< 1 \times 10^{-5}$ M. In combination with the values reported above of k_2 = 0·71 s^{-1} and k_{-2}/k_3 = 1·1, this yields the value $k_3 > 7 \times 10^4$ l mol^{-1} s^{-1}. $RhCl(PPh_3)_2$ is thus seen to be at least 10^4 times as reactive toward H_2 as either $RhCl(PPh_3)_3$ or $Rh_2Cl_2(PPh_3)_4$. Direct support is thus provided for the original suggestion of Wilkinson *et al.* concerning the high reactivity of the dissociated species $RhCl(PPh_3)_2$ and the probable importance of this species (despite its low concentration in solution) in $RhCl(PPh_3)_3$-catalysed hydrogenation and related reactions.

Support of this research through grants from the National Science Foundation is acknowledged.

(*Received, 6th June* 1973; *Com.* 810.)

---

[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[2] S. Siegel and D. Ohrt, *Tetrahedron Letters*, 1972, **8**, 15.

[3] H. Arai and J. Halpern, *Chem. Comm.*, 1971, 1571.

[4] P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 3240.

[5] C. A. Tolman, J. P. Jesson, and P. Meakin, Abstracts 165th National Meeting Amer. Chem. Soc., Dallas, 1973.