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A DISCUSSION OF THE DIFFERENT KINDS OF SOLUTE–SOLUTE AND SOLUTE—SOLVENT INTERACTIONS ACTING IN HOMOGENEOUS CATALYSIS BY TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

The subject of solute–solute and solute–solvent interactions has been widely discussed in coordination and organometallic chemistry, but not in the related field of homogeneous catalysis by transition metal complexes. This is not because these effects have little importance in homogeneous catalysis, on the contrary, they are often as significant as those in organic or even classical coordination chemistry, as will be seen. The real meaning of the above statement is that an effort has not been made to present this problem generally and to give in parallel a satisfactory analysis and classification of the many different cases reported in the literature.

The aim of this work was to examine the subject in general and to produce a tentative classification of the relevant features of the solvent–solute or solute–solute interactions in homogeneous catalysis. At least four types of effects can be identified. (a) The stabilisation of different organometallic species, often having different catalytic properties, as determined by the polarity or basicity/acidity of the solvent or solute. These are usually quite large effects, as regards both activity and selectivity. (b) The interaction between a solvent (behaving as a donor base) and the metal complex catalyst (behaving as an acid) can give rise to a poisoning effect, by occupation of a vacant site of the coordination sphere of the metal center. This is usually a strong effect.

Effects (a) and (b) are related to strong interactions between the solvent and catalyst; they have been studied in detail for various cases.

(c) Ion pairing between cations and anionic catalytic species (e.g. $[HFe(CO)_4]^-$, $[Co(CN)_5]^{3-}$ etc.) can have a significant influence on the activity of the catalyst and, in some cases, even on the selectivity. Such a type of solute–solute interaction has not been widely investigated with cationic catalytic species since often the anions used are weakly interacting (e.g. ClO_4^- or BF_4^-).

(d) The polarity or hydrogen-bonding properties of a protonic solvent can, by a classical solvation mechanism, affect the rates of catalytic homogeneous reactions or the stereoselectivity of enantioselective catalytic reactions such as the asymmetric hydrogenation of a prochiral double bond. In this latter case the transition states of a catalytic cycle are perturbed by relatively weak interactions such as dipole–dipole interactions or hydrogen bonding which can produce significant effects.

Effects (c) and (d) refer to relatively weak interactions and as such have been less well studied than effects (a) and (b), since they are related to more subtle phenomena and properties of the solutions. However, these effects may have important effects, particularly in the control of different kinds of selectivity, which is known to be a characteristic feature of homogeneous catalysis with transition metal complexes.

B. THE EFFECTS OF THE SOLVENT AND SOLUTE ON CATALYTIC ACTIVITY AND SELECTIVITY VIA THE STABILISATION OF DIFFERENT ORGANOMETALLIC SPECIES

Usually, solvents or solutes of high polarity or with particular basic or acidic properties interact strongly with metal complexes even under relatively mild conditions to produce new species, either by an electron-transfer process or more simply by protonation or solvolysis of ligands. It is obvious that these interactions must have a significant effect on the total catalytic activity, which can be increased or decreased depending on the nature of the new species formed in situ. These same interactions may operate on the selectivity and even on the enantioselectivity of a catalyst.

The organometallic chemistry of the interaction of different solvents with metal complexes has been widely investigated; consequently it is easy in many cases to correlate the observed changes in the properties of the catalytic solution with the known transformations of the metal complexes originally dissolved. There are numerous examples in the literature and for this reason we limit our discussion to a few extreme cases in order to show the extent to which this kind of organometallic chemistry can help in understanding the origin of particularly large effects on the catalytic activity and selectivity.

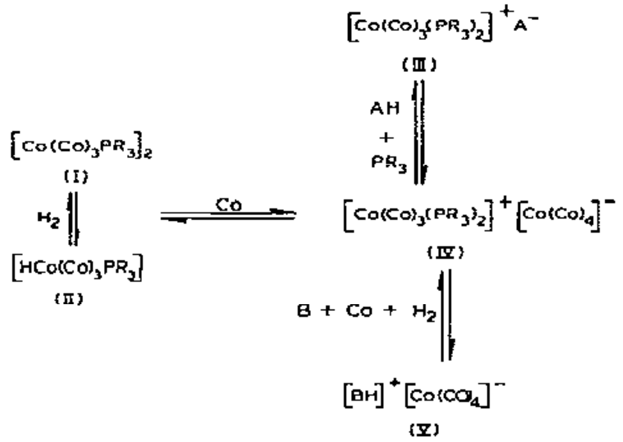
(i) Solvent effects in cobalt carbonyl hydroformylation modified by a tertiary phosphine

It is known that the addition of a tertiary phosphine to the classical olefin hydroformylation catalyst based on $Co_2(CO)_8$ improves the catalytic properties of the system, evidenced by the higher *normal* to *iso* ratio of the products and by the increased extent of hydrogenation of aldehydes to alcohols [1]. This observation forms the basis of the development of a new technique: the Shell process for olefin hydroformylation. A systematic analysis of the influence of the polarity and basicity (or acidity) of the solvent on this reaction [2] has been performed wherein the nature of the metal complexes, formed under differing conditions, was studied and correlated with the properties of the catalytic system. Scheme 1 shows the species present under the various reaction conditions; their relative concentrations can be evaluated

TABLE 1

The molecular composition and catalytic activity in different solvents of the cobalt catalyst [2]

Solvent	Dielectric constant	pK_{BH^+}	pK_{AH}	Cobalt species	Initial rate (mol l^{-1} h^{-1})
n-Hexane	1.93	-	-	(II)+(I)~100%	0.66
Methanol	32.6	−2.2	-	(II)+(I)<5%, (IV)>95%	0.28
Formic acid	58	-	3.75	(III)~100%	0.0
Acetic acid	6.2	-	4.76	(III)~100%	0.0
Triethanolamine	29.4	7.8	-	(V)~100%	0.0
Triethylamine	2.4	10.8	-	(II)+(I)~85%, (V)~15%	0.67



Scheme 1. Species formed under CO and H_2 in the presence of different solvents by interaction of $Co_2(CO)_8$ with PR_3; AH denotes an acidic protonic solvent and B a basic solvent. Species (I) is the precursor of the catalytic species (II). Species (III), (IV) and (V) are catalytically inactive.

almost quantitatively by IR spectroscopy (Table 1). It has been observed that the relative composition of the mixture of complexes is dictated by the properties of the solvent, the other variables (temperature, hydrogen and carbon monoxide partial pressures, phosphine concentration) showing a much less pronounced influence.

Dramatic solvent effects give rise to quantitative formation of one particular species (see Table 1), as with triethanolamine (only $[Co(CO)_4]^-$), or formic or acetic acid (only $[Co(CO)_3(PR_3)_2]^+$). Generally speaking, non-polar solvents favour the formation of covalent species [(I) and (II) of Scheme 1] while ionic species are stabilised in polar solvents. The basicity of the solvent has a significant influence on the ionic species distribution, but it does not affect the ratio of covalent to ionic complexes: cf. (Table 1) the behaviour of NEt_3 (high basicity, low polarity) and $N(CH_2CH_2OH)_3$ (high basicity, high polarity). Conversely, even a relatively weak acid, such as CH_3COOH, causes almost quantitative formation of cation (III) of Scheme 1 (see Table 1). These effects are quite dramatic, since well defined catalytic activity is observed only when covalent complexes are present; hydroformylation does not occur in solvents like acetic and formic acids or triethanolamine, which bring about quantitative formation of species (III) and (V) respectively, which are catalytically inert.

This major effect determines the relative composition of the equilibrium mixture of cobalt complexes and hence the amount of the true catalytic species [species (II) of Scheme 1, in this case]. In addition, there is a minor solvent effect which acts on the activity of this latter species, since it appears that polar solvents increase its activity. A higher specific hydroformylation rate is observed on addition of polar solvents; for instance, the substitution of DMF for only 4% of n-heptane resulted in an increase of about 100% in the rate of hydroformylation, although no appreciable variation in the concentration of the active species $[HCo(CO)_3PR_3]$ was detected. This latter effect is due to dipole–dipole specific interactions, a case that will be discussed in section E.

The combined action of the two effects (i.e. the concentration of (II) and the polarity of the solvent) gives rise to a maximum in catalytic activity when mixtures of two solvents of different polarity and very low basicity are used (e.g. n-heptane–ethanol mixtures, as in Fig. 1). The upward slope of Fig. 1(a) is due to a polarity effect on the reaction rate overwhelming the effect of a decreasing concentration of the hydridic species (II); the downward slope is

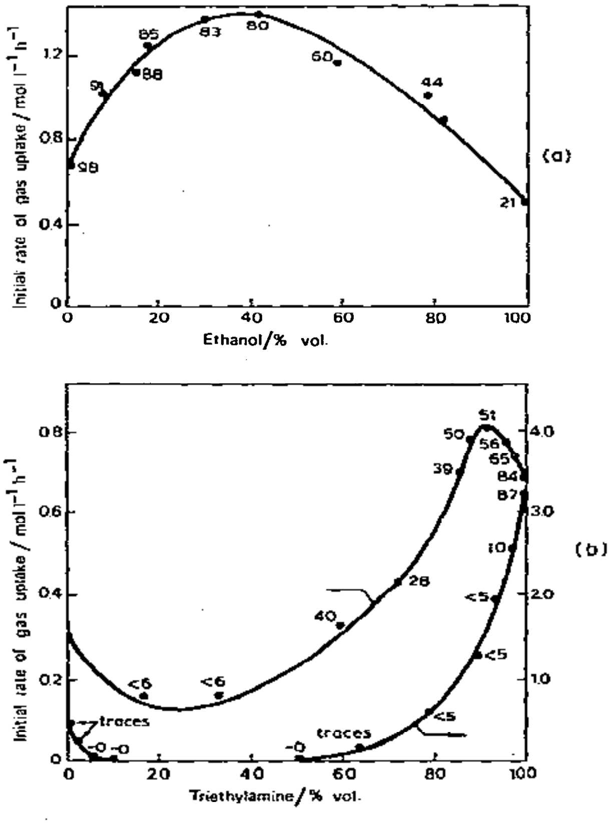


Fig. 1. (a) The hydroformylation rate with a $Co_2(CO)_8 + P(Bu^n)_3$ catalyst in n-heptane–ethanol mixtures. (b) The hydroformylation rate with a $Co_2(CO)_8 + P(Bu^n)_3$ catalyst in methanol–triethylamine (1) and DMF–triethylamine (2) mixtures. The numbers give the approximate percentage of cobalt as covalent species (I)+(II). Data taken from ref. 2.

due to the now predominant effect of a decrease in the cobalt hydride concentration.

Interestingly, the basicity of the solvent has no significant effect on the specific hydroformylation rate, since a constant hydroformylation rate was found for mixtures of two solvents of low polarity (such as benzene and triethylamine) but with very different basicity.

We have hence discussed a typical case in which highly polar solvents favor the formation of ionic species by a metal–metal bond heterolysis. In particular, the kinetics of the reaction

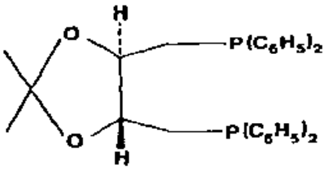
$$[Co(CO)_3(PR_3)_2]_2 \xrightarrow{CO} [Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$$

were investigated [3], showing that both polarity and the donor properties of the solvents are important in determining the electron-transfer process. This is a general effect; covalent asymmetric metal–metal bonds [e.g. in $R_3SnMn(CO)_5$ or $R_3SnCo(CO)_4$] can also give rise to ionic species in polar solvents [4]. This kind of electron transfer through a metal–metal bond is controlled by very delicate electronic effects; for instance, unlike the phosphine-modified catalytic system, pure $Co_2(CO)_8$ hydroformylates faster in ethanol than in n-heptane [5]. Although comparable amounts of the active catalytic species $HCo(CO)_4$ are present in both solvents, the polarity of the solvent determines the overall rate [3].

(ii) Solvent effects on the enantioselective hydrogenation of olefins catalysed by rhodium complexes with optically active chelating diphosphines

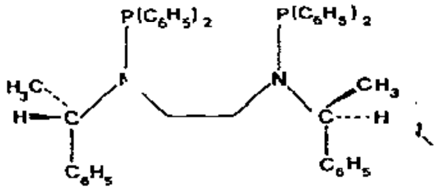
This is another case in which the polarity of the solvent stabilises ionic, rather than covalent, species, but via solvolysis of a metal–halogen bond; the effects on the selectivity of the catalytic system are immense.

The enamide $CH_2{=}CPhNHCOCH_3$ is reduced in ethanol to (*R*)-*N*-acetyl-α-phenylethylamine with 42.5% enantiomeric excess (e.e.) by adding the chelating diphosphine (+)-DIOP to $[RhCl(C_2H_4)_2]_2$ [6a]. DIOP, (+)- or (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, is the chiral diphosphine system of formula synthesized by Kagan et al. The same catalytic system reduces the enamide to (*S*)-*N*-acetyl-α-phenylethyl-



amine in benzene with a 44% e.e., but at a slower rate. When the preformed cationic complex $[Rh(COD)(+)DIOP]ClO_4$ is used as a catalyst in ethanol

(COD = 1,5-cyclooctadiene), the enamide $CH_2{=}CPhNHCOCH_3$ is reduced to (*R*)-*N*-acetyl-α-phenylethylamine at the same rate and with the same enantioselectivity found in ethanol for the system $[RhCl(C_2H_4)_2]$ and (+)DIOP [6b]. Similar results are reported by Pracejus and Pracejus [7] using a chelating diphosphine derived from *N*,*N*-bis[(*S*)-α-phenylethyl]ethylenediamine, of formula



The catalytic system (prepared in situ by addition of the diphosphine to $[Rh(C_2H_4)_2Cl]_2$ in a 1 : 1 ratio of rhodium to phosphine) reduces the methyl ester of (*Z*)-(2-acetoamido)cinnamic acid to the methyl ester of *R*-(*N*)-acetyl-α-phenylalanine with 9.0% e.e. in benzene but with 66.2% e.e in methanol. On the other hand, no significant differences in enantioselectivity were found in methanol between the catalytic behaviour of the neutral chloro complex $[Rh(diphosphine)Cl]_{1\,or\,2}$ and the cationic complex $[Rh(diphosphine)COD]^+$. The latter cationic complex has proved to be even more selective in benzene, reducing the methyl ester of (*Z*)-(2-acetoamido)cinnamic acid with 82.5% e.e.

It therefore appears that methanol stabilises the formation of the cationic species via solvolysis of the Rh–Cl bond, while in benzene substitution of the olefin is preferred to form a covalent monomeric or dimeric species.

The very large differences in enantioselectivity between covalent and ionic rhodium complexes carrying the same chiral diphosphine could be attributed to a different mode of bonding of the substrate to be hydrogenated [8d]. In covalent species the substrate interacts with the metal only via the olefinic double bond, while in ionic species a template effect is achieved by interactions via the double bond and the amide group. The detailed mechanism of such a template effect in hydrogenation reactions has been elucidated by an elegant combination of ^{13}C and ^{31}P NMR spectroscopy [8a,8b] and X-ray crystallography [8c]. Briefly, the stabilisation of the ionic species increases the number of available coordination sites on the metal by solvolytic expulsion of the chloride ligand.

(iii) The effect of protonic substances on the catalytic activation by zerovalent complexes

This is a typical case of solute–solute interaction, since the catalytic activity of zerovalent complexes [such as $Ni(CO)_4$ or $Pd(PPh_3)_3$] in a series

TABLE 2

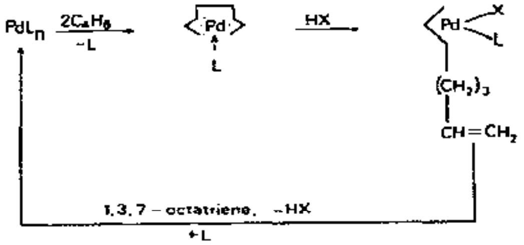
Dimerization of 1,3-butadiene in benzene solution in the presence of different cocatalysts at 100°C [a] [9]

Cocatalyst	pK_a	%Conversion [c]	% Selectivity [d]		
			1,3,7-Octatriene	Octatriene isomers	Vinylcyclohexene
Succinic acid	4.16	99.0	95.0	3.0	2.0
Benzoic acid	4.19	99.0	96.0	1.0	2.1
Adipic acid	4.43	99.0	93.5	5.5	0.8
Acetic acid	4.75	98.5	82.5	15.5	2.0
Propionic acid	4.87	98.0	81.5	11.0	0.5
Acetylacetone	8.83	68.5	45.5	6.0	48.5
Phenol	9.9	68.0	90.0	7.5	2.5
Methanol [b]	15.5	50.1	70.0	10.0	20.0

[a] $(PPh_3)_2PdCl_2$: 30 mmol l^{-1}; cocatalyst: 300 mmol l^{-1}; 1,3-butadiene: 20 mol l^{-1}.
[b] Cocatalyst: 1500 mmol l^{-1}.
[c] Reaction time: 6 h.
[d] Based on 98% reaction of butadiene.

of different reactions, such as the carbonylation of unsaturated substrates (olefins or acetylenic compounds) or the dimerisation of butadiene, is determined by the added protonic substances. The role of the proton is not quite clear, but two possible steps can be proposed: (a) direct protonation of the zerovalent metal having basic properties to form active metal hydrides or (b) electrophilic attack on a metal–carbon bond thus breaking it.

It was found [9] that in the linear dimerisation of butadiene to give 1,3,7-octatriene, the catalytic activity of zerovalent triphenylphosphinepalladium(0) complexes is greatly increased by the addition of a protonic substance (e.g. organic carboxylic acids, phenols, alcohols). The increase in activity and selectivity is related to the pK_a of the protonic cocatalyst



Scheme 2. The role of the protonic agent in the linear dimerisation of butadiene according to ref. 9; L = ligand, HX = protonic agent.

(Table 2). The role of the protonic substance has been attributed to the direct protonation of a bis(η^3-allyl)palladium(II) intermediate as in Scheme 2.

Likewise, Pd(0)(PPh_3) complexes catalyse the hydrocarboxylation of olefins only in the presence of a high acid [10]. In this case, the cocatalytic solute–solute interaction has been explained by the protonation of the zerovalent palladium atom to form an active palladium hydride.

C. THE POISONING OR ACTIVATING EFFECT OF THE SOLVENT AS A CONSEQUENCE OF OCCUPATION OF VACANT SITES OF COORDINATION

This is one of the most important common effects, which resembles the poisoning of the active centers of surfaces by adsorbates. We shall deal with only two typical extreme cases.

(i) Donor species in olefin epoxidation by organic hydroperoxides [11]

An important catalytic homogeneous reaction is olefin epoxidation by organic hydroperoxides (ROOH) catalysed by complexes of Mo, V, W, Ti, etc. In this particular reaction, one coproduct, namely the alcohol generated from the hydroperoxide, causes autoretardation. The reaction follows Michaelis–Menten type kinetics, since the general rate equation is given [11] by

$$-\frac{d[RO_2H]}{dt}=\frac{d[\text{epoxide}]}{dt}=\frac{k_3[\text{olefin}][RO_2H][M^{n+}]_0}{K_1+(K_1/K_2)[ROH]+[RO_2H]} \tag{1}$$

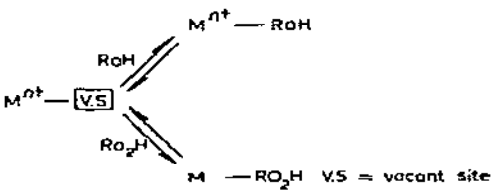
which corresponds to the possible mechanism of eqns. (2)–(4)

$$RO_2H+M^{n+}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}[M^{n+}RO_2H] \qquad K_1=k_{-1}/k_1 \tag{2}$$

$$ROH+M^{n+}\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}[M^{n+}ROH] \qquad K_2=k_{-2}/k_2 \tag{3}$$

$$\text{olefin}+[M^{n+}RO_2H]\xrightarrow{k_3}[M^{n+}ROH]+\text{epoxide} \tag{4}$$

where M^{n+} = Mo(VI), W(VI), V(V), Ti(IV), etc. Competing complex formation between the catalyst and the alcohol hinders the formation of the intermediate catalytically active hydroperoxide complex and, consequently, the reaction of the latter complex with the olefin. The extent of autoretardation or poisoning is related to the ratio of the equilibrium constants for the formation of catalyst–hydroperoxide and catalyst–alcohol complexes. This ratio varies with the metal catalyst, the extent of poisoning by t-butanol in epoxidation by t-butyl hydroperoxide increasing in the order $W < Mo < Ti$



$<$ V. The differences are especially great between V and Mo or W, since with the former epoxidation is strongly retarded by the addition of alcohol, whereas it is only slightly affected by alcohol in the presence of the latter two metals. The kinetic equation (1) can be rewritten as

$$-\frac{\mathrm{d}[\mathrm{RO_2H}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{epoxide}]}{\mathrm{d}t}=\frac{k_3[\mathrm{olefin}][\mathrm{M}^{n+}]_0}{K_1/[\mathrm{RO_2H}]+\dfrac{K_1}{K_2}\dfrac{[\mathrm{RO_2H}]_0}{[\mathrm{RO_2H}]}+\left(1-\dfrac{K_1}{K_2}\right)} \quad (5)$$

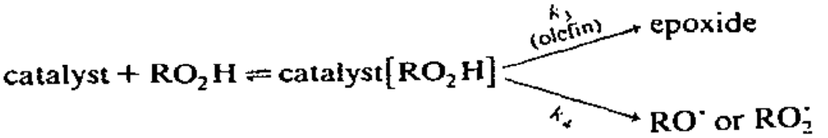
where $[\mathrm{ROH}]=[\mathrm{RO_2H}]_0-[\mathrm{RO_2H}]$. If $1-(K_1/K_2)$ is very small (i.e. $K_1 \simeq K_2$), the above equation becomes

$$-\frac{\mathrm{d}[\mathrm{RO_2H}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{epoxide}]}{\mathrm{d}t}=\frac{k_3[\mathrm{M}^{n+}]_0}{K_1+(K_1/K_2)[\mathrm{RO_2H}]_0}[\mathrm{olefin}][\mathrm{RO_2H}] \quad (6)$$

This rate equation explains the apparent first-order dependence on $[\mathrm{RO_2H}]$ originally found for Mo catalysts, for which the dissociation constants for the catalyst–hydroperoxide and the catalyst–alcohol complexes are approximately equal.

The inhibiting effect increases with both the donor power and the polarity of the solvent as follows: $\mathrm{H_2O} > \mathrm{CH_3OH} > \mathrm{C_2H_5OH} >$ n-BuOH $>$ t-BuOH. Donor solvents can form complexes with the catalyst and, hence, they lower the rate of epoxidation by hindering complex formation between the hydroperoxide and the metal catalyst.

In addition, unlike the rate of homolytic decomposition of the hydroperoxide complex (k_4), the rate at which the intermediate catalyst–hydroperoxide species reacts with the olefin (k_3) is expected to be lowered by coordinating solvent molecules hindering the approach of the hydrophobic olefin



$$\text{catalyst} + \mathrm{RO_2H} \rightleftharpoons \text{catalyst}[\mathrm{RO_2H}] \begin{cases} \xrightarrow[\text{(olefin)}]{k_3} \text{epoxide} \\ \xrightarrow{k_4} \mathrm{RO^{\bullet}} \text{ or } \mathrm{RO_2^{\bullet}} \end{cases}$$

This is observed experimentally; the rate and the selectivity being much lower in coordinating solvents, like alcohols, ethers, ketones and DMF, than in other non-donor solvents.

As in the epoxidation with organic peracids, higher rates are observed with non-coordinating polar solvents such as polychlorinated hydrocarbons.

(ii) The complex action of donor solvents on olefin catalysis by Pd(II)

The type of inhibiting effect discussed above is quite general when the catalyst is a metal ion in a high oxidation state (which implies a relatively strong Lewis acid of "hard" character). When catalysis is carried out on "soft" substrates like unsaturated hydrocarbons with low oxidation state metal complexes (weak acid of soft character), the inhibiting power of donor solvents (which are usually 'hard' bases) is expected to be weak. One particular case is given by the catalysis by Pd(II) ion, which is on the borderline between soft and hard. With this latter ion the presence of slightly soft donor solvents like DMSO (dimethyl sulphoxide) or even some nitriles can hinder or slow down the catalytic process, due to the strong coordinating interaction between the palladium(II) ion and the donor solvent.

An anomalous case is given by DMF (dimethylformamide) and related strongly basic solvents. It has been reported that DMF stabilises the palladium catalyst for ethylene oxidation (in particular vinyl acetate synthesis). However, with olefins containing allylic hydrogens the presence of DMF as solvent may either inhibit the catalytic reaction (e.g. in olefin isomerisation) or influence its selectivity (e.g. in oxidation of 1-olefins with acetic acid).

We have found [12] that DMF favours the abstraction of HCl from the intermediate η^2-palladium olefin complexes to form the corresponding η^3-allyl complexes, which are either completely inactive towards isomerisation of the olefins or react to the external attack of the acetate ion in a different manner to the corresponding η^2-palladium olefin complexes. In this example, the donor solvent, which coordinates to the metal, does not compete with the substrate (in this case an olefin) for the occupation of a vacant coordination site, but facilitates the transformation of the olefin–palladium complex into another organometallic species which behaves differently. This specific action is due to the ability of the solvent, in particular DMF, to trap the proton abstracted from the coordinated olefin. Thus, the coordination of DMF is merely a template action, in order to facilitate allylic hydrogen abstraction from the coordinated olefin.

D. THE EFFECT OF ION PAIRING ON REACTIONS INVOLVING IONIC CATALYSTS, IN PARTICULAR CARBONYL ANIONS

Ten years ago it was reported [13] that "ion-pairing phenomena may have hitherto unrecognized importance in the chemical reactivity of many metal carbonyl anions". Solute–solute and solute–solvent interactions have been

TABLE 3

The effect of solvent and counter-ion on the reaction:
$RFe(CO)_4^- \xrightarrow{Ph_3P,\ 25^\circ C} RCOFe(CO)_3PPh_3^-$

	Relative rate constant
Counter-ion ($R = n\text{-}C_{10}H_{21}$, THF solvent)	
Li^+	(1)
Na^+	0.17
Na^+(11-hexamethylphosphoramide)	0.036
Na^+(dicyclohexyl-18-crown-6)	0.001
$(Ph_3P)_2N^+$	0.00042
Solvent ($R = n\text{-}C_5H_{11}$, Na^+ counter-ion)	
THF	(1)
N-Methylpyrrolidone	0.0024

found to be important in several types of arbitrarily classified reactions which involve anionic metal carbonyls: (i) Metal–carbonyl migration or carbon monoxide insertion; (ii) ligand dissociation; (iii) nucleophilic displacement; and (iv) reduction of carbon monoxide.

(i) Metal–carbonyl migration or carbon monoxide insertion

Form the data of Table 3 it was concluded that "clearly ion-pairing effects are dominant" [14], the effects having been varied by changes in solute–solute and in solute–solvent [15] interactions in the reactants and transition states [16]. Strong ion pairing may therefore significantly affect the catalytic cycles of those carbonylation reactions in which carbon monoxide insertion is a rate-determining step.

(ii) Ligand dissociation

The effects of counter-ions and of solvent-modified counter-ions on several reactions formally classifiable as involving loss of a ligand have been reported.

Reaction of $HFe(CO)_4^-$ in THF	Na^+	$(Ph_3P)_2N^+$	Ref.
CO exchange	Readily	Not readily	17
O_2 (saturated solutions?)	$t_{1/2} \approx 5$ min	$t_{1/2} \approx 100$ min	18

$$\frac{Ph_3PFe(CO)_3COPh^- + Bu_3P \xrightarrow{THF} Bu_3PFe(CO)_3COPh^- + Ph_3P}{k(20/1\ HMPA/Li^+)/k(Li^+) = 10} \qquad 19$$

It has been reported [20] that the rate of decomposition of $[\{(ArO)_3P\}Fe(CO)_3CHO]^-$ (Ar = 3,5-dimethylphenyl) to $[HFe(CO)_4]^-$ was "insensitive to the nature of the counter-ion" but that the rate of the exchange reaction:

$$[\{(ArO)_3P\}Fe(CO)_3COCH_3]^- + (PhO)_3P \rightarrow [\{(PhO)_3P\}Fe(CO)_3COCH_3]^- + (ArO)_3P$$

"depends strongly on the nature of the counter-ion":

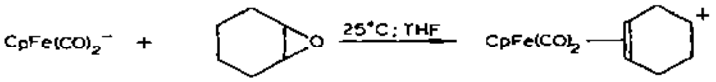
	Relative rate	
	Et_4N^+	Li^+
Formyl decomposition	(1)	0.58
Phosphite exchange	0.02	520

Such exchange reactions are also relevant to catalytic cycles.

(iii) Nucleophilic displacement

Several reactions which formally involve the displacement of a halide from carbon by a metal carbonyl anion have been studied (see Tables 4–7) [21].

A complex reaction the initial stages of which may be formulated as



involving nucleophilic displacement on carbon, has been found to be strongly influenced by the nature of the cation [26].

TABLE 4

The effects of the counter-ion and solvent on the reaction:
$Mn(CO)_5^- + PhCH_2Cl \xrightarrow{25°C} PhCH_2Mn(CO)_5 + Cl^-$ [22]

Counter-ion	Solvent	Relative rate constant
Li^+	THF	(1)
Li^+ (~15 equiv. HMPA)	THF	0.10
Na^+	THF	1.7
Na^+ (1 equiv. 15-crown-5)	THF	0.40
Na^+ (~15 equiv. HMPA)	THF	0.15
Na^+	Et_2O	72.0
Na^+	THF	1.7

TABLE 5

The effects of the counter-ion and solvent on the reaction:
$Co(CO)_4^- + PhCH_2Cl \xrightarrow{50°C} PhCH_2Co(CO)_4 + Cl^-$ [23]

Counter-ion	Solvent	Relative rate constant
Na^+	THF	(1)
Na^+ (1 equiv. 18-crown-6)	THF (same trend in other solvents)	0.003
K^+	THF	0.8
Cs^+	THF	0.5
Li^+	THF	0.1
$PhCH_2N^+Et_3$	THF	0.05
Na^+	Me_2EtCOH	55.
Na^+	PhOMe	33.
Na^+	$Me_2CHOCHMe_2$	28.
Na^+	MeOH	10.
Na^+	THF	(1)
Na^+	MeCN	0.05
Na^+	DMF	0.03

TABLE 6

The effects of the counter-ion and solvent on nucleophilic attack by $Fe(CO)_4^{2-}$ [24]

(*a*) $Fe(CO)_4^{2-} + Me_3CCH_2Br \xrightarrow{25°C,\ NMP} [Me_3CCH_2Fe(CO)_4]^- + Br^-$

Counter-ion	Relative rate constant
Na^+	(1)
Na^+ [1.3 equiv. (2.2.2) cryptand]	2.9

(*b*) $Fe(CO)_4^{2-} + n\text{-}C_{10}H_{21}Br \xrightarrow{25°C} [n\text{-}C_{10}H_{21}Fe(CO)_4]^- + Br^-$

Counter-ion	Solvent	Relative rate constant
Na^+	THF	(1)
Na^+ (1 equiv. dicyclohexyl-18-crown-6)	THF	59.0
Na^+	10/90 *N*-methylpyrrolidone/THF	19.0

TABLE 7

The effect of the counter-ion on the reaction [25]:
$\eta^5\text{-}C_5H_5Mo(CO)_3^- + RX \xrightarrow{25°C, THF} \eta^5\text{-}C_5H_5Mo(CO)_3R + X^-$

Alkyl halide	Counter-ion	Relative rate constant
n-C_4H_9I	Na^+	(1)
n-C_4H_9I	Na^+ (20 equiv. HMPA)	20
n-C_4H_9I	$(PPh_3)_2N^+$	19
n-C_4H_9Br	Na^+	0.021
n-C_4H_9Br	Na^+ (20 equiv. HMPA)	0.10
$C_6H_5CH_2Cl$	Na^+	1.4
$C_6H_5CH_2Cl$	Na^+ (20 equiv. HMPA)	0.45
$C_6H_5CH_2Cl$	$(PPh_3)_2N^+$	0.46

Counter-ion	Time for "complete" anion consumption
Li^+	2 min
Li^+ (1 equiv. HMPA)	No reaction
Na^+	4 h
Bu_4N^+	No reaction

In general, the effect on the rate of a reaction of certain changes in the nature or magnitude of solute–solute interactions is dependent upon the structural characteristics and charge distribution in the reactants relative to the transition state(s) of the rate-determining step(s); such factors can vary significantly as a result of seemingly minor changes in the composition of a chemical system. It is therefore impossible to make generally applicable statements regarding the effect of certain changes in, e.g. the nature of the solvent or of the counter-ion, on the rate of this particular type of reaction. Diverse trends are therefore to be expected *.

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* Note that, although the results above involving crown ethers, and other results in the literature suggest that a crown-complexed cation forms a weaker ion pair than the 'uncomplexed' (i.e. solvent-complexed) cation, this need not have been the outcome a priori [28]. Therefore, it would be inappropriate to conclude, for example, solely from the fact that addition of crown ether decreases the rate of a reaction, that the reaction is 'assisted by ion pairing'.

It has beeen reported [25] that 'it is apparent that counter-ion effects on oxidative addition reactions of transition metal carboxylates will add their own mechanistic subtleties to an already significant list of reaction pattern characteristics'.

(iv) Reduction of carbon monoxide [29]

The homogeneous rhodium/Lewis base-catalysed conversions of carbon monoxide and hydrogen to ethylene glycol [31] have recently been studied [30], typically at 200–300°C and 500–1000 atm.

Since the initial suggestion [32] that anionic rhodium carbonyl clusters are an important part of the catalyst system and that ion pairing decreases its reactivity, the involvement in the catalyst system of the solvent and of the components of the amine and salt Lewis-base cocatalysts has been investigated.

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 medium. The rate of formation of ethylene glycol is greatest in phosphine oxides, which are cation-complexing solvents of moderately high dielectric constant [28].*

It was found that, in general, amines and salts function as cocatalysts and that there is an optimum amount of cocatalyst for the formation of ethylene glycol, there being concurrent promotion and inhibition. The dependence of

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* Examples of the opposite behaviour have in fact been reported. (a) Addition of 18-crown-6 to a solution of KOMe in MeOH increased the extent of ion pairing with fluoradenide [27]. This result, for which no sound explanation could be offered, is rationalizable on an ad hoc basis in the following way. The degree of ion pairing is determined by the outcome of competition between anion and solvent for the cation. Methanol can specifically solvate K^+ sufficiently well to remove it from fluoradenide. However, methanol cannot solvate K^+(crown) nearly as well as it can solvate K^+. So, in the competition between fluoradenide and methanol for K^+(crown), methanol could lose since the interaction between fluoradenide and K^+, being mostly electrostatic and involving a diffuse negative charge (not dependent on specific, close contact with K^+, as is methanol), does not suffer when K^+ becomes K^+(crown) as much as in the methanol case. (b) Below −10°C in THF the ion-pair dissociation constants of fluorenyl sodium and fluorenyl strontium are greater than those of their dimethyldibenzo-18-crown-6 complexes [28a]. (c) The ion-pair association constant of sodium iodide in acetonitrile is significantly greater in the presence of dibenzo-18-crown-6 [28b].

TABLE 8

The effect of the counter-ion on the reaction [33]:

$$CH_3OH + H_2 + CO \xrightarrow[3\ h,\ 120\ kg\ cm^{-2},\ 180°C]{[RuCo_3(CO)_{12}]^-,\ CH_3I} CH_3CHO + CH_3CH(OCH_3)_2 + CH_3CH_2OH + CH_3CO_2CH_3$$

Counter-ion	% Yield		
	$CH_3CHO + CH_3CH(OCH_3)_2$	CH_3CH_2OH	$CH_3CO_2CH_3$
Na^+	7	16	4
Cs^+	3	18	6
Et_4N^+	2	21	0.4

promotion and inhibition on the properties of the cocatalysts, particularly their basicity and the ion-pairing ability of their counter-ions and conjugate acids, inherent and as modified by the solvent was studied.

Nevertheless, it is clear that ion-pairing effects are significant, since the complex mechanism of reaction probably involves steps such as carbon monoxide insertion, ligand exchange, etc., which are known to be sensitive to ion pairing [see sections (i), (ii) and (iii)].

The effect of the counter-ion on the $[RuCo_3(CO)_{12}]^-$ catalysed reductive carbonylation of neat methanol has been reported [33]. Results are shown in Table 8.

(v) The effects of the solvent and counter-cation on hydrogenation catalysed by the anionic cobalt cyanide system

The selective hydrogenation of cyclopentadiene in ethanol catalysed by the anion $[Co(CN)_5]^{3-}$, in the presence of the counter-cation Li^+ [34] has been investigated. It was found that the total catalytic activity is dependent upon the amount of water present. By influencing the strength of the ion pairing between Li^+ and $[Co(CN)_5]^{3-}$, water indirectly affects the activity of the latter ion. The addition of water increases the activity, suggesting that ion pairing is detrimental to the hydrogenation properties of $[Co(CN)_5]^{3-}$. This is confirmed by the complete absence of any hydrogen activation when the salt $[NR_4]_3[Co(CN)_5]$ was reacted with hydrogen in acetonitrile [35]. It is expected in this case that ion pairing must be significant. In addition, some evidence for ion pairing between Li^+ and $[Co(CN)_5]^{3-}$, even in ethanol, has been obtained by the isolation, from an ethanol solution, of lithium salts of both $[HCo(CN)_5]^{3-}$ and $[Co(CN)_5]^{3-}$ anions containing at least one molecule of LiCl, which cannot be separated after repeated washing with ethanol [34].

The effects of ion pairing and water solvation on the catalytic selectivity and stability (towards decomposition by reaction with H_2O) of the $[Co(CN)_5]^{3-}$ ion have also been examined by the phase-transfer technique and micellar solutions [36]. In the hydrogenation of methyl sorbate under phase-transfer conditions, the main product is *trans*-methyl-3-hexenoate, whereas *trans*-2-hexenoate derivatives are predominant when using $K_3[Co(CN)_5]$ in water.

As expected, if a solvent effect is involved, the micellar or phase-transfer conditions have only a modest effect on the product distribution in the hydrogenation of sodium sorbate which is soluble only in water [36].

In addition to altering product ratios, the presence of micelle-forming surfactants or of the phase-transfer reagent has a substantial effect on the lifetime of the catalyst. In general, the $K_3[Co(CN)_5]$ catalyst is not stable in aqueous solution and decomposes to an inactive species in a few hours whereas it is stable for days in the presence of surfactants or phase-transfer reagents [37].

It is thus apparent that ion pairing affects the activity, selectivity and lifetime of the $[Co(CN)_5]^{3-}$ catalyst. This is confirmed by the fact that substitution of potassium by lithium [38] in the cation not only allows the use of ethanol as solvent, but also stabilises the species with a $[CN^-]:[Co^{2+}]$ ratio of 4:1 instead of 5:1, which gives rise to complex spectroscopic data and catalytic behaviour. Unlike the $[Co(CN)_5]^{3-}$ anion, this Co(II) cyanide, which shows unusual electronic and EPR spectra, does not become diamagnetic on reaction with hydrogen and does not hydrogenate activated mono-olefins or acetylenic compounds, but only cyclic or linear *cis*-1,3-conjugated dienes. This catalytic system is very stable and produces rates about 10 times faster than those of an alcoholic solution of $Li_3[Co(CN)_5]$ of comparable total cobalt concentration. This new catalytic system shows a peculiar selectivity, since *trans*-1,3-dienes or cyclic non-conjugated dienes are not hydrogenated.

Although direct evidence is not available for ion pairing between the Li^+ cation and the anionic Co(II) cyanide species (with a 4:1 cyanide to cobalt ratio), it is quite possible that strong ion pairing may be one of the reasons for the stabilisation of this unusual catalyst, which cannot be obtained in water even in the presence of Li^+ ions.

E. RELATIVELY WEAK AND SIMPLE SOLVATION EFFECTS OPERATING ON RATES AND SELECTIVITIES OF HOMOGENEOUS CATALYTIC PROCESSES

These solvent effects, usually investigated in detail in organic and inorganic chemistry, have two main origins: electrostatic or field effects (dipole–dipole, dipole–induced dipole etc.) and hydrogen bonding. They are often quite relevant in organometallic chemistry and homogeneous catalysis, since they may act on transition states which are either highly polar, due to the presence of a metal, or relatively rigid, due to the coordination sphere.

We report here some particular examples which show significant results.

(i) The effect of solvent polarity on oxidative addition reactions and dioxygen activation by metal complexes

Many reactions, which are important steps in catalytic processes, such as oxidative addition of carbon–halogen bonds to low oxidation state metal complexes or dioxygen activation by Co(II) paramagnetic complexes with polydentate delocalised ligands (e.g. tetradentate Schiff bases, porphyrins etc.), are sensitive to the dielectric constant of the solvent [39,40].

The oxidative addition of heteropolar carbon–halogen bonds to low oxidation state metal complexes proceeds, in some cases, by a "pseudo-polar mechanism" [41]. The very large negative entropy of activation and the large dependence of the reaction rates on the dielectric constant of the solvent support highly polar transition states. When the final products of the oxidative addition are ionic species, such as in the addition of alkyl halides to η^5-$C_5H_5M(CO)PR_3$ ($M = Co$, Rh, Ir), the solvent effects on the reaction rates are remarkably large [42].

Another reaction, in which the formation of a polar $Co^{\delta+}$–$O_2^{\delta-}$ linkage causes solvent reorganisation to accommodate charge separation is the addition of dioxygen to Co(II) complexes with tetradentate Schiff bases and other polydentate ligands [39]

$$\text{Co(porphyrin) L} + O_2 \rightleftharpoons \text{Co(porphyrin)(L)}\ O_2$$

$$\text{Co(salen)(L)} + O_2 \rightleftharpoons \text{Co(salen)(L)}\ O_2$$

(L = base or donor solvent)

As in the transition state of oxidative addition, this reorganisation occurs more readily in very polar media such as DMF. The effect of going from DMF to solvents of low polarity such as pyridine or aromatic solvents is reflected in a decrease in affinity towards dioxygen of a factor of about 10^2–10^3. This observation is of interest in catalysts since some oxidation reactions of high selectivity on aromatic substrates catalysed by Co(II) Schiff-base complexes are dependent on the nature and polarity of the solvent; reactions such as the catalytic and selective oxygenation of indoles, the oxygenolysis of flavanols (similar to dioxygenase-type activity) and the catalytic hydroxylation of phenols (similar to monooxygenase or phenolase-type activity) are highly solvent dependent, although not always, and occur preferentially in highly polar solvents such as CH_2Cl_2, DMF and CH_3OH [43].

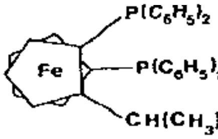
In the same category is the reaction

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

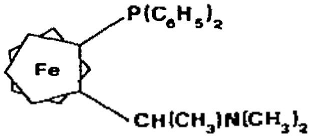
which is catalysed by $Rh_6(CO)_{16}$ [44]. In weakly donor solvents of low polarity, such as acetone, rather drastic conditions are required (80–100°C and 35 atm). In highly polar donor solvents, such as DMF, the reaction occurs very readily under mild conditions (25°C and about 1 atm). In our experience the role of the solvent is to break down the original cluster into active rhodium species, which are stabilised by the donor properties of DMF. The same solvent favours O_2 activation via its high polarity.

(ii) Solvent effects on the asymmetric catalytic reduction of olefins by cationic Rh(I) complexes

We have previously reported that solvents play a primary role in the stabilisation of cationic versus neutral complexes in Rh(I) catalysed asymmetric hydrogenation. However, other solvation effects can lead to less dramatic but significant effects acting on the e.e. in this kind of reaction. Kumada et al. [44] have reported a marked influence of the solvent on the reduction of (Z)-(2-acetoamido)cinnamic acids using the catalytic system composed of $[Rh(1,5\text{-hexadiene})Cl]_2$ and the diphosphine (*S*)-(*R*)-BPPFA (ratio Rh : P = 1 : 2.4) where (*S*)-(*R*)-BPPFA is (*S*)-α-(*R*)-1,2-bis(diphenylphosphino)ferrocenylethyldimethylamine of formula



This system, which requires rather severe conditions (P_{H_2} = 50 atm), reduces the (Z)-(2-acetoamido)cinnamic acid with 93% e.e. in MeOH and with 89% e.e. in H_2O–methanol (1 : 1); however, the same system reduces *para*-acetoxy-(Z)-(2-acetoamido)cinnamic acid with 87% e.e. in H_2O–methanol (3 : 1) but only with 8% e.e. in pure methanol. This large effect arises from competition between the various donor atoms of the chelating ligand. Thus the metal could be chelated through the P and N atoms located on the same ring, rather than the two P atoms or the chelating phosphine could even act as a monodentate ligand. Chelation through the P and N atoms on the same ring, has been demonstrated in the complex $[(PPFA)RhNBD]PF_6$ by X-ray crystallography; this is a good catalyst for asymmetric hydrogenation [46]. NBD denotes norbornadiene and PPFA is (*S*,*R*) or (*R*,*S*)-α(2-diphenylphosphinoferrocenyl)ethyldimethylamine of formula



Obviously, the nature of the protonic solvent selectively favors, probably via hydrogen-bonding solvation of the metal complex and of the substrate to be hydrogenated, the mode of bonding of the chelated ligand. This is reflected in large variations in the e.e. of the catalytic reduction.

Less dramatic solvent effects, usually protonic, on the kinetic parameters are observed. In the work of Frizuk and Bosnich [46], the cationic complex [Rh((*R*)-prophos)(NBD)]ClO_4, where (*R*)-prophos is (*R*)-(+)-1,2-bis(diphenylphosphino)propane, reduces *N*-(2-acetoamido)- or *N*-(2-benzoylamido)-cinnamic acids with high e.e., usually >90%. The latter parameter is not sensitive to the solvents used, e.g. THF or methanol. On the contrary, the cationic complex [Rh((*S*,*S*)-chiraphos)(NBD)]ClO_4, where (*S*,*S*)-chiraphos is (2*S*,3*S*)-(−)bis(diphenylphosphino)butane, reduces the same substrates again with high e.e., but e.e. values which are markedly influenced by the nature of the solvent. For instance, the reduction of (*Z*)-*N*-(2-(acetoamido)cinnamic acid is achieved with 74% e.e. in THF and 89% e.e. in ethanol.

F. CONCLUSIONS

This survey of various aspects of solvent–solute and solute–solute interactions in homogeneous catalysis shows that these effects are often significant. They may operate not only on the total activity of the catalytic systems, but also on subtle aspects of their selectivity, including enantioselectivity.

It appears that factors such as the donor and polar properties of the solvents, their complexing ability and the ion-pairing properties of particular ions play important roles in controlling homogeneous catalysis by transition metal complexes.

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