

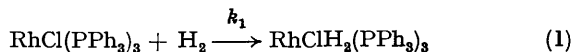
## Hydrogenation of Tris(triphenylphosphine)chlororhodium(I)

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

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

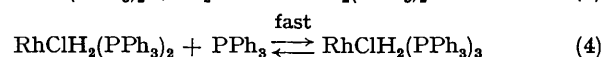
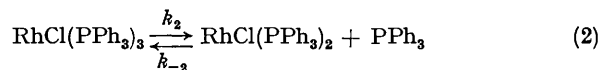


In view of the considerable interest in this catalytic system it is remarkable that the kinetics and mechanisms of reaction (1) do not appear to have been thus far directly examined. One possible explanation is that, unless inhibited by the addition of excess of  $\text{PPh}_3$ , reaction (1) is too 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  $\text{RhCl}(\text{PPh}_3)_2$  and  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ .<sup>1-4</sup>

Our kinetic measurements were performed in benzene solution at 25.0°. The rates of reaction of  $\text{RhCl}(\text{PPh}_3)_3$  with  $\text{H}_2$  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  $\text{PPh}_3$ ) with a Cary 14 spectrophotometer. The kinetic measurements encompassed the initial concentration ranges,  $6.0 \times 10^{-5}$  to  $4.2 \times 10^{-4}$  M  $\text{RhCl}(\text{PPh}_3)_3$ ,  $7.1 \times 10^{-4}$  M to  $2.8 \times 10^{-3}$  M  $\text{H}_2$ , and  $1.8 \times 10^{-3}$  to  $1.5 \times 10^{-1}$  M added  $\text{PPh}_3$ .

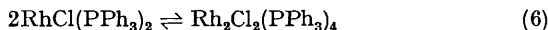
The results of these kinetic measurements are quantitatively accommodated by a mechanistic scheme which includes, in addition to the direct hydrogenation (1) a contribution from the dissociative reaction pathway described by equations (2)–(4).



Under the conditions of most of the kinetic measurements, *i.e.*, in the presence of added excess of  $\text{PPh}_3$ , dissociation of  $\text{RhCl}(\text{PPh}_3)_3$  [into  $\text{RhCl}(\text{PPh}_3)_2$  and/or  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ ] is slight,<sup>3,4</sup> so that  $[\text{RhCl}(\text{PPh}_3)_3] = ca. [\text{Rh}^I]_{\text{total}}$ , and the equilibrium (4) lies far to the left, *i.e.*, in favour of the undissociated hydride,  $\text{RhClH}_2(\text{PPh}_3)_3$ .<sup>4</sup> Application of the steady state approximation to  $\text{RhCl}(\text{PPh}_3)_2$ , accordingly, yields the rate-law described by equation (5) which was found to fit our kinetic data accurately for the values,  $k_1 = 4.81 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_2 = 0.71 \text{ s}^{-1}$ , and  $k_{-2}/k_3 = 1.1$ .

$$\frac{-d[\text{RhCl}(\text{PPh}_3)_3]}{dt} = \left[ k_1 + \frac{k_2 k_3}{k_{-2}[\text{PPh}_3] + k_3[\text{H}_2]} \right] \times [\text{H}_2][\text{RhCl}(\text{PPh}_3)_3] \quad (5)$$

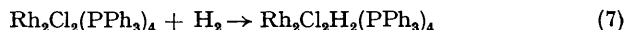
Extension of our earlier spectral measurements<sup>3</sup> on the dissociation of  $\text{RhCl}(\text{PPh}_3)_3$  over a sufficiently wide concentration range to establish this point serves to support the conclusion, also reached by Meakin *et al.*<sup>4</sup> on the basis of n.m.r. measurements, that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



Examination of equation (5) reveals that at sufficiently low  $\text{PPh}_3$  concentrations, such that  $k_{-2}[\text{PPh}_3] \ll k_3[\text{H}_2]$ , the pseudo-first-order rate constant for reaction with  $\text{H}_2$ , *i.e.*,  $\text{rate}/[\text{RhCl}(\text{PPh}_3)_3]$ , approaches the value  $(k_1[\text{H}_2] + k_2)$  which approximates to  $k_2$  since  $k_1[\text{H}_2]$  ( $= ca. 0.01 \text{ s}^{-1}$  at 1 atm  $\text{H}_2$ )  $\ll k_2$  ( $0.71 \text{ s}^{-1}$ ). Under these conditions, the dissociative reaction pathway [equations (2)—(4)] is the principal one so that the rate of reaction with  $\text{H}_2$  becomes limited by the rate of dissociation ( $k_2$ ) of  $\text{RhCl}(\text{PPh}_3)_3$  and is thus independent of  $[\text{H}_2]$ . We have confirmed this point experimentally.

In the absence of added  $\text{PPh}_3$  the preformed dimer  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$  was found to react directly with  $\text{H}_2$ , apparently in accord with equation (7), to form  $\text{Rh}_2\text{H}_2\text{Cl}_2(\text{PPh}_3)_4$  in which  $\text{H}_2$  has added to only one of the Rh atoms.<sup>5</sup>

Kinetic measurements, similar to those described above for  $\text{RhCl}(\text{PPh}_3)_3$ , yielded the rate law (8), with a value of  $k_8 = 5.4 \text{ l mol}^{-1} \text{ s}^{-1}$ , *i.e.*, close to that of  $k_1$ . The intrinsic reactivities toward  $\text{H}_2$  of the two four-co-ordinate  $\text{Rh}^{\text{I}}$  complexes,  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$  are thus very similar.



$$-d[\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4]/dt = 2k_8[\text{H}_2][\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4] \quad (8)$$

From the combination of the spectrally determined<sup>3</sup> equilibrium constant (*ca.*  $1 \times 10^{-4} \text{ M}$ ) for the dissociation reaction  $2\text{RhCl}(\text{PPh}_3)_3 \rightleftharpoons \text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4 + 2\text{PPh}_3$ , and the lower limit of *ca.*  $10^6 \text{ M}^{-1}$  that can be assigned to the equilibrium constant of reaction (6) [based on the absence of detectable dissociation of  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$  in *ca.*  $10^{-5} \text{ M}$  solutions of the latter], the value of the equilibrium constant of equation (2) (*i.e.*,  $k_2/k_{-2}$ ) can be deduced to be  $< 1 \times 10^{-5} \text{ M}$ . In combination with the values reported above of  $k_2 = 0.71 \text{ s}^{-1}$  and  $k_{-2}/k_3 = 1.1$ , this yields the value  $k_3 > 7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ .  $\text{RhCl}(\text{PPh}_3)_2$  is thus seen to be at least  $10^4$  times as reactive toward  $\text{H}_2$  as either  $\text{RhCl}(\text{PPh}_3)_3$  or  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ . Direct support is thus provided for the original suggestion of Wilkinson *et al.* concerning the high reactivity of the dissociated species  $\text{RhCl}(\text{PPh}_3)_2$  and the probable importance of this species (despite its low concentration in solution) in  $\text{RhCl}(\text{PPh}_3)_3$ -catalysed hydrogenation and related reactions.

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