THERMODYNAMICS, KINETICS, AND MECHANISMS OF SOLVATION, SOLVOLYSIS, AND
SUBSTITUTION IN NON-AQUEOUS MEDIA

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Abstract - Rate constants (k), and the various transition state theory
activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $T\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$), reflect barriers between
initial and transition states. Solvent effects on k and on $\Delta X^{\ddagger}$ can be
analysed into these two components if the reaction mechanism, kinetic
data, and thermodynamic transfer parameters for the reactant(s) are all
known. Examples of such analyses in organic and in inorganic chemistry,
for substitution and for redox processes, are reviewed. Detailed
consideration is given to a range of racemisation and isomerisation
reactions, involving charged and uncharged, hydrophobic and hydrophilic
substrates. Applications of such analyses to some organometallic
reactions are given. This review concludes with a discussion of the
use of volumes of activation in diagnosis of mechanism and of solvation
in these and other systems.

INTRODUCTION

This contribution is concerned with solvation and its kinetic consequences for a variety of
substitution processes. Most reactions discussed are of well-established mechanisms,
but in one case the use of solvation effects in indicating mechanism is involved. Most of
the discussion will deal with the analysis of solvent effects on reactivity into initial
state and transition state contributions, with a brief discussion about gaining information
about solvation changes from activation volume determinations. We aim to show here how
trends in kinetic parameters taken at face value often mask more complicated changes in
initial and transition state parameters. If the mechanism of a reaction in solution is to
be completely defined, an analysis along these lines is an essential aspect. An initial
state-transition state analysis of solvent effects on reactivity clearly requires thermo-
dynamic information as well as kinetic. Indeed the thermodynamic information is doubly
important, because it not only quantifies solvent effects on the initial state, but is also
essential for the calculation of transition state transfer parameters from the kinetic data,
as indicated in Fig.1. In most treatments of this type it seems to be tacitly assumed that
the transition state comes at the same position along the reaction coordinate axis, as
shown in Fig.1. This need not, of course, be so, in which case the arithmetical analysis
is still valid but the discussion of solvation changes now has to include one more variable.
This matter has recently been discussed, with particular application to Menschutkin
reactions (1). Change of solvent sometimes has the more dramatic effect of changing the
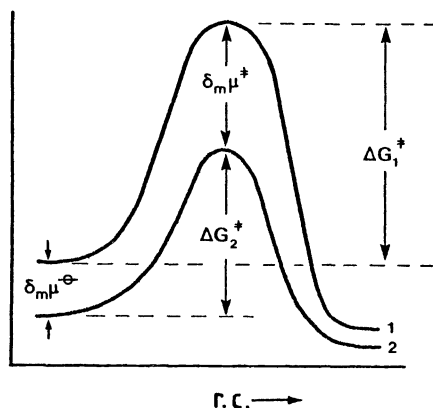mechanism of a reaction; we shall not be concerned with such extremes here.

Fig. 1. Solvent effects on initial
and transition states, and
on the activation barrier.

Initial state-transition state analyses have been carried out for solvent effects on
reactivity for a variety of organic and inorganic reactions, both for substitution and
for redox processes, in series of non-aqueous solvents and in binary aqueous solvent
mixtures (2-4). Examples, with some of the conclusions reached, are given in Table 1
(5-29). The unique properties of water, both structural and as a solvent for inorganic
electrolytes, both simple and complex, mean that it has to feature prominently even in a
discussion primarily concerned with non-aqueous solvents.

As will become apparent during the course of the following review, there are several
constraints on systems whose kinetic behaviour can be successfully and confidently
analysed into initial state and transition state solvation trends. Unimolecular reactions
must be rapid enough for convenient kinetic monitoring, but not so fast that it is
impossible to obtain accurate thermodynamic information on the initial state from calori-
metric or solubility measurements. Bimolecular reactions are much to be prefered, both
because their rates can generally be varied by suitable concentration control and because
thermodynamic parameters for the initial state can be obtained by measurements on the
reactants separately. Reactions which do not involve ions are also more attractive, as no
extrathermodynamic assumptions for obtaining single-ion values have to be introduced. A
number of techniques yield the transfer parameters for the constituent ions of a salt
between two solvents, i.e.

$$\delta_m \mu^{\ominus}(salt) = \nu_+ \delta_m \mu_+^{\ominus} + \nu_- \delta_m \mu_-^{\ominus},$$

but there is no absolute method for calculating single ion values. Several procedures
have been suggested, with concomitant debate about their validity. Nonetheless the broad
patterns which emerge are with few exceptions self-consistent.

The main portion of this review deals with two areas. The first area is that of racemisation
and isomerisation, the second is that of substitution at derivatives of Group VI carbonyls.
Both areas provide many examples of reactions of well-established and often simple
mechanisms; both areas also provide many opportunities to study systems which do not
involve ions and the attendant extrathermodynamic difficulties just mentioned. The review
will conclude with a brief discussion of the diagnostic use of activation volumes,
comparing their usefulness in assessing solvation effects in reactions of known mechanism
(cyanide attack at Group VI carbonyl derivatives) and in assessing mechanisms in simple
situations such as solvent exchange at transition metal cations.

RACEMISATION AND ISOMERISATION

Table 2 lists a selection of racemisation and isomerisation reactions of established
mechanism and varying characteristics. These processes range from indubitably intra-
molecular organic cases to almost certainly intermolecular inorganic reactions. The
reactions in Table 2 also cover the range from hydrophobic to hydrophilic substrates, and
include both uncharged and charged species. They will be discussed in order, with indi-
cations of what kinetic, mechanistic and thermodynamic information on solvent effects is
available, what information is needed, and what conclusions can be reached.

TABLE 2. Racemisation and isomerisation reactions

Compounds	Nature of periphery	Mechanism
Hindered biphenyls	Hydrophobic (usually)	Intramolecular
Metal β-diketonates	Hydrophobic	Intramolecular*
$Fe(phen)_3^{2+}$	Hydrophobic	Intramolecular
$Ni(phen)_3^{2+}$	Hydrophobic	Intermolecular
$Cr(oxalate)_3^{3-}$	Hydrophilic	Intramolecular*
$Co(en)_2Cl_2^+$	Mixed**	Intermolecular
$Pt(PEt_3)_2(C_6H_4X)Cl$	Mixed**	Intermolecular

* Though may involve unidentate intermediates/ts
** Hydrophilic leaving group

TABLE 1. Examples of initial state-transition state dissections (ΔG
          unless otherwise stated)

Substitution: organic

t-BuCl solvolysis (also ΔH)	is, ts trends opposed	(5)
$C_6H_5CH_2Cl$ solvolysis (ΔV)		(6)
Finkelstein: MeI + Cl^-	Cl^- transfer dominant	(2,7,8)
Menschutkin: Me_3N + MeI	is $\gg$ ts from water; is < ts non-aq	(9)
$\qquad Me_3N$ + ArCl*	is (destab) < ts (stab) non-aq	(9)
RCO_2R' hydrolysis		(10,11)
Alkene, alkyne hydration		(11)

Substitution: inorganic

Et_4Sn + $HgCl_2$ (also ΔH)	reactants, ts parallel; is > ts	(12)
R_4Pb + I_2		(13)
$Pt(bipy)Cl_2$ + tu*	reactants, ts parallel; is > ts	(14)
cis-$[Pt(4CNpy)_2Cl_2]$ + tu*		(15)
$PtCl_4^{2-}$ + CN^-	is $\sim$ ts $\sim$ $PtCl_4^{2-}$	(16)
$Fe(bipy)_3^{2+}$ + CN^-	bipy solvation dominates is and ts	(17)
$Co(NH_3)_5Cl^{2+}$ + Hg^{2+}	charge effects dominant $\quad$ is $\sim$ ts	(18)
$ReCl_6^{2-}$ + Hg^{2+}	$\quad$ is > ts	(18)
$Fe(CN)_5(4CNpy)^{3-}$ + CN^- (also ΔH)	is $\sim$ ts; both very solvent sensitive	(19)
$Fe(phen)_3^{2+}$ (also ΔH): +OH^-, +CN^-		
$\qquad$ aquation	is $\lesssim$ ts; phen solvation dominant	(20,21)
$PtCl_4^{2-}$ aquation	is < ts	(16)
M(formazan)L + PPh_3, tu, NCS^-*		(22)
Cu(R-salicylideneiminate)$_2$ subsn.		(23)
$Pd(OAc)_2$: styrene dimerisation	$Pd(OAc)_2$ solvation dominant	(24)

Redox

$IrCl_6^{2-}$ + I^-, catechol	is < ts	(25)
$CoW_{12}O_{40}^{5-}$ + I^-	is < ts; $CoW_{12}O_{40}^{5-}$ dominant	(26)
$Fe(phen)_3^{2+}$ + $S_2O_8^{2-}$	is > ts; reactant solvation opposed	(27)
$Fe(bipy)_2(CN)_2$ + $S_2O_8^{2-}$	is $\ll$ ts; reactant solvation balanced	(28)
$Co(NH_3)_5Cl^{2+}$ + Fe^{2+}	conclusion depends on s.i. split	(29)

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* Ar = p-$CH_2C_6H_4NO_2$; tu = thiourea; M = Pd or Pt; L = NH_3 or pyridine

Hindered Biphenyls

These could prove ideal substrates for initial state-transition state analysis of solvent
effects on reactivity for an intramolecular process of a hydrophobic organic non-electrolyte.
However here, and in the case of the tris-β-diketonate metal complexes discussed in the next
section, it is much easier to resolve charged species than uncharged. There are a few early
kinetic data on internal rotation within compounds of type I (30, 31), though early investi-
gators showed much more interest in varying substituents than in varying solvents (31).
However it was early demonstrated that the barrier to rotation in II was the same in
diphenyl ether as in the gas phase (32). Extensive series of rate constants in a range of
non-aqueous media are available for III with R = COOH, COOMe (33). Solvent effects on rate
constants for the ionic species IV (34,35) and V (36) have been discussed qualitatively in
terms of initial state and transition state contributions. A quantitative analysis will not
be possible until suitable solubility data have been obtained, and then an extrathermo-
dynamic assumption will be needed in the case of these charged species. In this connection,
some progress towards an initial state-transition state analysis could perhaps be made by
considering models such as VI, for solubilities and pK_a values in various solvents are
available for its conjugate acid (37).

Fig. 2.
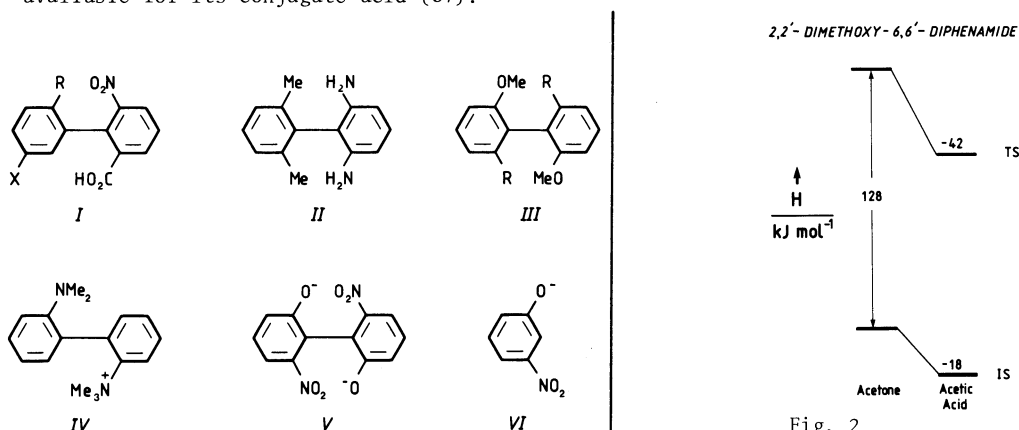Enthalpies of transfer for the initial
and transition state for hindered rotation
in III (R = $CONH_2$).

There has been one quantitative initial state-transition state analysis of enthalpy, for
hindered rotation in III, with R = $CONH_2$ (38). A combination of kinetic data and calori-
metric measurements led to the conclusion that transition state solvation dominated
(Fig. 2), at least for the two solvents treated.

For further initial state-transition state analyses, solubility and calorimetry experiments
are needed on III, R = COOH, COOMe, to complement the available kinetic data. We have
embarked on a kinetic and solubility examination of I, R = OMe, X = H, for which scanty
kinetic data exist (31). It would be interesting to extend this study to other organic
intramolecular processes, for example hindered rotation about C···N; kinetic data in
several solvents exist, for instance for 1-nitro-2-dimethylaminoethene (39).

Metal β-Diketonates

These provide a convenient link into inorganic chemistry. Metal(III) tris-β-diketonates are
uncharged, have a hydrophobic periphery, and racemise intramolecularly (40-42). The con-
siderable difficulties in resolving these complexes have resulted in very sparse kinetic
data. A recently described new resolution method (43) may lead to further kinetic studies.
In contrast to the paucity of kinetic data, there is an abundance of solubility data, mainly
arising from widespread interest in these compounds as ideal solutes in Hildebrand regular
solution treatments (44,45).

There is a general impression that barriers to racemisation are fairly insensitive to
solvent (40). Gibbs free energies of transfer range up to about 15 kJ mol^{-1} for, e.g.,
tris-acetylacetonatochromium(III). This suggests that small solvent effects on rates are
the small difference between larger changes in chemical potentials of initial and transition
states.

Activation parameters for racemisation of the tris-acetylacetonatogermanium(IV) cation are
given in Table 3 (46,47). The mechanism of racemisation is thought to be intramolecular,
but involving unidentate ligand intermediates and solvent interaction with the germanium
(from the correlation with Gutmann donor numbers, DN). The activation volume is said to
reflect this participation of a solvent molecule in the transition state.
If one deals with unsymmetrical β-diketones, then the situation becomes more complicated,
as there are mer- and fac- isomers of tris-complexes, both of which may exist as optical
isomers. There is much kinetic information on such systems (40), for example a full study

TABLE 3. Activation parameters for racemisation of $Ge(acac)_3^+$

Solvent	$\dfrac{\Delta H^{\ddagger}}{kJ\ mol^{-1}}$	$\dfrac{\Delta S^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\dfrac{\Delta V^{\ddagger}}{cm^3\ mol^{-1}}$	DN
1,1,2,2-tetrachloroethane	27.9	+4	+15.1	(0)
nitromethane	26.6	-1		2.7
propylene carbonate			+5.4	15.1
acetonitrile	24.3	-4	0	14.1
NN-dimethylformamide	23.3	-5	-4.1	26.6

of solvent effects and rate constants and activation parameters for several vanadium(III) complexes (48), but the situation is unattractively complicated for our present purposes.

A possible extension of this area would be to tris-dialkyldithiocarbamate complexes, for example of iron (49).

Tris-1,10-phenanthroline-iron(II)
Tris-diimine-iron(II) complexes are related to the tris-β-diketonates of the previous section. They have hydrophobic peripheries and racemise by an intramolecular mechanism (50,51). This has to be a trigonal twist; a one-end-off mechanism is precluded sterically. Again as for the tris-β-diketonates one can have symmetrical (e.g. 1,10-phenanthroline) or unsymmetrical (e.g. 4-methyl-1,10-phenanthroline) ligands, with the additional possibilities of mer- and fac- geometrical isomerism for the latter. However in contrast to the β-diketonate complexes, stereochemical change in complexes containing unsymmetrical diimine ligands has been little studied (52).

The diimine complexes of the tris-1,10-phenanthroline-iron(II) type differ from the metal(III) tris-β-diketonates in their 2+ charge. In practice this does not affect their solvation characteristics dramatically, for Gibbs free energies of transfer from water into non-aqueous solvents are negative (53). Indeed the marked curvature of the plot of Gibbs free energies of transfer for tris-1,10-phenanthroline-iron(II) (Fig. 3) suggests strong preferential solvation by the methanol in aqueous methanol solvent mixtures.

There are extensive sets of data on racemisation of the tris-1,10-phenanthroline-iron(II) cation in mixed aqueous (54,55) and in non-aqueous solvents (54-56). Figure 4 shows an initial state-transition state dissection for racemisation in non-aqueous solvents, using transfer parameters for the initial state from van Meter and Neumann (53). For all solvents both initial and transition states are stabilised on transfer from water. If we ignore the very viscous glycerol, then racemisation is faster in non-aqueous solvents than in water because the transition state is more stabilised than the initial state, with the two trends in step. Viscosity is clearly of importance in the case of glycerol, but cannot be a determining feature for the other solvents (cf. relative viscosities given at the foot of Fig. 4).
Initial state and transition state transfer enthalpies show almost parallel trends for both racemisation and aquation (57).

Tris-1,10-phenanthroline-nickel(II)
This cation provides an interesting comparison with the iron(II) analogue just discussed, as the weaker nickel (d^8)-nitrogen bonding permits intermolecular isomerisation in contrast
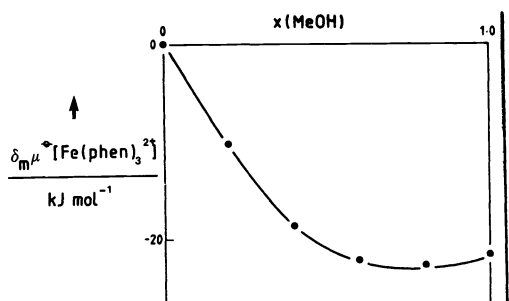

Fig. 3. Reflection of preferential solvation of $Fe(phen)_3^{2+}$.

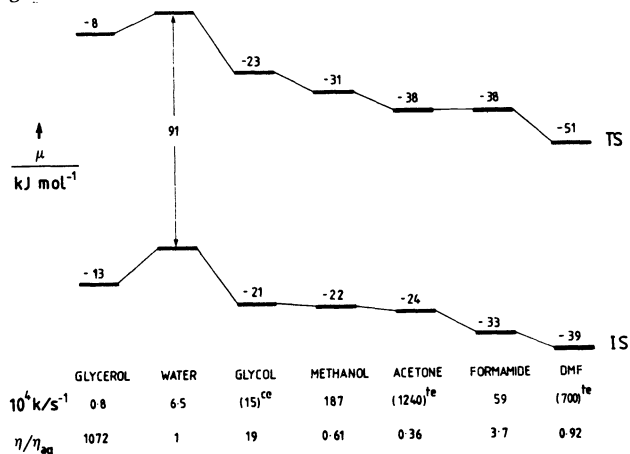Fig. 4. Initial state-transition state analysis for $Fe(phen)_3^{2+}$ racemisation.

to intramolecular for low-spin d^6 iron(II) (58). Unfortunately no transfer data exist for the nickel complex, but it would seem a close approximation to use data for the extremely similar iron complex. The initial state-transition state dissection (Fig. 5) differs, as one would expect, from that for the iron complex (Fig. 4), but there is too little information as yet for a detailed discussion of Fig. 5 and its trends. It would be interesting to extend this work to the analogous 2,2'-bipyridyl complexes, in most ways very similar to the 1,10-phenanthroline complexes, but having the key difference that unidentate ligand intermediates are feasible only for the former. There are some odd features in the solvent dependence of the racemisation rate constant for the 2,2'-bipyridyl and 1,10-phenanthroline complexes of nickel(II) (56,59) that invite further scrutiny.

Tris-oxalato-chromate(III)

It is now time to switch attention to a complex with a hydrophilic exterior. The tris-oxalato-chromate(III) anion has a periphery of hydrophilic oxygen atoms, and it racemises by an intramolecular mechanism, albeit in which there is a unidentate-oxalate transition state or intermediate (40). There are kinetic data for racemisation of this anion in several series of binary aqueous solvent mixtures, with organic cosolvents methanol, ethanol, n-propanol, iso-propanol, dioxan, and acetone (60,61). We have determined solubilities of the potassium salt of this anion in aqueous methanol and aqueous acetone. Thence Gibbs free energies of transfer of tris-oxalato-chromate(III) have been estimated using de Ligny's values for the potassium cation (62). The results of our initial state-transition state analysis are shown in Fig.6. De Ligny's values for transfer of the potassium cation are surprisingly negative for transfer into aqueous acetone; if the real values are less negative, then the destabilisation of the initial and transition states will be smaller than illustrated, but the overall pattern will not be significantly altered.

In both series of solvent mixtures, slower racemisation as the proportion of organic cosolvent increases is due to somewhat greater destabilisation of the transition state than of the initial state. This is just the opposite of the pattern for racemisation of the tris-1,10-phenanthroline-iron(II) cation (v.s.). This difference can be ascribed to the respectively hydrophilic and hydrophobic natures of the peripheries of the complexes. The greater effect on the transition state than on the initial state in both cases can be understood in terms of greater interaction with the solvent in the transition state. In the case of the tris-oxalato-chromate(III), the free end of unidentate oxalate will result in greater interaction with the solvent, whereas in the case of tris-1,10-phenanthroline-iron(II), the larger volume of the transition state (63) will again increase interaction with solvent.
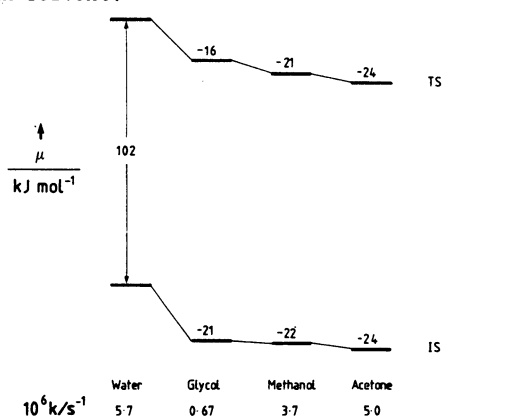

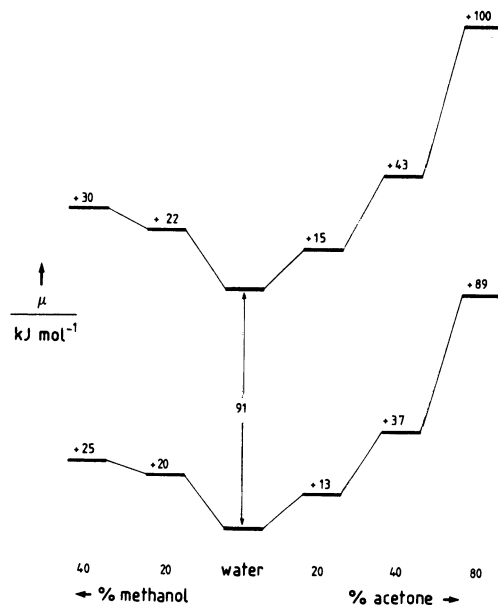Fig. 5.   Initial state-transition state analysis for Ni(phen)$_3^{2+}$ racemisation.

Fig. 6.   Initial state-transition state analysis for Cr(ox)$_3^{3-}$ racemisation.

Bis-ethylenediamine-dichloro-cobalt(III)

Solvent effects on solvolysis and isomerisation of the cis-bis-ethylenediamine-dichloro-cobalt(III) cation (64) were discussed at 4ICNAS (Vienna, 1974) (65). Solvent effects on initial and transition states were both important in determining reactivity, with changes in solvent interaction both with leaving chloride and the Co(en)$_2$Cl^{2+} moiety significant in determining observed reactivity trends. For solvolysis in methanol, DMF, and DMSO, chloride solvation (66) seems to dominate (18).

Cis-[Pt(PEt$_3$)$_2$(m-C$_6$H$_4$CH$_3$)Cl]

The final system in this section is more controversial; an initial state-transition state analysis seems here to make a positive contribution towards the problem of mechanism

elucidation. For isomerisation of the platinum(II) complexes cis-bis-triethylphosphine-aryl-chloro-platinum(II), one group has presented a variety of evidence in favour of a dissociative mechanism (67,68), another has argued in favour of the operation of a "normal" associative mode of activation (69), while an autocatalytic mechanism has also been suggested (70) and discussed (71). We shall now show that the reported solvent variation of rate constants (68) can be rationalised rather well in terms of a dissociative mechanism with solvent effects on reactivity determined by solvation of the leaving chloride (72):

TABLE 4. Prediction of relative rates of isomerisation of cis-$[Pt(PEt_3)_2(m-C_6H_4CH_3)Cl]$ in aliphatic alcohols

	$\delta_m\mu^{\ominus}/kJ\ mol^{-1}$		$\log_{10}\dfrac{k(MeOH)}{k(ROH)}$	
	KCl	Cl$^-$	forecast	actual
EtOH	+14.5	+7.8	1.30	1.26
1-PrOH	+22.1	+11.9	1.98	1.71
1-BuOH	+25.7	+13.9	2.32	2.06
2-BuOH	+27.1	+14.6	2.43	2.31

No single-assumption set of Gibbs free energies of transfer of chloride between the range of aliphatic alcohols seems to exist, but available solubility data for alkali metal halides permits their estimation. From solubilities of potassium chloride (73), and the assumptions

$$\gamma_\pm(ROH)/\gamma_\pm(MeOH) = 1.00$$

$$\delta_m\mu^{\ominus}(Cl^-) = 0.54\gamma_m\mu^{\ominus}(KCl),$$

respectively reasonable and justified elsewhere (72), we obtain the transfer parameters for chloride given in Table 4. Hence ratios of rate constants can be calculated assuming a limiting dissociative (D) mechanism and that transfer of chloride alone determines the dependence of rate constant on medium. Ratios of rate constants thus forecast are compared with ratios of measured rate constants in Table 4. The good agreement provides strong support for the mechanism assumed here. The fact that the ratios of actual rate constants are all about 90% of the forecast ratios suggests that the platinum-chloride bond is indeed nearly broken in the transition state, with the leaving chloride having an approximately 0.9- charge.

Obviously we require Gibbs free energies of transfer of the platinum complex to do this analysis properly, in the manner equivalent to the iron(II) and chromium(III) complexes discussed above. We are currently assessing the most suitable complex to use for a full initial state-transition state analysis, not only of racemisation but also of solvolysis and thiourea substitution, in a range of non-aqueous solvents.

SOLVOLYSIS AND SUBSTITUTION

The last two sections have dealt with isomerisations that are closely related to solvolysis, itself a special case of substitution. As already hinted above, initial state-transition state analyses of solvent effects on rate constants for substitution are complicated by the need for single-ion assumptions when the complex or a leaving or entering group are charged. Such is very often the case for classical coordination complexes, but single-ion problems can frequently be avoided in the area of organometallic substitution. An indication of some preliminary efforts and conclusions in this area follows.

Tetracarbonylmolybdenum(0) Derivatives

Our interest in this area developed from our studies of nucleophilic attack at iron(II)-diimine complexes (74), with the initial kinetic investigation being of cyanide attack at $Mo(CO)_4(bipy)$:

$$Mo(CO)_4(bipy) + 2CN^- = Mo(CO)_4(CN)_2^{2-} + bipy$$
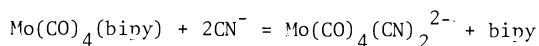
in several non-aqueous solvents and in dimethyl sulphoxide-water mixtures (75). More recently we have studied analogous reactions which do not involve ions (v.i.).

The rate law for the above reaction is

$$-d[Mo(CO)_4(bipy)]/dt = \{k_1 + k_2[CN^-]\}[Mo(CO)_4(bipy)].$$

Here the first-order term corresponds to a dissociative or solvolytic pathway, the second-

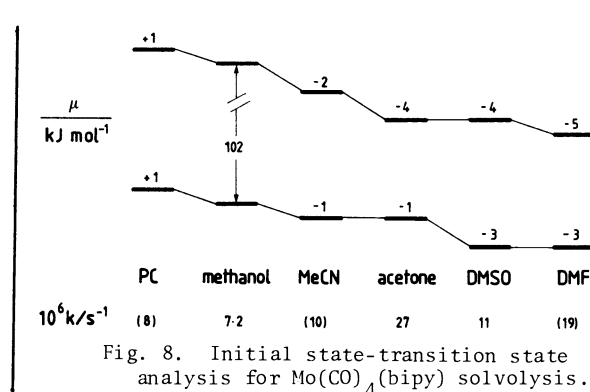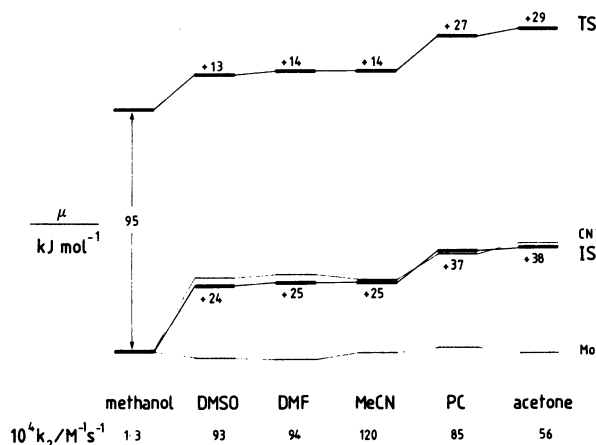Fig. 7. Initial state-transition state analysis for $Mo(CO)_4(bipy)$ plus cyanide.

Fig. 8. Initial state-transition state analysis for $Mo(CO)_4(bipy)$ solvolysis.

order term to bimolecular reaction with cyanide. Whether the latter attack takes place at the molybdenum or initially at the coordinated ligand is a matter of current lively controversy, especially for analogous iron(II), ruthenium(II), and platinum(II) diimine complexes (76), but does not affect our initial state-transition state analysis. We have analysed reactivity trends with these contributions both for solvolysis and for cyanide attack, assuming a dissociative mechanism for the former. Measured solubilities of the molybdenum compound give its Gibbs free energies of transfer. Such values for cyanide are derived from potassium cyanide solubilities (17). The initial state-transition state analyses are shown in Figs. 7 and 8. Solvent effects on the molybdenum compound are very small, on the cyanide ion large (Figs. 7 and 8 are to different scales). So solvation changes and trends are subtle for solvolysis, but dominated by the cyanide in nucleophilic attack by this anion.

For the reaction with cyanide, initial state and transition state chemical potential changes are parallel, with the former larger. Presumably the cyanide has a smaller interaction with the solvent when it is incorporated into the transition state. On the other hand, transition state effects are somewhat larger than initial state effects in the solvolysis (k_1) path:

Examples of simple substitution reactions involving only non-electrolytes are provided by displacement of piperidine or of triphenylphosphine from their bis-ligand-tetracarbonyl-molybdenum(0) complexes by Group V donors. Results of preliminary kinetic studies of the reaction

$$Mo(CO)_4(PPh_3)_2 + LL = Mo(CO)_4(LL) + 2PPh_3,$$
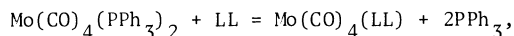
where LL = bipy or phen, in toluene, chloroform, and methanol show that rates are independent of the nature and concentration of the incoming ligand LL, and are thus dissociative in mechanism (77). From these rate constants and measured solubilities of the bis-triphenyl-phosphine compound in methanol and in toluene, the initial state-transition state analysis shown in Fig.9 has been derived. In contrast to solvolysis of 2,2'-bipyridyl-tetracarbonyl-molybdenum(0) above, but in common with a large number of organic substitutions, initial state solvation dominates over transition state solvation.

Substitution at the compound $Mo(CO)_4(btz)$ where btz is a dithio-diimine ligand (the complex is shown in Figs. 10 and 11 below), should provide further useful examples of substitution reactions for initial state-transition state analysis of solvent effects. At present we
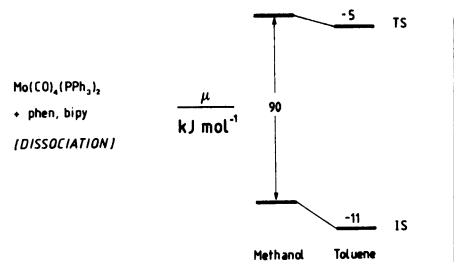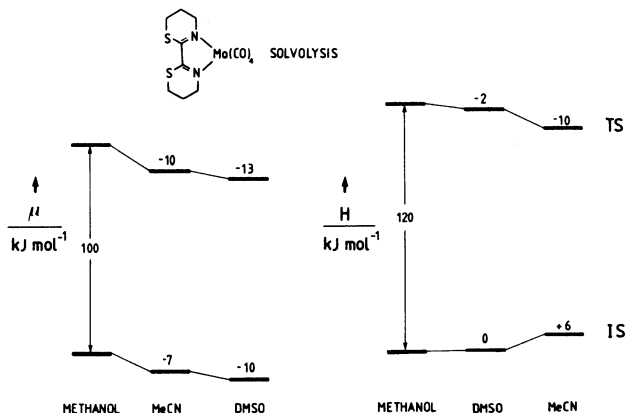

Fig. 9. Initial state-transition state analysis for $Mo(CO)_4(PPh_3)_2$.

Fig. 10. Initial state-transition state analysis for $Mo(CO)_4(btz)$

have only kinetic data for solvolysis, but we do have both Gibbs free energy and enthalpy data, with appropriate solubilities and enthalpies of solvation (78). Figure 10 shows initial state-transition state dissections of solvent effects in terms of G and of H. The chemical potential (G) analysis shows similar trends to those shown in Fig. 8 for solvolysis of the 2,2'-bipyridyl analogue. It is interesting that changes are more marked for the btz compound than for its bipy analogue; the btz is the more soluble and thus interacts more strongly with solvents.

There is an interesting spectroscopic digression from the initial state-transition state analysis for this btz compound. This compound is markedly solvatochromic, like the closely related series of diimine compounds $M(CO)_4(LL)$ where M = Cr, Mo, or W, and LL = 2,2'-bipyridyl or (substituted) 1,10-phenanthroline (79-81), and the less closely related series $Fe(LL)_2(CN)_2$ (82). Solvatochromism indicates a difference between solvation changes at the ground and excited states for the observed transition, charge-transfer in these cases, for different solvents. A ground state-excited state analysis of solvatochromism can be conducted in a manner similar to the initial state-transition state analyses of reactivities which form the main subject of this review; indeed several such analyses have been carried out, for example for the dioxan-iodine complex (83). The kinetic initial state and solvatochromic ground state are identical, of course, but the solvatochromic and kinetic excited and transition states differ. The spectroscopic charge-transfer takes place so quickly that the geometry of the excited state solvation shell is identical with that of the ground state (Frank-Condon) (84), but the kinetic transition state is formed at a slower rate such that the solvation shell can alter its geometry appropriately. Similar considerations show that the spectroscopic analysis (E) should be compared with kinetic activation enthalpies (H). Thus the ground state-excited state analysis of solvent effects on the charge-transfer spectrum of the btz compound (Fig. 11) should be compared with the right hand half of Fig. 10. There is no clear parallel or distinction; data for more solvents are needed before trends can be established. As in organic examples, both ground and excited state solvation changes are significant. Detailed analysis of solvent effects on spectra of carbonyl (85, 86) and azo (86) compounds showed complicated patterns of ground state and excited state effects. There is no reason to believe that our organometallic systems should not also be complicated.

Fig. 11. Ground state-excited state analysis for $Mo(CO)_4(btz)$.
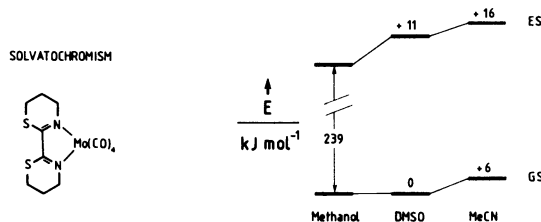
Activation Volumes

In the main body of this review we have dealt with solvation changes of initial and transition states on transfer between media. In these last sections we shall deal mainly with differences in solvation between initial and transition states, and how these differences change with solvent. The link between this section and previous sections is provided by molybdenum(0) and iron(II) complexes already encountered, specifically in their reactions with cyanide:

$$Mo(CO)_4(bipy) + 2CN^- = Mo(CO)_4(CN)_2^{2-} + bipy$$

$$Fe(phen)_3^{2+} + 2CN^- = Fe(phen)_2(CN)_2 + phen.$$
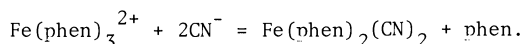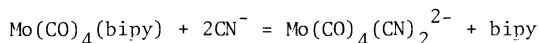
In terms of initial state-transition state analyses, it is interesting to see how solvation of various entities dominates in different media. Thus, as shown above, for the molybdenum system in non-aqueous media it is the cyanide ion and its solvation changes which dominate. However for the iron(II) system in water-rich binary mixtures, reactivity trends are dominated by solvation changes at the iron(II) cation (cf. Fig. 3 above) as the cyanide ion appears to maintain a fairly constant solvation (presumably predominantly hydration) shell in various water-rich mixtures (17). The relation of this to the initially puzzling activation volume data is developed into the following paragraphs.

Initial reports of activation volumes for nucleophilic attack at diimine complexes of iron(II) gave values in the range of +19 to +22 cm^3 mol^{-1} for reaction of the tris-1,10-phenanthroline and tris-2,2'-bipyridyl complexes with hydroxide and with cyanide. These activation volumes were interpreted in terms of a dissociative mechanism (87), which indeed they do seem to indicate. However such a conclusion is in conflict with all other discussions, which, though they may differ in proposing nucleophilic attack either at the iron or initially at the ligand (88), all agree that substitution is bimolecular. Subsequent determinations of activation volumes for nucleophilic attack at other iron(II) complexes in water, and at molybdenum(0) complexes in non-aqueous solvents, listed in Table 5 (89-91), indicate that the nature of the solvent is of great importance in determining not only the magnitude but also the sign of the activation volume.

The most plausible rationalisation of the results in Table 5 is that the big differences between water, methanol, and dimethyl sulphoxide values may be attributed to cyanide desolvation. In water the heavily hydrated cyanide loses much electrostricted water on entering the transition state, and it is the expansion of this solvent on moving from the hydration shell to bulk water that causes the positive activation volume. In dimethyl sulphoxide the cyanide is only very lightly solvated, and thus there are no solvent volume changes from its desolvation to mask the intrinsically negative activation volume for bimolecular attack. This rationalisation must be an oversimplification, for it takes no account of the small but real effect of change of ligand on activation volume. This importance of ligand nature is perhaps even more simply demonstrated by the results for aquation of iron(II)-phenanthroline complexes given in Table 6 (92) below. However further information, including especially more data on solvation and solvation changes for iron(II)-diimine complexes, will help to resolve these difficulties and complexities.

TABLE 5.   Activation volumes for nucleophilic attack at diimine complexes

Reactants	Solvent	$\Delta V^{\ddagger}/cm^3 mol^{-1}$	Ref.
$Fe(LL)_3^{2+} + OH^-, CN^-$	water	+19 to +22	(89)
$Fe(4Mephen)_3^{2+} + CN^-$	water	+10	(90)
$Mo(CO)_4(bipy) + CN^-$	methanol	+4	(91)
$Mo(CO)_4(bipy) + CN^-$	DMSO	-9	(91)

TABLE 6.   Activation volumes for aquation of iron(II)-phenanthroline complexes, in aqueous solution at 298.2K (92)

	$\Delta V^{\ddagger}/cm^3 mol^{-1}$
$Fe(5NO_2phen)_3^{2+}$	+17.9
$Fe(phen)_3^{2+}$	+15.4
$Fe(4,7-diCH_3phen)_3^{2+}$	+11.6

In these reactions with the often strongly solvated nucleophiles cyanide and hydroxide, it seems that measured activation volumes can be determined as much, or even more, by solvation than by the intrinsic positive or negative volume change on going from the initial to the transition state in a dissociative or associative activation step respectively. We would like to conclude this review by contrasting this solvation-dominated area with the area of solvent exchange, where activation volumes have recently revealed important fundamental mechanistic trends, with interpretation untrammelled by solvation of charged leaving or incoming groups.

Solvent Exchange

Table 7 shows trends in activation volumes for methanol (92) and for water (93) exchange across the first row transition metal 2+ cations. The change from negative values for manganese(II) to markedly positive values for cobalt(II) and nickel(II) has been taken as strong evidence for a change of mechanism from associative to dissociative in this direction (92-94). Although this interpretation has been criticised (95), it has received support from other quarters (96). Not surprisingly, activation volumes for solvent exchange at $Cr^{3+}aq$, where $\Delta V^{\ddagger}$ values are between -6 and -12 $cm^3 mol^{-1}$ for water, DMF, and DMSO (97), and at Fe^{3+} aq, where $\Delta V^{\ddagger} = -5.4$ $cm^3 mol^{-1}$ for water exchange (98), are also indicative of associative activation. Interestingly, water exchange at $FeOH^{2+}$ aq is characterised by an activation volume of +7.0 $cm^3 mol^{-1}$, indicating dissociative exchange at this hydroxo-cation (98).

TABLE 7.   Activation volumes $(cm^3 mol^{-1})$ for solvent exchange.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
Methanol	-5.0	+0.4	+8.9	+11.4
Water	-5.4	+3.8	+6.1	+ 7.2

Thus it is clear that activation volumes may in appropriate cases give clear indication of mechanism or of the role of solvation, but that their interpretation is more difficult and contentious where both mechanism and solvation effects are to be assessed.

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