Solvent Effects in Homogeneous Catalysis by Metal Complexes

The Evidence of Solute–Solute and Solute–Solvent Interactions in Homogeneous Catalysis with Transition Metal Complexes: an Introduction

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The effects of solute–solvent interactions in homogeneous catalysis with transition metal complexes have never been studied in great detail although it is quite well known that they can be relevant in a large number of cases.

In fact at least four different kinds of effect can be identified.

a) The stabilisation of different complexes, in relation with the polarity or basicity or acidity of the solvent; these complexes can play a different role in the catalytic cycles. A typical case is given by the oxosynthesis of olefins catalysed by the system $Co_2(CO)_8$ + PR_3 (so called Shell catalysis) [1]; the polarity of the solvent has a great influence on the equilibrium:

$$\underset{\text{(catalytically active)}}{[Co_2(CO)_6(PR_3)_2]} \overset{CO}{\rightleftharpoons} \underset{\text{(catalytically inactive)}}{[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-}$$

b) The poisoning effect of the coordination of donor solvents to the active sites of the catalytic complexes as for instance in the epoxidation of olefins by hydroperoxides in the presence of Mo complexes (so called Halcon Catalysis) [2].

c) The role of solvents on the ion pairing between different cations and anionic catalytic species (like $Co(CN)_5^{3-}$, $HFe(CO)_4^-$ etc.), such kind of solute–solute interactions can introduce a relevant perturbation of the activity and also selectivity of the anionic complexes (for instance probably in the Union Carbide synthesis of polyalcohols from syn. gas) [3].

d) The polarity or the protonic character of the solvent can influence the enantiomeric yields of enantioselective reactions like for instance the asymmetric hydrogenation of olefins with rhodium chiral phosphines complexes (for instance in the Monsanto catalysis to produce L-Dopa) [4].

In conclusion these effects perturb the nature of the catalysts either by strong interactions (like in *a*) and *b*)) or by relatively weak perturbations (like in *c*) and *d*)).

However the fundamental organometallic chemistry necessary to understand in detail the origin of these effects is still lacking.

References

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Phase Transfer Approach to Homogeneous Catalysis with Metal Complexes

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Since 1976, when the first examples of the application of phase transfer catalysis to organometallic chemistry appeared in the literature, significant progress has been made in this area of chemistry. Of particular note is the demonstrated utility of this technique in effecting homogeneous catalysis with transition metal complexes under exceedingly mild conditions.

Some recent developments in this subject will be highlighted, including metal carbonyl catalyzed reduction, dehydrogenation, and carbonylation processes (*e.g.* 1 → 2, 3 → 4) which are of considerable industrial interest.