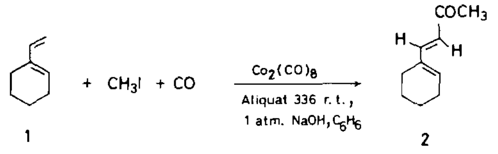

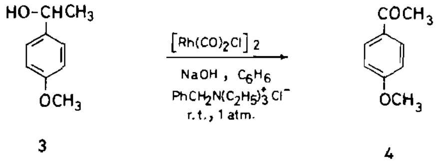

Solvent effects on these reactions will be discussed.

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

1 U.S. Patent 3833634 (1974) to Union Carbide Corporation.
2 J. N. Cawse, unpublished work.

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

1 G. Fachinetti, C. Floriani *et al., J. Am. Chem. Soc., 100,* 7405 (1978); *Inorg. Chem., 18,* 3469 (1979).
2 M. Pasquali, C. Floriani *et al., J. Chem. Soc. Chem. Comm.,* 197 and 937 (1979).
3 M. Pasquali, C. Floriani *et al., J. Am. Chem. Soc.,* submitted.