SOLVENT AND PRESSURE EFFECTS ON KINETICS OF REACTIONS OF COMPLEXES

Michael J. Blandamer and John Burgess

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

Abstract - Effects of solvent and of pressure are described and discussed
for a variety of reactions of coordination complexes in water and in binary
aqueous solvent mixtures. Activation volumes, for reactions of established
mechanism, are considered in relation to solvation changes involved in
generating transition states, while analyses of kinetic and appropriate
ancillary thermodynamic data are considered in relation to solvation
changes consequent on transferring reactants and transition states from
water into mixed aqueous solvents. Such information, often complementary
from these two approaches and in a few cases supplemented by data concern-
ing model transition states, is presented and discussed with particular
reference to the following reactions:

(i)   substitution at pentacyanoferrates(II);

(ii)   racemisation of tris-oxalato-chromate(III);

(iii)   nucleophilic attack at diimine complexes;

(iv)   formation of nickel(II) complexes;

(v)   mercury(II)-catalysed aquation;

(vi)   outer-sphere redox: $IrCl_6^{2-} + I^-$;

(vii)   inner-sphere redox: $Co(NH_3)_5Cl^{2+} + Fe^{2+}$.

INTRODUCTION

This contribution deals with the effects of medium and of pressure on kinetics of reactions
of inorganic complexes in water and in water-rich binary aqueous solvent mixtures. The
influence of solvent composition and of pressure on kinetic parameters will be discussed
with particular reference to solvation of reactants and of transition states. The two
approaches can provide complementary information on the role of solvation. Pressure effects
give indications of changes in solvation on going from the initial to the transition state,
while solvent effects give indications of changes in solvation of the initial and transition
states individually on transfer between media.

Activation volumes, $\Delta V^{\ddagger}$, derived from the pressure dependence of rate constants, can be
divided into intrinsic and solvation contributions:

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{intr} + \Delta V^{\ddagger}_{solvn}.$$

If one or other of these contributions can reasonably be taken to predominate, then
activation volumes can be used interpretatively. Thus in weakly solvating solvents, or in
the gas phase, the distinction between positive activation volumes for dissociative
processes and negative for associative processes has frequently proved valuable in diagnosis
or confirmation of mechanism. Even in aqueous solution activation volumes have proved
invaluable in establishing mechanisms of water exchange, as solvation effects will be small
for an uncharged leaving and entering group, but in reactions involving ions in aqueous
solution, solvation effects may dominate over intrinsic effects in determining the size
and even the sign of the activation volume, as will be seen below.

Solvent effects on rate constants and activation parameters, on the other hand, reflect
solvation changes on the initial and transition states as these are transferred from, say,
water into a mixed aqueous solvent. If solvent effects on the initial state can be
established from thermodynamic data, then solvent effects on the transition state can be
calculated (assuming constancy of mechanism and the validity of transition state theory).
Figure 1 shows the interrelation of kinetic and thermodynamic parameters for Gibbs free
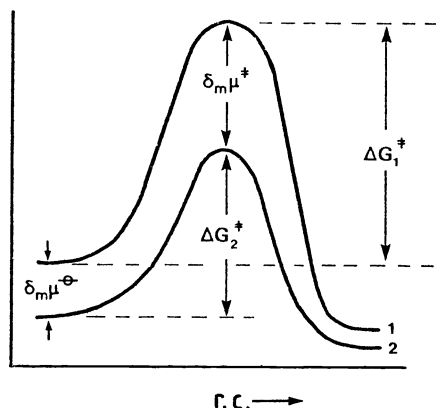
Fig. 1. Solvent effects on initial
         and transition states, and
         on the activation barrier.

energies (chemical potentials); analogous diagrams apply for enthalpies, entropies, volumes, and other parameters. For Gibbs free energy analyses, initial state transfer functions can be derived from solubility or vapour pressure measurements. For enthalpies, initial state transfer functions can be derived calorimetrically or, less attractively, using the van't Hoff isochore on the temperature dependence of solubilities. Several factors affect the ease of carrying out the experimental work and of interpreting the results and the initial state-transition state analysis. These factors are set out in the following paragraphs (i) to (iii).

(i)   Bimolecular reactions are preferable to unimolecular. For the latter one is restricted to reactions slow enough for equilibrium measurements on the initial state to be feasible, yet not so slow that kinetic measurements take an inordinate time. For bimolecular reactions one can carry out the initial state measurements on each reactant separately, and there is also the possibility of controlling half-lives by concentration variation.

(ii)   For reactions involving ions, the derivation of the required transfer parameters involves controversial extrathermodynamic assumptions. However it is obvious that a coordination chemist can hardly restrict himself to uncharged reactants!

(iii) Transition state transfer parameters are always the indirect resultant from initial state and activation barrier measurements, and are by definition inaccessible to direct measurement. However in suitable systems, as will be illustrated below, it is possible to obtain supporting evidence from measurements on transition state models.

The initial state-transition state dissection exercise is rather more than a simple juggling of arithmetical values of the various thermodynamic values, satisfying though this can be. Rather we attempt to show how the outcome of such analyses can be used to probe details of reaction mechanisms and show factors governing observed trends in kinetic parameters. Thus in several cases outlined here, observed trends can mask quite striking solvent variation in the initial and transition states as the solvent is varied. The self-consistency between patterns described here lends some support to the idea that, despite its obvious shortenings, transition state theory provides a useful basis for analysing kinetic data.

Analysis of solvent effects on reactivity into initial state and transition state components has been carried out on a variety of organic reactions, some substitutions at sp-block elements, a few organometallic reactions, and some reactions of coordination complexes of the transition metals. These analyses have been fully documented elsewhere recently (1-3). In this review we discuss initial state-transition state analyses of solvent effects on reactivities for several reactions, both substitution and redox, of transition metal complexes. We also try to show how these and pressure effects can provide complementary information on the role of solvation, and, in two cases, how transition state modelling may assist in interpretation.

We end this introduction by noting that investigations of the effect of solvent on activation volumes are rare, though values have been reported for pyridine substitution in $PtCl(NO_2)(py)_2$ in methanol, ethanol, nitromethane, and dichloromethane (4). Also it may be noted that initial state-transition state analyses in terms of volumes are also rare, though such an analysis has been carried out for benzyl chloride solvolysis (5).

SUBSTITUTION AT PENTACYANOFERRATES(II)
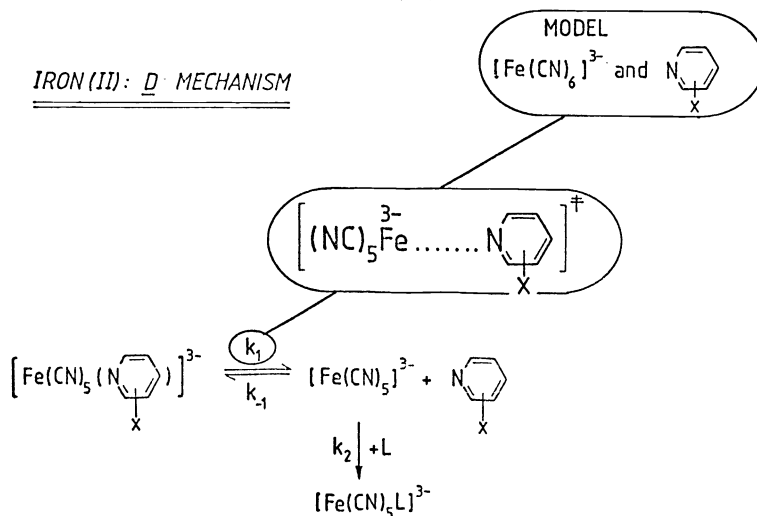
Reactions in this category proceed by limiting dissociative mechanism (S_N1(Lim) or D) (6). Operationally they share the benefits of bimolecular systems in that equilibrium (initial state) measurements can be conducted at leisure, with reactions only proceeding in the presence of an excess of the incoming competing nucleophile. They also provide the opportunity for simple transition state modelling, though, as the schematic diagram indicates, the use of the leaving group itself as part of the transition state model is less than entirely satisfactory in that the hydrophilic portion of (substituted) pyridine is still associated with the iron(II) and therefore not fully available for interacting with water in the solvent. We have tried to minimise this complication by using such leaving groups as 4-cyanopyridine and 2-methylpyrazine, which have hydrophilic centres not associated with the metal ion. Finally the study of reactions of complexes of this sort is helped by the extensive documentation of properties for a large number of such anions (7). All the discussion which follows relates to the limiting rate constants (k_1 of the Scheme) corresponding to the breaking of the iron(II)-leaving ligand bond.

Activation volumes for dissociation of four complexes of this type are listed in Table 1 (8,9). They show the expected lack of dependence on the nature of the incoming group. These large positive values appear dominated by the intrinsic contribution from the dissociative character of these reactions, with similar values for the four similarly-sized leaving groups. This apparent lack of sensitivity to solvation effects is consistent with the very small sensitivity of rate constants to solvent composition for reactions of this type in water-rich binary mixtures (10). This activation volume picture may be contrasted with that reported for solvolysis of $Co(NH_3)_5X^{2+}$ cations (11), where a range of negative activation volumes was observed, attributable to solvation effects at the small hydrophilic leaving anions.

TABLE 1. Activation volumes ($cm^3 mol^{-1}$)* for substitution in pentacyanoferrates(II), $Fe(CN)_5L^{3-}$, in aqueous solution.

Incoming Ligand:	CN^-	pz	imidH	
L = 3,5Me$_2$py	+20.5	+21.2	+20.3	(8)
3CNpy	+20.6			(8)
4CNpy	+20.6			(9)
2Mepz	+19.4			(9)

py = pyridine; pz = pyrazine; imidH = imidazole.

* Standard errors between $\pm$ 0.5 and $\pm$ 1.0 $cm^3 mol^{-1}$

The Table 1 results indicate that the activation volume for dissociation of these penta-cyanoferrates(II) is independent of the nature of the leaving group. We note that this is not the case for the very similar aquation reactions of tris-diimine complexes of iron(II) (Table 2 (12,13)).

TABLE 2. Activation volumes $(cm^3 mol^{-1})$ for aquation of tris-diimine-iron(II) complexes, $Fe(LL)_3^{2+}$, in aqueous acid.

LL		$\Delta V^{\ddagger}$	
$5NO_2$phen		+17.9	(12)
phen	1 M H_2SO_4	+15.4	(12)
4,7 Me_2phen		+11.6	(12)
bipy	1 M HCl	+12.3	(13)
	0.01M HCl	+14.8	(13)

An initial state-transition state analysis of the reactivity trend established for sub-stitution (limiting rate constant k_1 in Scheme above) in the $Fe(CN)_5(4CNpy)^{3-}$ anion is shown in Fig.2 (14). The Gibbs free energies of transfer of the initial state and of the model transition state component $Fe(CN)_6^{3-}$ were calculated from measured solubilities of $[Cr(en)_3][Fe(CN)_5(4CNpy)]$, $[Cr(en)_3]Cl_3$, and $K_3[Fe(CN)_6]$ using de Ligny's values for transfer of K^+ and Cl^- (15). Figure 2a shows how the very small change in rate constant masks large, and of course almost equal, changes in initial state and transition state transfer potentials. This is illustrated again in Fig.3, which emphasises how large these changes are in comparison with the activation barrier - the change in chemical potentials of initial and transition states on transfer from water into 80% methanol are one-third of the barrier. Figure 2b shows that the model transition state solvation changes are fairly close to those deduced for the actual transition state. In general the addition of methanol causes a marked destabilisation of pentacyanoferrates and related ions, presumably attri-butable to the 3-charge and the hydrophilic character of the five (or six) cyanide ligands.
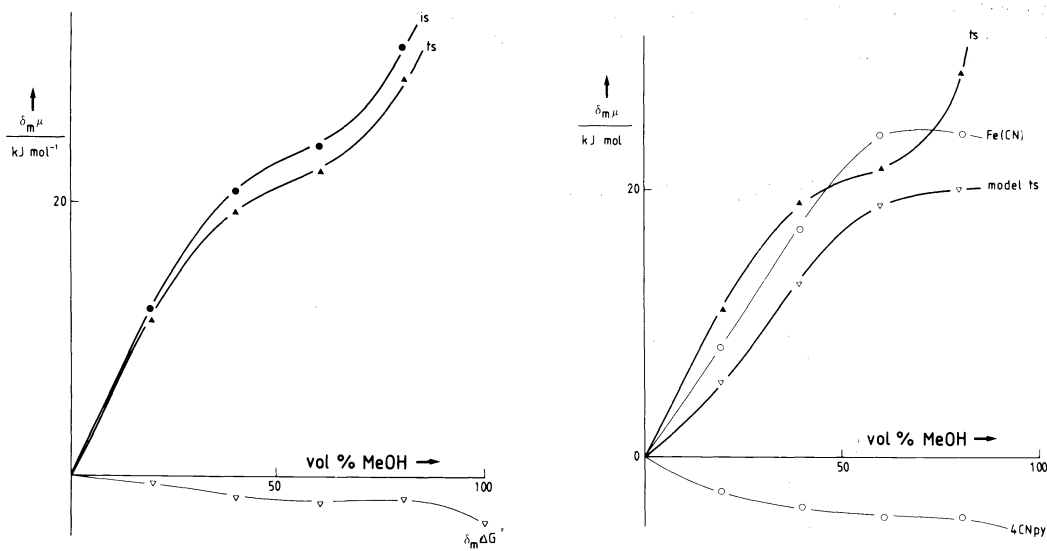

Fig. 2. Initial state-transition state analysis for $Fe(CN)_5(4CNpy)^{3-}$ dissociation.

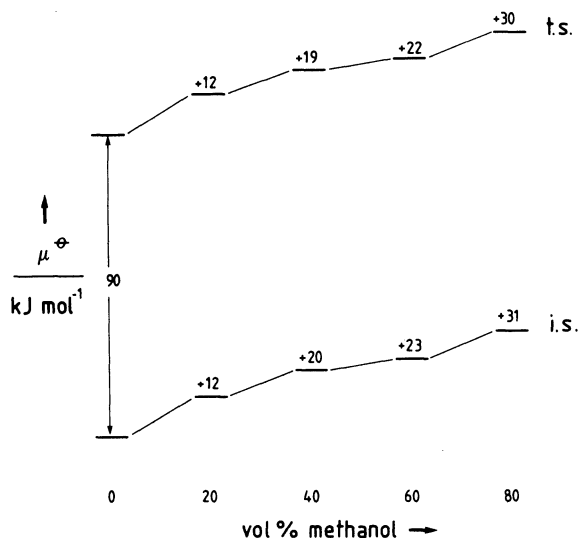Fig. 3. Relation of initial state and transition state changes to the
rate constant activation barrier for $Fe(CN)_5(4CNpy)^{3-}$ dissociation.

A similar pattern is emerging for enthalpies, with an observed small sensitivity of activation enthalpy to medium masking much larger changes in enthalpies of transfer of the initial and transition states. An analogous analysis of entropies would not at the moment be meaningful, as the single ion assumptions used for G and for H are not the same and may be incompatible.

Thus the two approaches are consistent in this case, with rate constant trends and activation volumes suggesting that changes in solvation on going from the initial to the transition state are much less significant than changes in both on transfer between different solvent media.

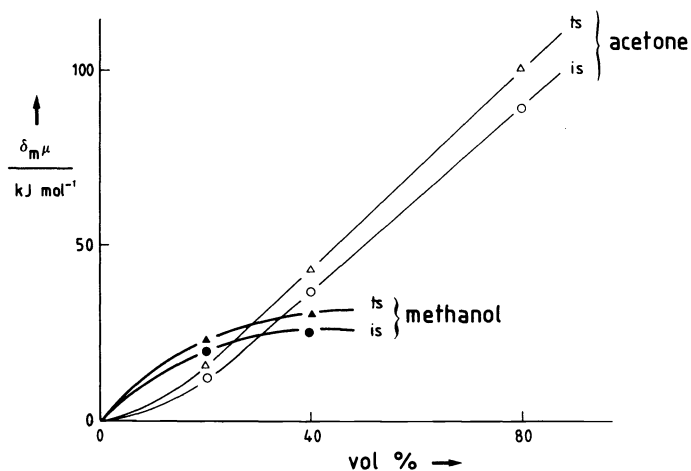

Fig. 4. Initial state-transition state analysis for $Cr(ox)_3^{3-}$ racemisation.

TRIS-OXALATOCHROMATE(III) RACEMISATION

This is a unimolecular process, involving dissociation of one end of bidentate oxalate (16).
Kinetic data are available in a variety of binary aqueous mixtures, with cosolvents
including methanol, ethanol, n-propanol, iso-propanol, dioxan, and acetone (17,18). From
our solubility measurements on potassium trisoxalatochromate(III) in methanol- and acetone-
water mixtures we have estimated Gibbs free energies of transfer for this anion, using
published data for K^+ (15,19), and thence carried out the initial state-transition state
analysis in Fig. 4.

For both cosolvents, slower racemisation as the proportion of organic component increases
represents an increasing activation barrier arising from a significantly greater destabil-
isation of the transition state than of the initial state. As the transition state has a
rather larger hydrophilic periphery than the initial state this is an intuitively reasonable
picture.

Activation volumes for racemisation of $Cr(ox)_3^{3-}$ (20) and for isomerisation of trans-$Cr(ox)_2$
$(OH_2)_2^-$ (21) are both -16 cm^3mol^{-1}, attributed to electrostriction of water around the
released hydrophilic end of the unidentate oxalate in the transition state and entirely
consistent with the view expressed in the previous paragraph. It is interesting to compare
these markedly negative activation volumes with that of +3.3 cm^3mol^{-1} reported for race-
misation of $Cr(phen)_3^{3+}$ (20), where the periphery is hydrophobic and there is for geo-
metrical reasons no likelihood of a one-end-off mechanism. For comparison, the activation
volume for the indubitably intramolecular inversion of cyclohexane rings is very close to
zero (22).

NUCLEOPHILIC ATTACK AT DIIMINE COMPLEXES

The dominant term in the rate law for reaction of cyanide or hydroxide with such diimine
complexes as $Fe(phen)_3^{2+}$, $Fe(bipy)_3^{2+}$, and $Mo(CO)_4(bipy)$:

$$\text{e.g.} \quad Fe(phen)_3^{2+} + 2CN^- = Fe(phen)_2(CN)_2 + phen$$
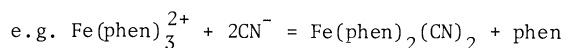
is second-order, indicating associative attack (23-26). Solvent effects are important both
in terms of activation volumes and of initial state-transition state analysis, with a marked
change in emphasis on going from water-rich media to non-aqueous solvents.

The most striking feature concerns activation volumes. Several years ago values of between
+19 and +22 cm^3mol^{-1} were reported for reaction of $Fe(bipy)_3^{2+}$ and of $Fe(phen)_3^{2+}$ with
hydroxide and with cyanide in aqueous solution (27), an unexpected result for associative
reactions. More recently, activation volumes of +4 and -9 cm^3mol^{-1} for reaction of
$Mo(CO)_4(bipy)$ with cyanide in methanol and in dimethyl sulphoxide respectively (28) suggest
that the desolvation of cyanide or hydroxide necessary for transition state formation may
dominate the observed activation volume in water, but may be negligible in dimethyl
sulphoxide. It is of interest that the activation volume for reaction of the anionic
complex $Fe(fz)_3^{4-}$* with hydroxide in water is zero(9); solvation changes on transition
state formation are likely to differ markedly between this 4- plus 1- reaction and
the 2+ plus 1- reactions mentioned above.

Complementary evidence for the importance of strong hydration of cyanide or of hydroxide
in determining reactivities in these systems comes from initial state-transition state
analyses of reactions of tris-diimine-iron(II) complexes in water-rich solvent mixtures.
Thus such an analysis for reaction of $Fe(bipy)_3^{2+}$ with cyanide (29) in 0 to 30% methanol
shows that the modest increase in rate can be attributed to slightly greater stabilisation
of the transition state than of the initial state as the proportion of methanol increases.
Both are, however, markedly stabilised by adding methanol, the situation being dominated
by the hydrophobic periphery of the coordinated bipyridyls. The chemical potential of the
cyanide changes by less than 1 kJ mol^{-1} over this solvent range, presumably as this anion
is sufficiently hydrophilic (30) to retain its hydration shell essentially intact.

ferrozine (fz) :
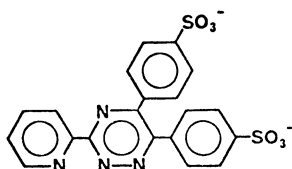
Turning to non-aqueous media and to the reaction of $Mo(CO)_4(bipy)$ with cyanide, changes in rate constant with solvent are again relatively small, but now it is the chemical potential of the cyanide which changes markedly with solvent, dominating Gibbs free energies of transfer both of the initial state and the transition state. The hydrophobic molybdenum compound is comparably solvated by all the non-aqueous solvents involved, to judge by the near constancy of its chemical potential (26). Finally the two regions of water-rich and non-aqueous behaviour can be linked by the initial state-transition state analysis of this $Mo(CO)_4(bipy)$ plus cyanide reaction in dimethyl sulphoxide-water mixtures, where the change-over from cyanide solvation control to hydrophobic complex control can be seen (26).

The question of transition state modelling is particularly interesting in this area. There has for some time been controversy as to whether the nucleophile attacks at the metal atom or initially at the coordinated diimine (31). There are some strong indications of the latter, especially when the diimine ligand contains an electron-withdrawing substituent such as a nitro- (32), sulphonato- (33), or chloro- (34) group. Recently spectroscopic evidence interpretable in terms of reaction via initial attack at the ligand has been presented for the reaction of $Fe(fz)_3^{4-}$ with hydroxide (33). $\Delta V^{\ominus}$ for the initial reversible reaction with hydroxide is zero, as is $\Delta V^{\ddagger}$ for transfer of the hydroxide to the iron. This latter result is hardly surprising, since the solvation change on forming the transition state for such a process is likely to be very small. Interestingly the solvent effect on rate constants for the analogous process
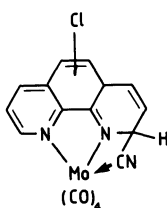
is, consistently, also very small (26).

COMPLEX FORMATION

The Eigen-Wilkins mechanism for the formation of complexes is a two-stage process, which has been taken into account in the interpretation of measured activation volumes (35). Values of around +10 $cm^3 mol^{-1}$ for the interchange step in reaction of Ni^{2+} with several monodentate ligands are consistent with the well-established dissociative interchange nature of this process. Solvation effects should be of minor importance here, but for the initial outer-sphere association equilibrium there is likely to be a significant volume contribution from the release of electrostricted solvent, especially when anionic ligands are involved. Thus the association of several M^{2+} cations with sulphate has $\Delta V^{\ominus}$ = +10 to +12 $cm^3 mol^{-1}$, attributed to the extrusion of about three water molecules (36). In the extreme, $\Delta V^{\ominus}$ for reaction of Ni^{2+} with $edta^{4-}$ has $\Delta V^{\ominus}$ = +25.5 $cm^3 mol^{-1}$ (37). A recent high pressure T-jump study of the reaction of Ni^{2+} with malonate gave an overall $\Delta V^{\ddagger}$ of +16 $cm^3 mol^{-1}$, which was separated into contributions of +7.3 $cm^3 mol^{-1}$ for the initial association equilibrium and +8.7 $cm^3 mol^{-1}$ for the interchange step (38).

An initial state-transition state analysis of rate constants is complicated by the two-stage nature of the mechanism and the lack of Gibbs free energies of transfer for Ni^{2+} (though values for Cu^{2+} (39) could be used without introducing too much uncertainty, one feels). We have carried out a preliminary analysis of enthalpies for formation of mono-2,2'-bipy-ridyl-nickel(II) in aqueous methanol (40), using Bennetto and Caldin's kinetic data (41), measured enthalpies of solution of anhydrous nickel chloride, Krestov and Klopov's enthalpies of transfer for chloride (42), and the assumption of a one-step mechanism. Figure 5 shows an updated version of this analysis, using better enthalpy of solution data, this time for nickel chloride hexahydrate (making the appropriate small correction for enthalpies of transfer of the six water molecules). The small changes in activation enthalpy as methanol is added to water again represent the balance between much larger and almost compensating changes for the initial and transition states. Both reactants contribute to these changes, but the 2,2'-bipyridyl is the more affected by change of solvent composition in the range of mixtures studied.
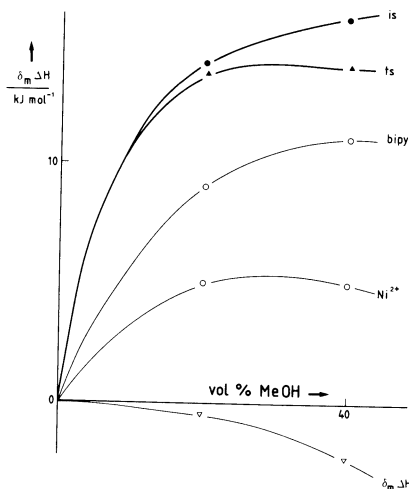
Fig. 5. Initial state-transition state analysis (enthalpies) for the
formation of mono-2,2'-bipyridyl-nickel(II).

MERCURY(II)-CATALYSED AQUATION

Mercury(II)-catalysed aquations of halide complexes of inert transition metal cations
provides another area where initial state-transition state analyses and activation volumes
are available. Application of the former approach to $Co(NH_3)_5Cl^{2+}$ and $ReCl_6^{2-}$ provided a
dramatic illustration of the importance of reactant charges, with very different patterns
for the augmentation (2+ plus 2+) and cancellation (2- plus 2+) of charge in formation of
the respective transition states (43). Unfortunately there is no activation volume
available for the $ReCl_6^{2-}$ plus Hg^{2+} reaction to show the consequences of release of
electrostricted water in transition state formation (though see inner-sphere redox below).
However, mercury(II)-catalysed of complexes $M(NH_3)_5X^{2+}$, where four combinations from M = Co,
Cr, Rh, and X = Cl, Br have been studied, have activation volumes close to zero (between
-1.7 and +0.8 cm^3mol^{-1} (44)), strongly suggesting a significant contribution from solvation
changes balancing the expected negative value for associative reaction.

In fact this type of reaction is generally two-stage:

$$M-X^{n+} + Hg^{2+} \rightleftharpoons M-X-Hg^{(n+2)+} \rightarrow M^{(n+1)+} + HgX^+$$
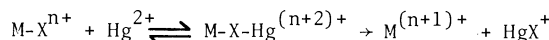
with the M-X-Hg species anything from a transition state to a stable intermediate. In
aquation of $Rh(NH_3)_5I^{2+}$, the binuclear intermediate is sufficiently stable and inert for
high pressure kinetics to have established $\Delta V^{\ominus}$ for the initial equilibrium and $\Delta V^{\ddagger}$ for
departure of HgI^+ from the rhodium. The value for $\Delta V^{\ominus}$, -1.7 cm^3mol^{-1}, again suggests the
importance of solvation changes in the production of the Rh-I-Hg intermediate, while the
value of +1.2 for $\Delta V^{\ddagger}$ also indicates a solvation contribution offsetting the intrinsic
positive $\Delta V^{\ddagger}$ for a dissociative process (45). Modelling has proved useful in analysing
solvent effects in systems of this type, in several ways. Thus, for example, the stable
intermediate in reactions of the $Rh(NH_3)_5I^{2+}/Hg^{2+}$ type can be used as model transition
state for, e.g., $Co(NH_3)_5Cl^{2+}/Hg^{2+}$, while for the loss of $HgCl^+$ from the fairly stable
binuclear species cis-$Rh(en)_2Cl(ClHg)^{3+}$ it proved convenient to use the transition state
for the trans-$Co(en)_2Cl_2^+/Hg^{2+}$ reaction (46).

REDOX REACTIONS

Only a small amount of time and space remain to deal with redox reactions, most of which
will be devoted to the outer-sphere electron transfer between hexachloroiridate(IV) and
iodide (47). An initial state-transition analysis has been carried out in aqueous methanol,
including use of $IrCl_6^{3-}$ as a reasonable transition state model (48) (Fig. 6). This analysis
is based on published Gibbs free energies of transfer of iodide (49) and measured solubili-
ties of potassium hexachloroiridate(III) and hexachloroiridate(IV). Similar patterns have
been established for hexachloroiridate(IV)-catechol (48) and 12-tungstocobaltate-iodide (50)
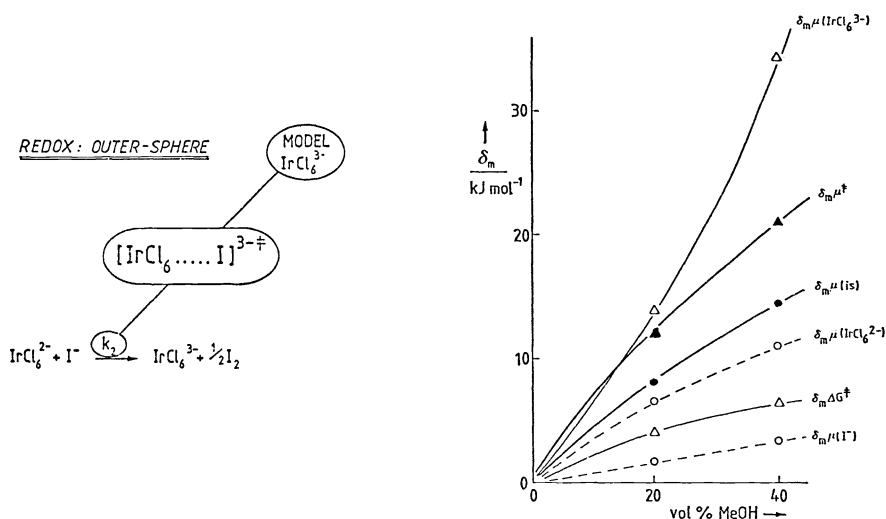electron transfer reactions.

Fig. 6. Scheme and initial state-transition state analysis of solvent
effects for the outer-sphere redox reaction $IrCl_6^{2-}/I^-$.

No activation volumes are available for these reactions, but it would not be surprising to
find reasonably negative values of similar size to those found for electron exchange between
pairs of cations, -13 to -20 cm^3mol^{-1} for $Tl^+aq/Tl^{3+}aq$, $Fe^{2+}aq/Fe^{3+}aq$, and $Co(en)_3^{2+}/Co(en)_3^{3+}$.
These values have been discussed in terms of solvent electrostriction around the highly
charged transition states (51), and indeed they are in striking contrast to the activation
volume of +36 cm^3mol^{-1} established for oxidation of the molybdenum(V) anion $Mo_2O_4(edta)^{2-}$ by
the cobalt(III) cation $Co_2O_2(NH_3)_{10}^{5+}$ (52). In turn this large positive value for partial
charge cancellation accords well with large negative values reported for several classes of
inorganic and organic reactions wherein transition state formation involves charge
separation. Examples include reactions of dimethylmercury with hydrogen halides (-22 to
-37 cm^3mol^{-1} (53)), Menschutkin reactions of alkyl halides with amines (-25 to -45 cm^3mol^{-1}
(54)), reactions of aliphatic amines with carbon acids (-9 to -20 cm^3mol^{-1} (55,56)), and
the reaction of di-n-butylamine with quinone (-54 to -67 cm^3mol^{-1} (57)), in various solvents.

Taube's original inner-sphere reaction (58) is unsuitable for our present approaches, but
replacement of chromium(II) as reductant by iron(II) (59) gives systems whose kinetics have
been studied under pressure in water (60) and in dimethyl sulphoxide (61) and which are
currently being analysed into initial state and transition state contributions. Such an
analysis is possible, since Gibbs free energies of transfer of $Fe^{2+}aq$ have been derived
recently (62) from transfer parameters for $Fe(phen)_3^{2+}$, themselves derived from solubili-
ties (63), for the phen ligand (again from solubilities (64)), and for the stability
constant (β_3) for the formation of this complex (65). Both this analysis and the measured
activation volumes (60,61) demonstrate the importance of solvation changes in determining
reactivities (51) in these inner-sphere electron transfer reactions, as in the substitution
reactions discussed earlier in this contribution.

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