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Mild Hydroformylation of Olefins using Rhodium Catalysts

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CERTAIN complexes of rhodium(III) have been shown to activate molecular hydrogen under very mild conditions of temperature and pressure.[1] We now report that not only are other rhodium complexes more effective catalysts for the homogeneous hydrogenation of olefins, but that such systems also catalyse the homogeneous hydroformylation of olefins under conditions milder than those required in the conventional process using cobalt carbonyl catalysts.[2]

Examples of homogeneous hydrogenation are the conversion of hex-1-ene into n-hexane by ethanol–benzene solutions of tertiary phosphine and arsine complexes such as 1,2,3-tris-(triphenylphosphine)trichlororhodium(III), and its dimethylphenylarsine analogue, and by ethanolic solutions of the solvated rhodium(I) chlorine-bridged stannous chloride complex.[3]

When carbon monoxide is present additionally, hydroformylation proceeds readily. Thus at 55°c and 90 atmospheres total pressure ($H_2:CO \approx 1:1$) for 12 hours, hex-1-ene is converted into n-heptaldehyde (~70%) and 2-methylhexanoaldehyde (~20%) when 1,2,3-$(Ph_3P)_3RhCl_3$ at a concentration of *ca.* 1% that of the olefin in ethanol–benzene solution (1 : 1) is employed. Under similar conditions in ethanol, 1,2,6-py_3RhCl_3 and $Rh_2Cl_2(SnCl_2, EtOH)_4$ are effective. Other olefins such as oct-1-ene, hept-1-ene, and butadiene also are hydroformylated.

At higher temperatures, *ca.* 100°, and with $H_2:CO$ ratios $>1:1$, further conversion of the aldehyde into alcohol appears to occur, and also with increasing hydrogen concentration the simple hydrogenation reaction begins to compete.

We have also shown that n-heptaldehyde is quantitatively reduced to n-heptanol by hydrogen (50 atm.) at 110° in presence of the above catalysts using, for example, $(Ph_3P)_3RhCl_3$ in ethanol–benzene or the rhodium–tin complex in ethanol. Since it is also possible to use as solvent the alcohol being produced by hydroformylation from an olefin, a convenient two-stage process could involve hydroformylation to the aldehyde followed by hydrogenation to the alcohol; this would allow stripping of the product and re-use of the catalyst.

The mechanism of these hydroformylations is presumably similar to that generally accepted[2] for the cobalt system involving formation of a metal–hydrogen bond, addition to the olefin, and insertion of CO into the metal–carbon bond so produced.

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[1] R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284.

[2] See, *e.g.*, C. W. Bird, *Chem. Rev.*, 1962, **62**, 283.

[3] A. G. Davies, G. Wilkinson, and J. F. Young, *J. Amer. Chem. Soc.*, 1963, **85**, 1692.