

SOLVENT EFFECTS ON INITIAL STATES AND TRANSITION STATES FOR REACTIONS OF INORGANIC COMPLEXES

Michael J. Blandamer and John Burgess

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

Abstract - The use of solvent effects on reactivities in the diagnosis of inorganic substitution mechanisms is discussed, and the converse approach, the use of reactions of known mechanism to probe solvent structural properties, mentioned. Solvent effects on reactivity trends can be analysed into initial state and transition state components by the use of appropriate thermodynamic parameters for the reactant(s). Such an analysis has been carried out for a variety of substitutions at inorganic centres, for example cobalt(III), iron(II), and platinum(II), and for peroxodisulphate oxidation of iron(II) species.

INTRODUCTION

The establishment of solvent effects on reactivities was carried out many decades ago in efforts to establish mechanisms of substitution at carbon centres. This approach was subsequently extended to substitution at a few other *sp*-block elements, and then to substitution in inorganic complexes. Meanwhile one or two inorganic reactions of established mechanism were being employed to probe solvent structural properties, in non-aqueous and in mixed aqueous media. Many years ago solvent effects on reactivities in some organic systems were analysed into their initial state and transition state components in order to gain greater insight into mechanisms. Subsequently this approach was extended to *sp*-element compounds, and then to inorganic complexes. We shall follow this chronologically-based sequence in the discussion which follows.

MECHANISM DIAGNOSIS

The early qualitative ideas of Hughes and Ingold were applied in a quantitative manner by Grunwald and Winstein (1) to the problem of distinguishing between dissociative and associative mechanisms of substitution at carbon. Subsequent extension to substitution at halides of other *sp*-block elements is indicated in Table 1, which shows the substrates and solvent sensitivity parameter *m*.

TABLE 1. Grunwald-Winstein *m* values for *sp*-element substitutions

Bond	Compound	<i>m</i>	
Carbon-chlorine	t-Butyl chloride	1.00	} (1)
Carbon-bromine	t-Butyl bromide	0.9	
Phosphorus-chlorine	(Me ₂ N) ₂ POCl	0.3	(2)
Sulphur-chlorine	Me ₂ N.SO ₂ Cl	0.7	(3)
Boron-bromine	Me ₃ N.BH ₂ Br	0.6	(4)

Langford hinted at the possible usefulness of this analysis of solvent effects in diagnosing mechanisms of substitution at halogeno-cobalt(III) complexes (5). Since then the correlation of substitution rates with Grunwald-Winstein solvent *Y* values has been used for several transition metal centres, as indicated by the examples listed in Table 2.

Applications have also been reported in organometallic chemistry, for example in establishing mechanisms of isomerisation of haloalkene complexes of platinum(0) to halovinyl derivatives (15). When correlation with *Y* values is impracticable, correlations with other parameters, for example with Reichardt's *E_T* parameter in oxidative additions to *trans*-IrCl(CO)(PPh₃)₂, may prove informative (16).

Table 2. Grunwald-Winstein m values for transition metal complex substitutions

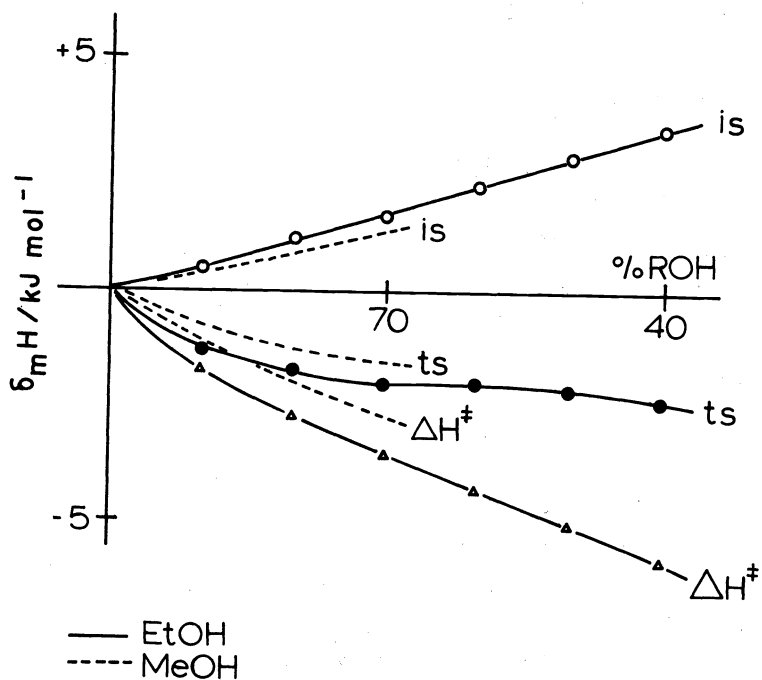
Bond	Complex	m	
Cobalt(III)-chloride	<u>cis</u> -[Co(en) ₂ Cl ₂] ⁺ etc.	0.25-0.35	(6)
Rhodium(III)-chloride	<u>trans</u> -[Rh(dmgH) ₂ (NO ₂)Cl] ⁻	0.32	(7)
Iridium(III)-chloride	<u>trans</u> -[Ir(en) ₂ Cl ₂] ⁺	0.3	(8)
Chromium(III)-chloride	[Cr(NH ₃) ₅ Cl] ²⁺	0.12	(9)
Ruthenium(II)-chloride	[Ru(NH ₃) ₅ Cl] ⁺	0.23	(10)
Palladium(II)-chloride	[Pd(Et ₄ dien)Cl] ⁺	0.4	{ (11) (12)
Rhenium(IV)-bromide	[ReBr ₆] ²⁻	-0.55	(13)
Manganese(I)-bromide	<u>cis</u> -[Mn(CO) ₄ Br ₂] ⁻	0.3	(14)

SOLVENT STRUCTURE

In order to probe solvent structure one needs a reaction of known mechanism whose rate is sensitive to changes in solvent environment. Aquation of cobalt(III) complexes or formation of nickel(II) complexes (dissociative), and substitution at square-planar d^8 complexes (associative) have been or are potentially useful. Aquation of the $Fe(5NO_2phen)_3^{2+}$ cation, whose activation volume indicates a dissociative mechanism (17), is useful here as rates are particularly sensitive to changes in solvent medium. Aquation at cobalt(III) or low-spin iron(II) centres reflects structure breaking and making in *t*-butyl alcohol + water mixtures (18), while the reaction of nickel(II) with bipy or pada reflects solvent structural properties in both non-aqueous and mixed aqueous media (19). These reactions, and substitution at the $Pd(Et_4dien)Cl^+$ cation, show an interesting correlation between reaction rate and the Gibbs excess function of mixing, G^E , of the solvent components at least in water-rich "typically aqueous" (G^E positive; $TS^E > H^E$) mixtures (12,20).

INITIAL STATE AND TRANSITION STATE SOLVATION

Further progress in understanding solvent effects on reactivity requires dissection of the composite rate constant trends into their component initial state and transition state solvation trends. This was first attempted for solvolysis of *t*-butyl chloride (21). The results of this analysis, for enthalpies, are illustrated for alcohol + water mixtures in Figure 1.

Fig. 1. Initial state and transition state effects in solvolysis of *t*-butyl chloride in alcohol + water mixtures.

This shows that initial state effects are greater than transition state effects, as did a similar analysis on volumes for solvolysis of benzyl chloride (22).

Similar conclusions were subsequently reached for the Menshutkin reaction of trimethylamine with methyl iodide (23), and for the reaction of tetraethyltin with mercury(II) chloride (24). Extension to an inorganic complex substitution reaction, that of Pt(bipy)Cl₂ with thiourea (25), is detailed in Figure 2, which shows the variation with solvent composition of the chemical potentials of the reactants and of the Gibbs activation function ΔG^\ddagger , all expressed in terms of the solvent operator δ_m . Here again the initial state solvation changes dominate over the transition state solvation changes.

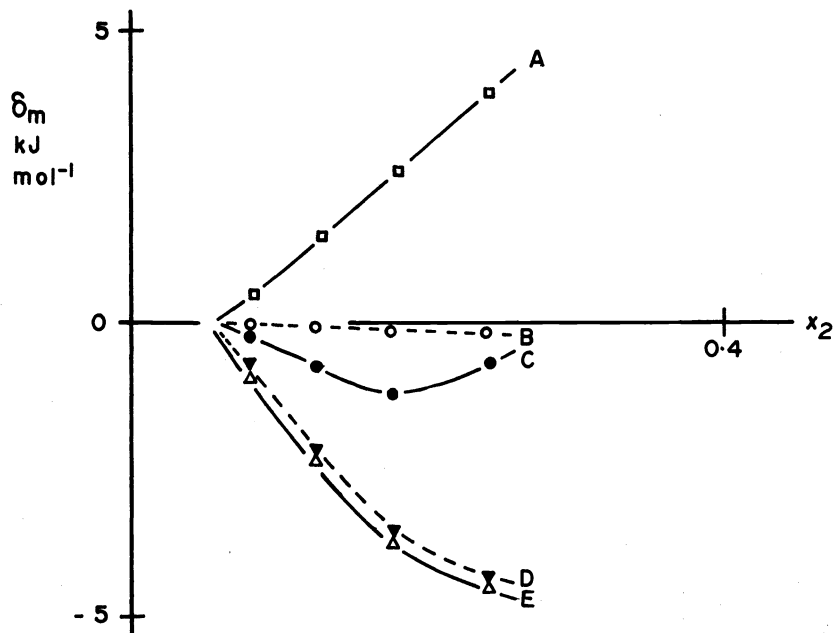


Fig. 2. Initial state and transition state effects in substitution of thiourea at Pt(bipy)Cl₂ in aqueous dioxan.

A = $\delta_m \Delta G^\ddagger$; B = $\delta_m \mu^\ominus(\text{tu})$; C = $\delta_m \mu^\ddagger$; D = $\delta_m \mu^\ominus(\text{Pt}^{\text{II}})$; E = $\delta_m \mu^\ominus(\text{is})$

Thus far we have restricted ourselves to reactions involving uncharged molecules, whose enthalpies of transfer or chemical potential changes can be observed fairly directly and satisfactorily. However the majority of inorganic complexes are charged, as are many potential nucleophiles. Now the estimation of transfer properties for reactants is complicated by the difficulties in establishing single ion values, in which process it is necessary to make assumptions, sometimes on none too firm foundations. Nonetheless it is often possible to make qualitative deductions even if these cannot be expressed quantitatively with confidence. This is illustrated by Figure 3, in which solvent effects on the reaction of Fe(bipy)₃²⁺ with cyanide are analysed into initial and transition state components on two different bases for transfer parameters for the iron(II) cation (different assumptions regarding the cyanide ion only make a small difference here). Regardless of assumption, the solvent effect on reactivity is a small resultant of similar solvation effects on the iron(II) moiety of the initial state and of the transition state; the hydrophobic periphery of this complex dominates (26).

The mercury(II)-catalysed aquation of the Co(NH₃)₅Cl²⁺ cation provides another example where small changes in rate constant with solvent composition are the result of large but almost identical initial state and transition state effects. However in mercury(II)-catalysed aquation of the ReCl₆²⁻ anion initial state effects are twice as large as transition state effects (Figure 4).

The results of these solvent effects on reactivity dissections are summarised in Table 3, which also shows the results of our preliminary studies of (outer-sphere) peroxodisulphate oxidation of low-spin iron(II) species. The majority of the results presented refer to mixed aqueous solvents; the reactions of Mo(CO)₄(bipy) with such nucleophiles as triphenyl phosphine, cyanide, and azide are currently being assessed for similar treatment in a range of non-aqueous solvents. While it is possible to derive transfer parameters more or less satisfactorily for reactant species, it is of course not possible to derive these directly

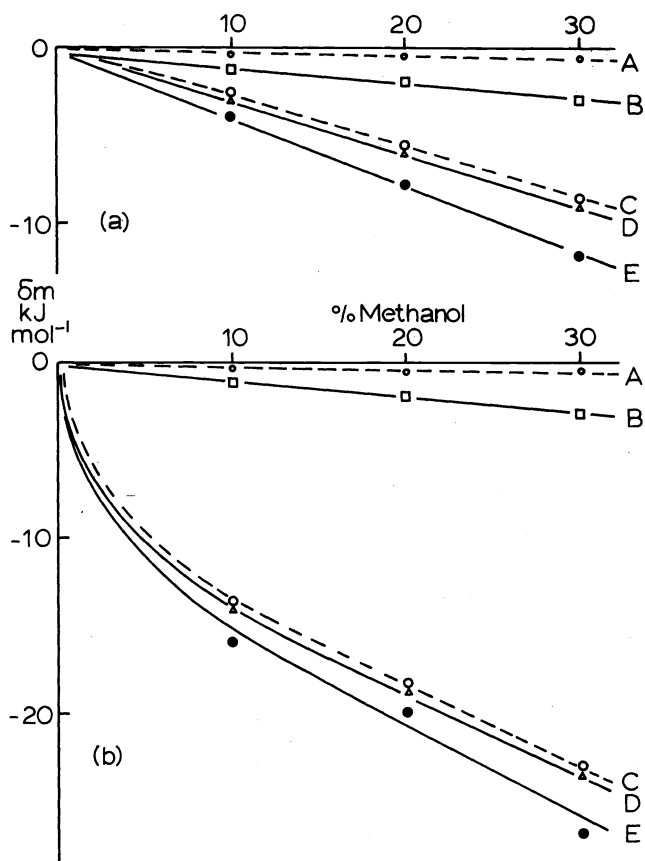


Fig. 3. Initial state and transition state effects in cyanide attack at $\text{Fe}(\text{bipy})_3^{2+}$ in aqueous methanol. Graph (a) uses Fe^{II} chemical potentials calculated by van Meter and Neumann (27); graph (b) uses Fe^{II} chemical potentials derived from $\text{Fe}(\text{bipy})_3(\text{BPh}_4)_2$ solubilities.

A = $\delta_{\text{m}\mu}^{\ominus}(\text{CN}^-)$; B = $\delta_{\text{m}}\Delta G^{\ddagger}$; C = $\delta_{\text{m}\mu}(\text{Fe}^{\text{II}})$; D = $\delta_{\text{m}\mu}^{\ominus}(\text{is})$; E = $\delta_{\text{m}\mu}^{\ddagger}$

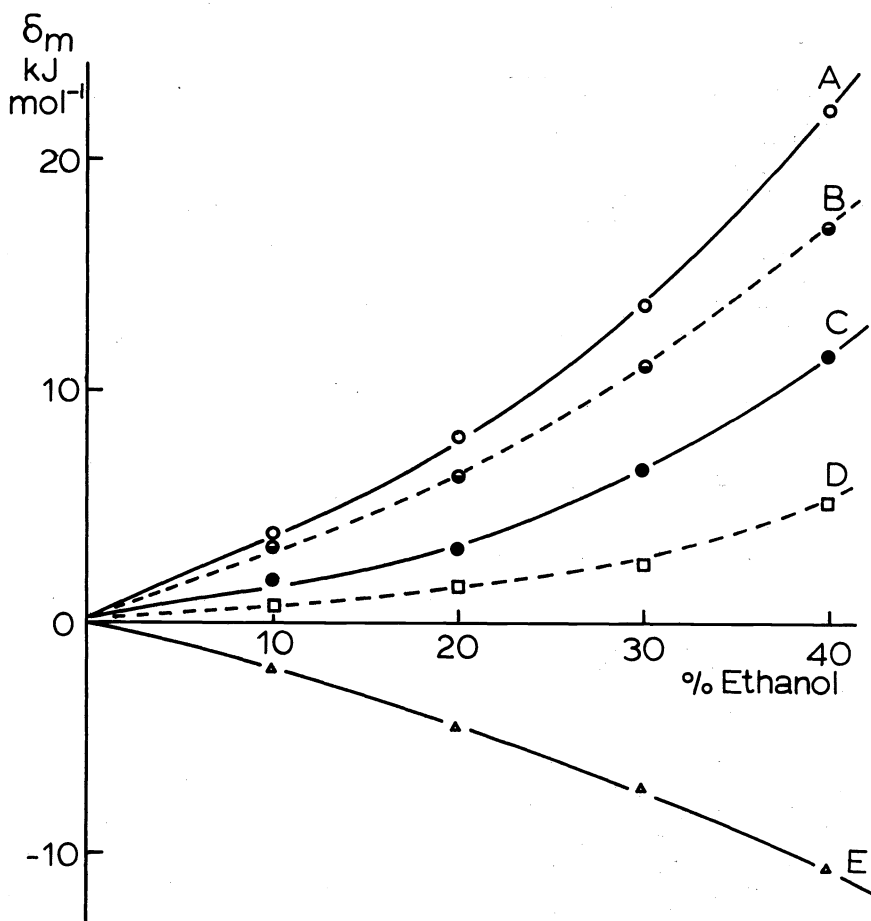


Fig. 4. Initial state and transition state effects in the mercury(II)-catalysed aquation of the ReCl_6^{2-} anion (in ethanol + water).

A = $\delta_{m\mu}^{\ominus}(\text{is})$; B = $\delta_{m\mu}^{\ominus}(\text{Hg-II})$; C = $\delta_{m\mu}^{\ddagger}$; D = $\delta_{m\mu}^{\ominus}(\text{Re-IV})$; E = $\delta_{m\mu}^{\ddagger}\Delta G^{\ddagger}$

Table 3. Summary of initial state/transition state dissections (ΔG unless otherwise stated)

t-BuCl solvolysis (ΔH)	is>ts	is, ts trends opposed	(21)
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ solvolysis (ΔV)	is>ts		(22)
Menschutkin $\text{Me}_3\text{N} + \text{MeI}$	is>>ts		(23)
$\text{Me}_3\text{N} + \text{pO}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$	is<ts		(23)
$\text{Et}_4\text{Sn} + \text{HgCl}_2$ (also ΔH)	is>ts	reactants and ts trends parallel	(24)
$\text{R}_4\text{Pb} + \text{I}_2$	is∇ts		(28)
$\text{Pt}(\text{bipy})\text{Cl}_2 + \text{tu}$	is>>ts	}reactants (and ts) trends parallel	(25)
$\text{Pt}(\text{4CNpy})_2\text{Cl}_2 + \text{tu}$	is>ts		(29)
$\text{Fe}(\text{bipy})_2^{2+} + \text{CN}^-$	is∇ts	bipy solvation dominates is and ts	(26)
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Hg}^{2+}$	is∇ts	} all reactant trends parallel:	
$\text{ReCl}_6^{2-} + \text{Hg}^{2+}$	is>ts		cf. charges is→ts
$\text{Fe}(\text{phen})_2^{2+} + \text{S}_2\text{O}_8^{2-}$	is>ts	reactant solvation trends opposed:	(30)
$\text{Fe}(\text{bipy})_2(\text{CN})_2 + \text{S}_2\text{O}_8^{2-}$	is<<ts	reactant solvation trends equal and opposite	(30)

for transition states. However it is possible in some cases to estimate such transfer parameters by the use of suitable models for the transition state. This has been attempted in, for example, t-butyl chloride solvolysis by the use of tetraalkylammonium chlorides as transition state models (21), and in solvolysis of, and hydroxide attack at, iron (II)-diimine complexes using naphthalene and naphthol (31).

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