Effect of Water on the Mechanism of Hydrogenations Catalysed by Rhodium Phosphine Complexes

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On the action of H_2 in aqueous solutions, the water soluble analogue of Wilkinson's catalyst, [RhCl(tppms)$_3$] [tppms=P(C$_6$H$_5$)$_2$(C$_6$H$_4$SO$_3$Na)], gives [RhH(tppms)$_3$] instead of [RhH$_2$Cl(tppms)$_3$] and this is reflected in the rates and selectivities of hydrogenations using this catalyst.

Within the important field of aqueous organometallic catalysis[1] there are indications that water is often not an inert solvent but influences the rates and selectivities of the processes.[1] Reactions of, or catalysed by, [RhClL$_3$] [L = tppts *i.e.* P(C$_6$H$_4$SO$_3$Na)$_3$ or tppms] show examples of such influence. The formation of hydroxorhodium complexes such as [Rh(OH)(tppts)$_3$], [{Rh(μ-OH)(tppts)$_2$}$_2$] or *trans*-[Rh(OH)(CO)(tppts)$_2$][2,3] is greatly facilitated. The *cis-mer* and *cis-fac* dihydrides, [RhH$_2$Cl(tppms)$_3$], were characterized by ^{1}H and ^{31}P NMR studies in aqueous solution in the presence of HCl (1 mol dm^{-3}), HClO$_4$ or NaCl. However, these complexes were shown to be rather poor catalysts for olefin hydrogenation.[4] On the other hand, [RhCl(tppms)$_3$] readily catalyses the hydrogenation of olefinic substrates in neutral or only slightly acidic solution. In one particular example,[5] maleic acid (MA) was hydrogenated much more slowly than its *trans*-isomer (fumaric acid, FA) in contrast to what could be expected from a formal analogue of [RhH$_2$Cl(PPh$_3$)$_3$].[6] In D$_2$O, reductions with H_2 catalysed by [RhClL$_3$] complexes of various sulfonated phosphines (including tppms and tppts) extensive deuteriation of the product was observed.[7]

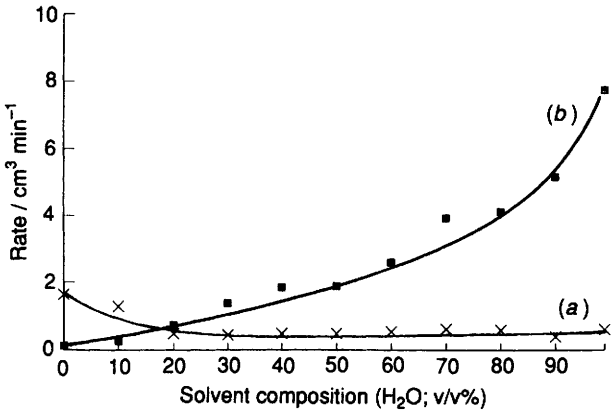

Fig. 1 Rates of hydrogenation of MA (*a*) and FA (*b*) in diglyme–water mixtures as a function of solvent composition; [Rh] = 0.001 mol dm^{-3}, [substrate]=0.05 mol dm^{-3}, T = 333 K, P_{total} = 0.1 MPa

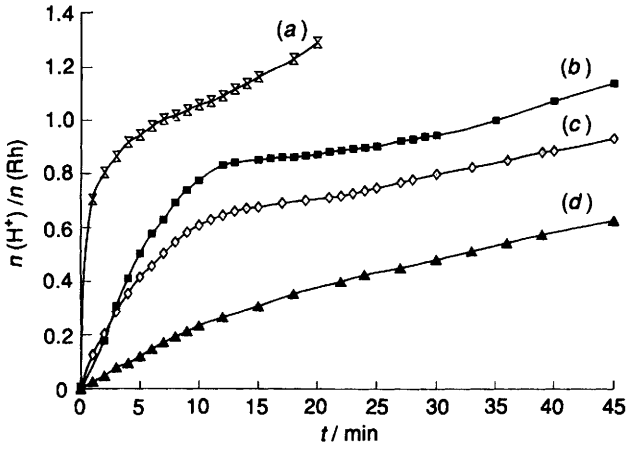

Fig. 2 Proton production during hydrogenation of [RhCl(tppms)$_3$] as measured by pH-static titrations; [Rh] = 0.02 mol dm^{-3}, T = 333 K, P_{total} = 0.1 MPa: pH, (*a*) 9.00, (*b*) 7.00, (*c*) 5.50, (*d*) 4.00

To get a deeper insight into the role of water in these reactions we compared the behaviour of the same catalyst, [RhCl(tppms)$_3$], in a strictly anhydrous solution and in solutions with increasing water content in the hydrogenation of MA and FA. As a low-polarity, aprotic, water miscible organic solvent diethyleneglycol dimethyl ether (diglyme) was chosen. In pure diglyme, the catalyst was prepared in the reaction of [{RhCl(cod)$_2$}$_2$] + 6 tppms + 6 [Bu_4N][HSO_4] (cod = cycloocta-1,5-diene) and aliquots of this stock solution were added (after removing Na[HSO_4] by filtration) at most solvent compositions. Only in highly aqueous solutions was the solid [RhCl(tppms)$_3$] used; the change in the cation had no effect on reaction rates. Results are shown on Fig. 1.

In anhydrous diglyme MA is hydrogenated faster (initial rate 1.64 cm^3 min^{-1}) than FA (initial rate 0.13 cm^3 min^{-1}). Under the same conditions [RhCl(PPh_3)$_3$] gave initial rates of 0.49 and 0.14 cm^3 min^{-1}, respectively. Obviously, with both catalysts the *cis*-olefin is reduced faster than the *trans*-isomer, in accordance with the well-established selectivity[6] of Wilkinson's catalyst. However, on increasing water concentration the selectivity reverses and in pure water solutions hydrogenation of FA is much faster than that of MA. (In these unbuffered aqueous solutions the pH is around 3, depending on the substrate and its concentration). It can be concluded therefore, that the peculiar selectivity is brought about by the aqueous solvent and not by the sulfonation of the ligand.

When hydrogen gas was bubbled through a 0.02 mol dm^{-3} aqueous solution of [RhCl(tppms)$_3$] the pH of the solution gradually dropped close to 2. Quantitative measurements of proton production were therefore undertaken. Solutions of [RhCl(tppms)$_3$] were hydrogenated in the vessel of a pH-stat at different starting pHs. If required, 0.2 mol dm^{-3} KOH solution was delivered by a pump to keep the pH constant throughout the hydrogenation, and the volume of the KOH solution was measured by an automatic burette.

It is clear from these measurements (Fig. 2) that at 60 °C, in neutral aqueous solutions approximately 1 mol H^+ per 1 mol Rh is liberated in the first, relatively fast phase of the reaction. This is accompanied by the uptake of 1 mol H_2 per 1 mol Rh during the same period. At the same pH there was only 10% proton production (based on Rh) when the solution was bubbled with argon which may be attributed to the hydrolysis of the complex. In acidic solutions hydrolysis is retarded, however both hydrogen uptake and proton production is slower. On prolonged treatment with hydrogen, there is a second, slow phase of proton liberation, and the H_2 consumed and the H^+ produced may well exceed the amount of rhodium present. Around the reaction times corresponding to the break on the graphs the yellow solutions become dark and finally a black precipitate is formed. This second phase of the reaction was not investigated in detail.

These observations may be explained by reactions (1)–(3).

$$[RhCl(tppms)_3] + H_2 \rightleftharpoons [RhH(tppms)_3] + Cl^- + H^+ \quad (1)$$

$$[RhCl(tppms)_3] + H_2O \rightleftharpoons [Rh(OH)(tppms)_3] + Cl^- + H^+ \quad (2)$$

$$[Rh(OH)(tppms)_3] + H_2 \rightleftharpoons [RhH(tppms)_3] + H_2O \quad (3)$$

Unfortunately, despite all our efforts, we could not detect a hydride resonance in the ^1H NMR spectrum of the hydrogenated complex in D_2O probably because of a fast exchange with the solvent. It is recalled here, that there is no ^1H NMR data in the literature for Rh^I-monohydrides in aqueous solution. Both H^+ and Cl^- push the equilibria (1) and (2) backwards and under those conditions the Rh^{III}-dihydrides observed by Larpent and Patin[4] may form.

The predominance of [RhH(tppms)$_3$] brings about substantial changes in the mechanism of hydrogenation. In a monohydridic mechanism of olefin hydrogenation the product must be liberated from the intermediate alkyl derivative either by hydrogenolysis or by protonation by H^+ (D^+) of the solvent. Clearly, in aqueous solutions the latter reaction may be favoured. As a consequence, in agreement with earlier observations,[6] we found extensive deuterium incorporation {80% from ^1H NMR (δ 4.4) and FTIR [ν(CD) 2183 cm^{-1}]} when *Z*-α-acetamidocinnamic acid was hydrogenated in D_2O with H_2 at 60 °C catalysed by [RhCl(tppms)$_3$] ([substrate]=0.8 mol dm^{-3}, [Rh]=0.01 mol dm^{-3}, P_{total}=0.1 MPa). Another consequence of a monohydridic mechanism may be the lowering or loss of enantioselectivity[8,9] in aqueous hydrogenations relative to the same reaction in low-polarity, aprotic solvents, and its restoration on the effect of surfactants.[10]

[RhH(tppms)$_3$] may, as well, arise from a reductive dehydrochlorination[11] of [RhH_2Cl(tppms)$_3$] formed by the oxidative addition of H_2 on [RhCl(tppms)$_3$]. The analogous reaction of [RhCl(PPh_3)$_3$] in organic solvents requires addition of bases (mostly amines).[12] In aqueous solutions water itself plays the role of a base and because of the large solvation energies of H^+ and OH^- dehydrochlorination is strongly facilitated. With [RhCl(PPh_3)$_3$] in organic/aqueous biphasic systems, HCl or Base·HCl is extracted into the aqueous phase leaving [RhH(PPh_3)$_3$] in the organic phase. This reaction explains unusual rates and selectivities in hydrogenation of acetophenone[13] and alkadienoic[14] acids.

It should be noted that in this paper we do not address the question of phosphine dissociation equilibria of the particular rhodium complexes, nor do we consider other factors which influence the mechanism of hydrogenations.[15]

In conclusion, we emphasize that in homogeneous aqueous solutions or in aqueous/organic biphasic systems formation of monohydridorhodium phosphine derivatives is a strong possi-

bility and has important influence on the outcome of reactions catalysed by [$RhClL_n$]-type complexes. Meaningful mechanistic results may be obtained only from studies on buffered solutions.

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