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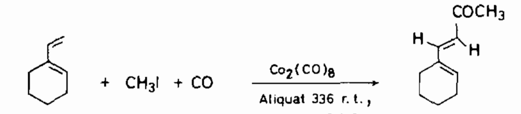
Since 1976, when the first examples of the application of phase transfer catalysis to organometallic chemistry appeared in the literature, significant progress has been made in this area of chemistry. Of particular note is the demonstrated utility of this technique in effecting homogeneous catalysis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



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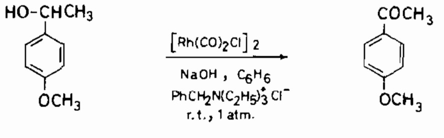

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Solvent effects on these reactions will be discussed.

Solvent and Solute Interactions in Organic Synthesis and Homogeneous Catalysis Involving Anionic Metal Carbonyls

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The effects of solvent and ion pairing on the chemistry of metal carbonyl anions will be selectively surveyed and then an illustrated outline of our work on the conversion of carbon monoxide and hydrogen to ethylene glycol will be presented.

The homogeneous rhodium/Lewis base-catalyzed conversion of carbon monoxide and hydrogen to ethylene glycol [1] has more recently been studied typically at 200–300 °C and 500–1000 atm.

Since the initial suggestion [2] that anionic rhodium carbonyl clusters are an important part of the catalyst system and that ion pairing decreases its reactivity, we have studied the involvement in the catalyst system of the solvent and of the components of the amine and salt Lewis base co-catalysts.

The solvents in which the highest rates of formation of ethylene glycol are observed are those which facilitate separation of ions without attendant complexation of the catalyst, either by ligation or solvation. Solvents of high dielectric constant, such as sulfolane and butyrolactone, and those capable of complexing cations, such as tetraglyme and crown ethers, are particularly good reaction media; even better are binary mixtures containing a component of each class. This is the first use of crown ethers as a reaction solvent. The rate of formation of ethylene glycol is greatest in phosphine oxides, which are cation complexing solvents of moderately high dielectric constant.

We have found that, in general, amines and salts function as co-catalysts and that there is an amount of co-catalyst optimum for formation of ethylene glycol, there being concurrent promotion and inhibition. We have studied the dependence of the promotion and inhibition on the properties of the co-catalysts, particularly their basicity and the ion pairing ability of their counterions and conjugate acids, inherent and as modified by the solvent.

References

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Binuclear Solvent-Dependent Nature of Some Complexes Relevant to Molecular Activation Processes

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A brief account will be given on the ion-pair nature of very well known organometallic species, with regards to their role in the activation of organic substrates and small molecules.

Two classes of co-ordination compounds will be discussed in this context; 'acid–base' transition metal–alkali cations and dinuclear copper(I) complexes. While the first type includes ion-pair species active in carbon dioxide fixation, the dinuclear copper(I) complexes may play a relevant role in carbon monoxide and dioxygen activation.

The attention will be mainly focused on the following points:

i) the co-ordination of alkali cations by transition metal complexes, producing acid–base compounds, and their role in the interaction with carbon dioxide and carbon dioxide-like molecules;

ii) some problems related to the CO_2 activation, which seems to require 'acid–base' complexes;

iii) the solvent-dependent synthesis of some dinuclear copper(I) complexes, in which both coppers(I) interact with the same substrate;

iiii) the problems associated with the high kinetic lability of some copper(I) complexes, to be used in molecular activation.

References

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