Rhodium Catalysts for the Homogeneous Hydrogenation of Ketones

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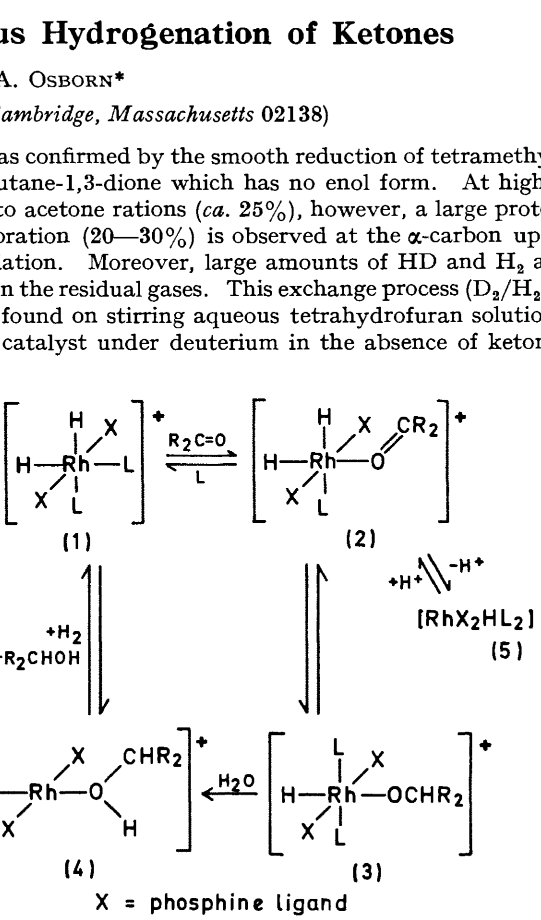
Summary Certain soluble rhodium complexes can function as homogeneous catalysts for the hydrogenation of ketones when promoted by small quantities of water.

DURING the last few years several effective homogeneous hydrogenation catalysts have been described,[1] but their utility has generally been limited to the reduction of unsaturated carbon–carbon bonds. We have previously reported[2] that the cationic species, $[RhH_2(PPh_3)_2L_2]^+$ (L = solvent), catalyses very efficiently the hydrogenation of olefins, diolefins, and acetylenes. We now find that the analogous complexes with more basic phosphines as ligands (*e.g.* PPh_2Me, $PPhMe_2$, PMe_3) also catalyse the reduction of ketones under mild conditions.†

A 3mM-solution of $[RhH_2(PPhMe_2)_2L_2]^+$ (as PF_6^-, ClO_4^- salts) in 1% aqueous acetone readily takes up molecular hydrogen at 25° and atmospheric pressure without an induction period (initial rate *ca.* 4 ml min.$^{-1}$). N.m.r. and g.l.c. analysis of the resultant solution confirms the presence of isopropyl alcohol. Other ketones, *e.g.* cyclohexanone acetophenone, and butan-2-one, are also readily hydrogenated using this catalyst. Benzophenone, however, is not readily hydrogenated; a stable complex appears to be formed. The reduction of 4-t-butylcyclohexanone takes place to yield predominantly *trans*-4-t-butylcyclohexanol (*ca.* 86% *trans* and 14% *cis*).

Several points of interest may be noted concerning the catalytic process. It is found that using *dry* acetone the rate of reduction is *extremely slow* (*ca.* 0·13 ml min.$^{-1}$) under the conditions described above. Incremental additions of water to this solution increase the rate markedly, reaching a maximum after the addition of *ca.* 1% water by volume. On further addition of water a slight decrease in rate is observed. Other ketones were found to show similar behaviour. However, the reduction of olefins is *inhibited* by the addition of water.

Reduction of 1% aqueous acetone with deuterium yields isopropyl alcohol labelled at the α-carbon, none being detectable at the β-carbon. The enol form of the ketone thus plays no significant role in the catalytic process. This was confirmed by the smooth reduction of tetramethylcyclobutane-1,3-dione which has no enol form. At higher water to acetone rations (*ca.* 25%), however, a large proton incorporation (20—30%) is observed at the α-carbon upon deuteriation. Moreover, large amounts of HD and H_2 are found in the residual gases. This exchange process (D_2/H_2O) is also found on stirring aqueous tetrahydrofuran solutions of the catalyst under deuterium in the absence of ketone.



SCHEME 1

As yet we have been unable to obtain fully reproducible kinetic data. However, it may be noted that the initial rate of reduction of $(CD_3)_2CO$ containing 1% D_2O (v/v) with deuterium gas is identical (±5%) with the initial rate of hydrogenation of a 1% aqueous acetone solution, indicating that no primary isotope effect is operative in the reduction of acetone under these conditions.

A mechanism consistent with the above observations is

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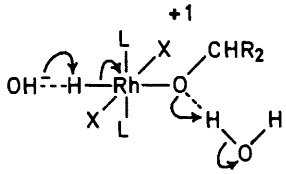
† Aldehydes are also initially reduced but a rapid decrease in catalytic activity is soon observed.

presented below (Scheme 1). Replacement of solvent by ketone on (**1**) (probably *via* an S_N1 process) yields (**2**) with co-ordinated ketone.[2] It is suggested that a *step-wise* process then occurs, initially involving a 1,3-hydride migration from a *cis*-site on the metal to the positive carbon on the keto-group (**2** → **3**). This step would account for deuterium incorporation at this carbon atom. We suggest that the second proton-transfer step (**3** → **4**) is promoted by small quantities of water. This process is presented diagrammatically in Scheme 2.



SCHEME 2

Deprotonation may be carried out by hydroxyl ion (as depicted) or by a water molecule and protonation of the alkoxy-group may occur simultaneously or more probably in a subsequent step. The amphiprotic nature of water thus facilitates this process but other species, *e.g.* ethanol, also are found to promote this reduction.‡ Indeed, the reduction of dry ketones is noticeably autocatalytic.

The catalytic cycle is completed by dissociation of the product alcohol away from the catalyst. This may occur either before or after the addition of one mole of hydrogen to the catalyst by a $d^8 \rightarrow d^6$ oxidative addition process to re-form (**1**) (see Scheme 1).

Deprotonation of the cationic dihydrido- species (**1**)—or (**2**)—can occur (to some extent even with water or alcohols) to yield a neutral monohydride species.§ An acetone solution of this species (**5**; X = PPh_2Me), generated *in situ*, does not absorb hydrogen. However, on addition of one mole of tetrafluoroboric acid hydrogenation of acetone proceeds. This reversible deprotonation–protonation process also facilitates the observed D_2–H_2O exchange.

Stable analogues have been isolated for all the intermediates except (**3**).

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‡ Small quantities of base (Et_3N) initially also promote reduction but then rapid inhibition occurs as a result of deprotonation of the active dihydrido-complex.

§ On treating a solution of the cation $[RhH_2(PPh_3)_2L_2]^+$ with one mole of base (Et_3N) and an excess of PPh_3 the known complex $Rh(PPh_3)_4H$ can be isolated. In absence of an excess of phosphine, species such as (**6**) are generated in solution. Analogous species are also produced by treatment of an acetone solution of $Rh(NBD)(CH_3)(PPh_2Me)_2$ with hydrogen.

[1] M. E. Vol'pin and I. S. Kolomnikov, *Russ. Chem. Rev.*, 1969, **38**, 273.

[2] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1969, **91**, 2816.