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INITIAL STATE AND TRANSITION STATE SOLVATION IN INORGANIC REACTIONS

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CONTENTS

A. INTRODUCTION

In the context of the analysis of the effects of solvents on the rate constants of reactions in solution, a notable landmark is provided by the tables published by Ingold [1]. In broad outline, these showed how the rate constants for different types of nucleophilic substitution reactions would change when the solvent is changed. The analysis, outlined in Table 1, is noteworthy because it sets down the basic principles for the analysis of solvent effects. Thus one asks whether on changing the solvent, the reactants are stabilised or destabilised. The same question is posed with reference to the activated complex/transition state and so by difference it is possible to predict the overall effect on the height of the energy barrier and, by extension, the rate constant for reaction. This separation of solvent effects on rate constants (and, thence,

TABLE 1

Predicted and observed solvent effects on rates of nucleophilic substitutions[a]

Charge disposition (is → ts)	Effect of increased solvent polarity on rate							
	Predicted	Obs. rate const.[b] in EtOH + H_2O (vol. % H_2O)		0	20	40	60	100
$Y^- + RX \rightarrow \overset{\delta^-}{Y}\cdots R\cdots\overset{\delta^-}{X}$	Small decrease	$Pr^iBr + OH^-$	$10^5 k_{55}$	6.0	4.9	3.0		
$Y + RX \rightarrow \overset{\delta^+}{Y}\cdots R\cdots\overset{\delta^-}{X}$	Large increase	$Pr^iBr + H_2O$	$10^7 k_{55}$	1.73	23.6	66.7		
$Y^- + RX^+ \rightarrow \overset{\delta^-}{Y}\cdots R\cdots\overset{\delta^+}{X}$	Large decrease	$Me_3S^+ + OH^-$	$10^4 k_{100}$	7240	178	15.1		0.37
$Y + RX^+ \rightarrow \overset{\delta^+}{Y}\cdots R\cdots\overset{\delta^+}{X}$	Small decrease	$Me_3S^+ + NMe_3$	$10^5 k_{45}$	6.67				0.65
$RX \rightarrow \overset{\delta^+}{R}\cdots\overset{\delta^-}{X}$	Large increase	Bu^tCl	$10^6 k_{25}$		9.14	126	1294	
$RX^+ \rightarrow \overset{\delta^+}{R}\cdots\overset{\delta^+}{X}$	Small decrease	$Bu^tMe_2S^+$	$10^5 k_{50}$	1.90	1.24			0.60

[a] Based on Tables 25-2 and 25-3 of C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N.Y., 1953, pp. 347 and 349. [b] Subscripts indicate temperature in °C.

to derived parameters such as enthalpies and volumes of activation) is the theme of this review.

Some time ago, Parker [2] in a detailed review of solvent effects on initial and transition states in organic reactions made passing reference to solvent effects on substitution reactions involving platinum complexes. In the intervening years considerable effort has been made to extend the analysis to other inorganic reactions, particularly those involving inorganic complexes. These new developments are the subject matter of this review.

The analysis of solvent effects on rates of reaction is conveniently made using the formalism of transition state theory [3] whereby the rate constant for a particular reaction in a given solvent at fixed temperature and pressure is related to $\Delta G^{\ddagger}$, the activation Gibbs function. Some indication of the complexities which can emerge in the analysis of solvent effects on $\Delta G^{\ddagger}$ is shown in Fig. 1 where we summarise what might happen to $\Delta G^{\ddagger}$ for a hypothetical reaction, initial state → transition state. In Fig. 1a, the centre vertical line represents the activation process (in terms of $\Delta G^{\ddagger}$) for reaction in a reference solvent. The diagram shows how on going to a second solvent an increase in rate constant (i.e. a decrease in $\Delta G^{\ddagger}$ at fixed temperature and pressure) can stem from either (i) a destabilisation of both states with the initial state being stabilised to a larger extent, or (ii) a stabilisation of both states with the transition state being stabilised to a larger extent. In Fig. 1b we show two cases where on changing the solvent, initial and transition states are affected differently leading to either (i) an increase, or (ii) a decrease in $\Delta G^{\ddagger}$. The trends illustrated in Fig. 1 do not, of course, exhaust all the possibilities which can arise. Indeed if the reaction involves two reactants (e.g. A + B → reactants) then the solutes A and B may be affected differently on going to a new solvent, e.g. one stabilised, the other destabilised. However, it is clear that an understanding of the factors which control the dependence of kinetic parameters on solvent requires an identification of the direction and magnitude of the changes in the properties of initial and transition states. Indeed, such an analysis is a prerequisite to an analysis of the role of solvent structure in kinetics of reactions. However it also follows that measurements of rate constants (and hence $\Delta G^{\ddagger}$) as a function of solvent cannot yield detailed information concerning the underlying trends in initial and transition states stabilities. In other words information from other non-kinetic measurements is required. Nevertheless where this additional evidence is unavailable, other approaches to the analysis of solvent effects on kinetics are extremely valuable. In this context, we merely draw attention to correlations involving solvent Y values [4] and, for reactions in aqueous mixtures, the thermodynamic properties of the mixtures. For example, we have probed possible correlations between $\Delta G^{\ddagger}$ and the excess molar Gibbs function of mixing for the binary aqueous solvent system [5].

In this review we shall survey the results of the analysis of kinetic parameters for reactions of inorganic complexes in terms of initial and transition state quantities. We review briefly the background theory for this analysis and

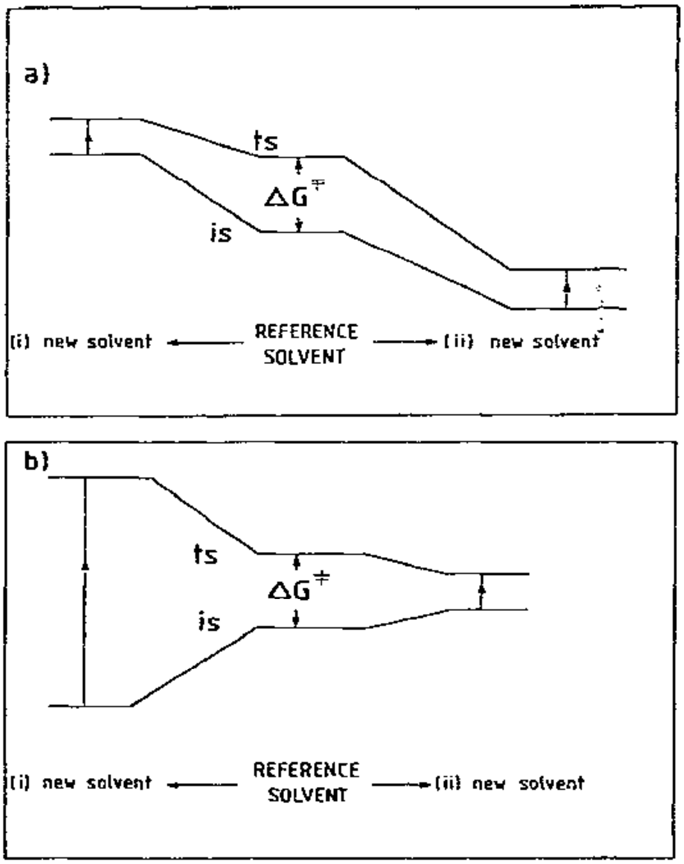


Fig. 1. Formalised representation of the effect of changing the solvent on the activation Gibbs function, $\Delta G^{\ddagger}$, and the initial and transition states; (a) $\Delta G^{\ddagger}$ decreases as a result of (i) destabilisation and (ii) stabilisation of both states; (b) $\Delta G^{\ddagger}$ (i) increases and (ii) decreases as a result of differing effects of solvent on initial and transition states.

indicate how the necessary experimental information is obtained. In particular we consider a variety of reaction types and attempt to draw some pattern from the trends which emerge. Initially we examine reactions involving neutral molecules and then turn our attention to reactions involving ions. Here the analysis is less straightforward because we are forced to make one or more extra thermodynamic assumptions in order to obtain the dependence on solvent of single-ion quantities.

The historical background to this subject can be found in the literature relevant to physical-organic chemistry [1,2]. In addition the importance of initial state solvation in determining activation parameters has been emphasised by Moelwyn-Hughes and Glew [6] and, more recently, by Robertson [7]. The analyses of rate data by Winstein and Fainberg [8], of enthalpies of activation by Arnett et al. [9] and of volumes of activation by Dickson and Hyne [10] are noteworthy, and in view of their importance to this subject we comment briefly on them below.

B. PRINCIPLES OF THE ANALYSIS

The type of analysis described here requires that the essential features of the reaction mechanism are well established. If this is not the case, quite misleading conclusions will be drawn. However we do not discuss at great length reaction mechanisms in this review, simply pointing out some important details. We must also assume that the kinetic data have been analysed correctly to yield the rate constants and related parameters for each reaction.

We start by assuming that the reaction involves a single step of the type shown in eqn. (1) where A and B are reactants and $(AB)^{\ddagger}$ is the transition state.

$$A + B \rightarrow (AB)^{\ddagger} \rightarrow \text{product} \qquad (1)$$

For reactions in solution, the solvent plays a key role in determining the energetics of activation. However it is not always obvious how this role can be formulated; it is very rarely incorporated into stoichiometric equations for reactions. One approach is to use the concept of solvent co-spheres along the lines suggested by Gurney [11]. Thus each solute (i.e. reactants A and B, and transition state $(AB)^{\ddagger}$ in eqn. (1)) is surrounded by an imaginary sphere which encloses solvent molecules whose organisation depends on the nature of the solute [12]. Implicit therefore in eqn. (1) is the associated co-sphere contribution to the reaction. At fixed temperature and pressure the second order rate constant (e.g. expressed in $dm^3\ mol^{-1}\ s^{-1}$) is used to obtain the activation Gibbs function, $\Delta G^{\ddagger}$. If the solvent is a binary mixture where the mole fraction of one component is x_2, then in this solvent $\Delta G^{\ddagger}(x_2)$ is given by eqn. (2)

$$\Delta G^{\ddagger}(x_2) = \mu^{\ddagger} - (\mu^{\ominus}(A) + \mu^{\ominus}(B)) \qquad (2)$$

Here $\mu^{\ominus}(A)$ and $\mu^{\ominus}(B)$ are the standard chemical potentials of the reactants A and B, and $\mu^{\ddagger}$ is the chemical potential of the transition state. Thus $\Delta G^{\ddagger}(x_2)$ is given by the difference between the chemical potentials of transition and initial states in their respective solution standard states. If the rate constant is expressed in $dm^3\ mol^{-1}\ s^{-1}$, the relevant standard state is the hypothetical solution where the concentration is 1.0 mol dm^{-3} and the corresponding activity coefficient is unity. For a first order reaction (e.g. $A \rightarrow A^{\ddagger} \rightarrow$ products), then $\Delta G^{\ddagger}(x_2)$ is given by eqn. (3)

$$\Delta G^{\ddagger}(x_2) = \mu^{\ddagger} - \mu^{\ominus}(A) \qquad (3)$$

The Gibbs function is however just one of a hierachy of thermodynamic variables and so, for example, eqn. (2) can be generalised as shown in eqn. (4)

$$\Delta X^{\ddagger}(x_2) = X^{\ddagger} - (X^{\ominus}(A) + X^{\ominus}(B)) \qquad (4)$$

Here X may represent G, H (enthalpy), S (entropy), V (volume), Cp (heat capacity) ..., these being derived from the appropriate dependence of rate constant on temperature and pressure [3,10]. In this review we concentrate most of our attention on factors influencing the magnitude of $\Delta G^{\ddagger}$, since the majority of currently available data pertaining to reaction of inorganic complexes involve the Gibbs function G (e.g. rate constants, solubilities). The dependence of rate constant on the composition of a binary solvent mixture leads to the corresponding dependence of $\Delta G^{\ddagger}(x_2)$ on x_2. The problems in this subject stem from the observation that there is no obvious correlation between this dependence and the corresponding solvent dependence of $\mu^{\ddagger}$, $\mu^{\ominus}(\mathrm{A})$ and $\mu^{\ominus}(\mathrm{B})$.

To avoid any confusion which might arise on using the symbol Δ to indicate changes consequent both on chemical reaction and on medium effects, it is convenient to use a solvent operator δ_{m} for the latter [13]. For a thermodynamic variable X this is defined by eqn. (5). The reference solvent is generally, especially for an inorganic chemist, water, i.e. the solvent or medium where $x_2 = 0$. The variable X may be, for example, the chemical potential of a solute. Then the difference in chemical potential on transferring the solute from the reference solvent to the medium M will be $\delta_{\mathrm{m}}\mu^{\ominus}(\text{solute})$, equivalent to $\Delta G_{\mathrm{tr}}(\text{solute})$ in the alternative terminology of some other authors. Kinetic data lead, according to transition state theory, to Gibbs free energies of activation $\Delta G^{\ddagger}$; the change in rate constant on going from water to a medium of mole fraction x_2, $\delta_{\mathrm{m}}\Delta G^{\ddagger}$, will be equal to $\Delta G^{\ddagger}(x_2)$ minus $\Delta G^{\ddagger}(x_2 = 0)$.

$$\delta_{\mathrm{m}}X = X_{\text{medium M}} - X_{\text{reference solvent}} \tag{5}$$

Equations (2) and (3) can be rewritten using the medium operator in conjunction with the chemical potentials.

$$\text{1st order:}\quad \delta_{\mathrm{m}}\Delta G^{\ddagger} = \delta_{\mathrm{m}}\mu^{\ddagger} - \delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{A}) \tag{6}$$

$$\text{2nd order:}\quad \delta_{\mathrm{m}}\Delta G^{\ddagger} = \delta_{\mathrm{m}}\mu^{\ddagger} - \{\delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{A}) + \delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{B})\} \tag{7}$$

Thus kinetics yield the double difference quantity, $\delta_{\mathrm{m}}\Delta G^{\ddagger}$. If the rate constant increases on going from pure solvent (i.e. $x_2 = 0$) to a mixture (i.e. $x_2 > 0$), then $\delta_{\mathrm{m}}\Delta G^{\ddagger} < 0$, but if the rate constant decreases, $\delta_{\mathrm{m}}\Delta G^{\ddagger} > 0$. Similarly if a solute (i.e. initial or transition state) is stabilised, $\delta_{\mathrm{m}}\mu^{\ominus} < 0$, but if it is destabilised $\delta_{\mathrm{m}}\mu^{\ominus} > 0$.

It follows from eqns. (6) and (7), that if we can obtain independently a value for one quantity on the right hand side of eqn. (6), or for two quantities on the right hand side of eqn. (7), a complete picture of the solvent effect on the rate constant will emerge. It is possible to glean such information from a variety of sources. If, for example, one of the reactants (e.g. A in eqn. (1)) is involatile, $\delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{A})$ can be obtained from the dependence of the solubility of the pure solid on solvent. If reactant A is volatile, then $\delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{A})$ can again be obtained from solubility measurements [14]. In both cases, the required quantity is given by eqn. (8), where we have made the usually reasonable assumption that the ratio of activity coefficients, $y(\mathrm{A}, x_2 = 0)/y(\mathrm{A}, x_2)$ is unity.

$$\delta_{\mathrm{m}}\mu^{\ominus}(\mathrm{A}) = RT \ln\{S(\mathrm{A}, x_2 = 0)/S(\mathrm{A}, x_2)\} \tag{8}$$

Thermodynamic transfer functions for solutes in aqueous mixtures can also be calculated from vapour pressures [15].

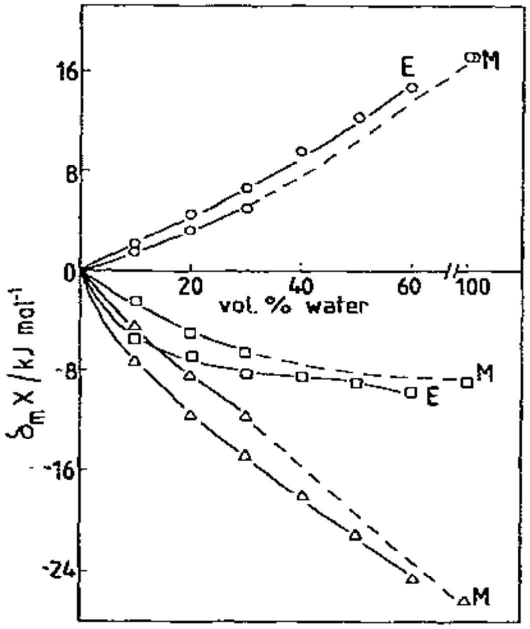
The ephemeral nature of the transition state means that $\delta_m\mu^{\ddagger}$ cannot be directly obtained although some indication of its value can be obtained from other sources. For example it is often possible to measure the transfer parameters for a solute whose solvation characteristics resemble those of some postulated transition state. However if both $\delta_m\Delta G^{\ddagger}$ and $\delta_m\mu^{\ominus}(\mathrm{A})$ are known for some first order reaction, we can calculate $\delta_m\mu^{\ddagger}$ directly from eqn. (6). If the experiments are repeated over a range of x_2-values, a plot can be constructed showing the dependence of the three quantities, $\delta_m\Delta G^{\ddagger}$, $\delta_m\mu^{\ddagger}$ and $\delta_m\mu^{\ominus}(\mathrm{A})$ on x_2. Where the reaction is second order (cf. eqn. (2)) we have found it helpful to plot, in addition to $\delta_m\Delta G^{\ddagger}$, $\delta_m\mu^{\ddagger}$, $\delta_m\mu^{\ominus}(\mathrm{A})$ and $\delta_m\mu^{\ominus}(\mathrm{B})$, the quantity $\delta_m\mu^{\ominus}$ (reactants), ($= \delta_m\mu^{\ominus}(\mathrm{A}) + \delta_m\mu^{\ominus}(\mathrm{B})$), against x_2. These plots show at a glance the essential features of the pattern for the solvent effects on the kinetics of reaction. If the solvent effects on the initial states are the dominant factor, the curves for $\delta_m\Delta G^{\ddagger}$ and $\delta_m\mu^{\ominus}$ (reactants) are mirror images across the composition axis. If, however, the solvent effects on the transition state are dominant, the curves for $\delta_m\mu^{\ddagger}$ and $\delta_m\Delta G^{\ddagger}$ will be close together.

The actual values of the thermodynamic parameters depend on the definition of the solution standard states. Some authors use the mole fraction scale, others the molal scale and others the molar scale. In this review, we use the molar scale. Indeed Ben-Naim has enumerated the advantages of using this scale when discussing transfer parameters for solutes [16]. Fortunately the interconversion between scales is a task involving simple arithmetic [17]. This is not to underplay the importance of defining the standard states.

C. REACTIONS INVOLVING NEUTRAL REACTANTS

Formally at least, the analysis of solvent effects on simple first order unimolecular reactions involving neutral reactants poses the least number of problems (e.g. eqn. (6)). One of the first systems to be extensively studied [8] was the solvolysis of tert-butyl chloride in alcohol and water mixtures.

When water is added to a solution of tert-butyl chloride in either methyl or ethyl alcohol, the rate constant increases (i.e. $\Delta G^{\ddagger}$ decreases). The solubilities of tert-butyl chloride in the mixtures yield (cf. eqn. (8)) the quantity $\delta_m\mu^{\ominus}(\text{t-BuCl})$. Combining this latter quantity with $\delta_m\Delta G^{\ddagger}$, we can calculate $\delta_m\mu^{\ddagger}$ and plot the data as shown in Fig. 2, where the reference solvent is the pure alcohol. For both methyl and ethyl alcohol, $\delta_m\Delta G^{\ddagger}$ decreases as the mole fraction of water in the mixture increases. In addition, both $\delta_m\mu^{\ddagger}$ and $\delta_m\mu^{\ominus}$(tert-butyl chloride) change gradually but in opposite directions. Thus the transition state is stabilised by adding water, contributing to a decrease in $\Delta G^{\ddagger}$. However the initial state is dramatically destabilised and, as more water is added, the effect of solvent on the initial state becomes the dominant feature. Indeed on going from methyl alcohol to water, the magnitude of $\delta_m\mu^{\ominus}$-



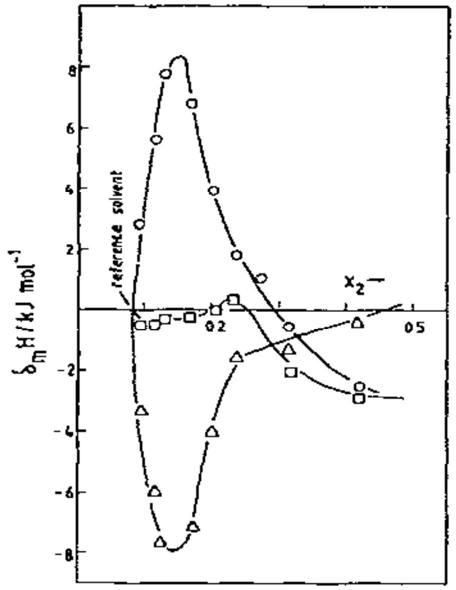


Fig. 2. Solvolysis of tert-butyl chloride in methyl alcohol (M) and ethyl alcohol (E). Effect of added water on the activation Gibbs function, $\delta_m\Delta G^{\ddagger}$, (△), and chemical potentials of initial, $\delta_m\mu^{\ominus}$ (○) and transition state, $\delta_m\mu^{\ddagger}$ (□).

Fig. 3. Solvolysis of tert-butyl chloride in water. Effect of added ethyl alcohol on the enthalpy of activation, $\delta_m\Delta H^{\ddagger}$ (△) and the partial molar enthalpies of initial, $\delta_m H^{\ominus}$(○) and transition states, $\delta_m H^{\ddagger}$ (□). The reference solvent is a mixture where $x_2 = 0.071$; component 2 = ethyl alcohol.

(t-BuCl) is nearly twice that for $\delta_m\mu^{\ddagger}$ [8].

The potential importance of trends in initial state quantities for solutions in water-rich mixtures is confirmed by the enthalpy data for the above solvolytic reaction. Combination of enthalpies of solution for tert-butyl chloride in water + ethyl alcohol mixtures with enthalpies of activation [9] shows that the extremum in $\delta_m\Delta H^{\ddagger}$ (Fig. 3) mirrors the extremum in $\delta_m H^{\ominus}$(t-BuCl), $\delta_m\Delta H^{\ddagger}$ being almost independent of composition. In a similar fashion analysis of volumetric properties for the solvolysis of benzyl chloride in water and either ethyl alcohol [18] or tert-butyl alcohol [10] shows that the extremum in $\delta_m\Delta V^{\ddagger}$ is to a large extent determined by the trend in $\delta_m V^{\ominus}$ (benzyl chloride) [19] (Fig. 4).

These three well documented examples (Figs. 2—4) indicate the general form of the analysis to be examined in this review. These examples are relatively clear cut although there is one interesting practical feature. The chemical reactions proceed at a moderate rate and so the kinetic data can be conveniently obtained, and $\delta_m\Delta G^{\ddagger}$ calculated accordingly. However special techniques must be used to obtain the thermodynamic properties of the ini-

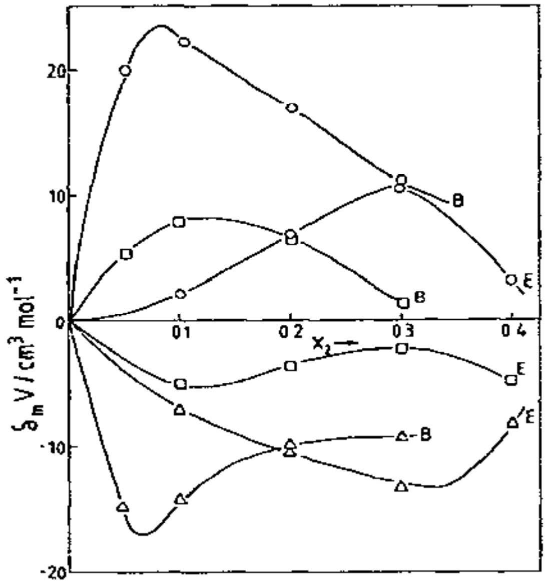


Fig. 4. Solvolysis of benzyl chloride in water; effect of adding either ethyl alcohol (E) or tert-butyl alcohol (B) on the volume of activation, $\delta_m \Delta V^{\ddagger}$, (△) and partial molar volumes of initial, $\delta_m V^{\ominus}$, (○) and transition, $\delta_m V^{\ddagger}$, (□) states.

tial state. Thus it was necessary to measure the enthalpies of solution for tert-butyl chloride almost instantaneously before significant chemical reaction occurred [9]. Comparable problems are not encountered when the reaction is second order-bimolecular (cf. eqn. (7)) because the properties of each solute in solution can be examined in the absence of the other reactants. The importance of changes in the chemical potential of the initial state is also evident in the bimolecular reaction (eqn. (9)) of the square-planar complex 2,2′-bipyridyldichloroplatinum(II), [Pt(bipy)Cl$_2$] with thiourea (tu), in dioxan and water and tetrahydrofuran (THF) and water mixtures [20].

$$[\mathrm{Pt(bipy)Cl_2}] + \mathrm{tu} \rightarrow [\mathrm{Pt(bipy)Cl(tu)}]^+ + \mathrm{Cl^-} \qquad (9)$$

The quantity $\delta_m\mu^{\ominus}$(Pt(bipy)Cl$_2$) was determined from solubility data although the low solubility in water means that the reference solvent is a mixture where e.g. $x_{\mathrm{diox}} = 0.05$. In addition $\delta_m\mu^{\ominus}$(tu) was calculated from either the effect of thiourea on the vapour pressure of THF—water mixtures [21] or solubility data [20]. With increase in mole fraction of co-solvent, the platinum complex and thiourea are stabilised, resulting in an increase in $\Delta G^{\ddagger}$. By comparison the effect of added solvent on the transition state (i.e. $\delta_m\mu^{\ddagger}$) is small (Fig. 5). The stabilisation of the platinum complex by added co-solvent is not unexpected if the hydration characteristics are dominated by the large and hydrophobic bipyridyl ring systems. The solubilities of apolar solutes in water are generally small and increase when an organic co-solvent is added [22]. It was therefore interesting to examine the impact of introducing a polar substi-

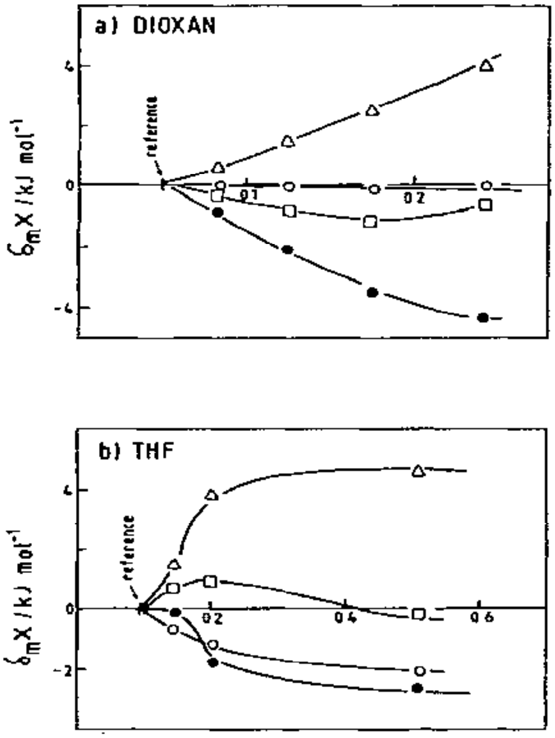


Fig. 5. Reaction of thiourea and 2,2'-bipyridyldichloroplatinum(II) in water; effect of added (a) dioxan and (b) tetrahydrofuran on $\delta_m\Delta G^\ddagger$, (△) and on the chemical potentials of thiourea, $\delta_m\mu^\ominus$(tu) (○), platinum complex, $\delta_m\mu^\ominus$(complex), (●) and transition state $\delta_m\mu^\ddagger$ (□).

tuent in the hydrophobic ring systems. The immediate effect is to increase the solubility of the platinum(II) complex and to make possible the use of water as a reference solvent. A marked decrease in the importance of the solvent dependence of the initial state is now observed [23]. Comparison of the data in Fig. 5 [20] and Fig. 6 [23] shows that the initial state for the reaction of *cis*-[Pt(4CN-py)$_2$Cl$_2$] with thiourea is considerably more sensitive to solvent than in the case of the reaction of [Pt(bipy)Cl$_2$] with thiourea. The possibility of direct solvent-ligand interaction has apparently rendered the former platinum(II) complex more sensitive to its environment.

An example of the importance of the solvent dependence of the partial molar enthalpies of initial states is found in the reaction between tetraethyltin and mercury(II) chloride [24]. Combination of enthalpies of solution and activation enthalpies leads to the pattern shown in Fig. 7 for this reaction, eqn. (10).

$$Et_4Sn + HgCl_2 \rightarrow EtHgCl + Et_3SnCl \tag{10}$$

The reference solvent is methyl alcohol and, on adding water, the enthalpy of

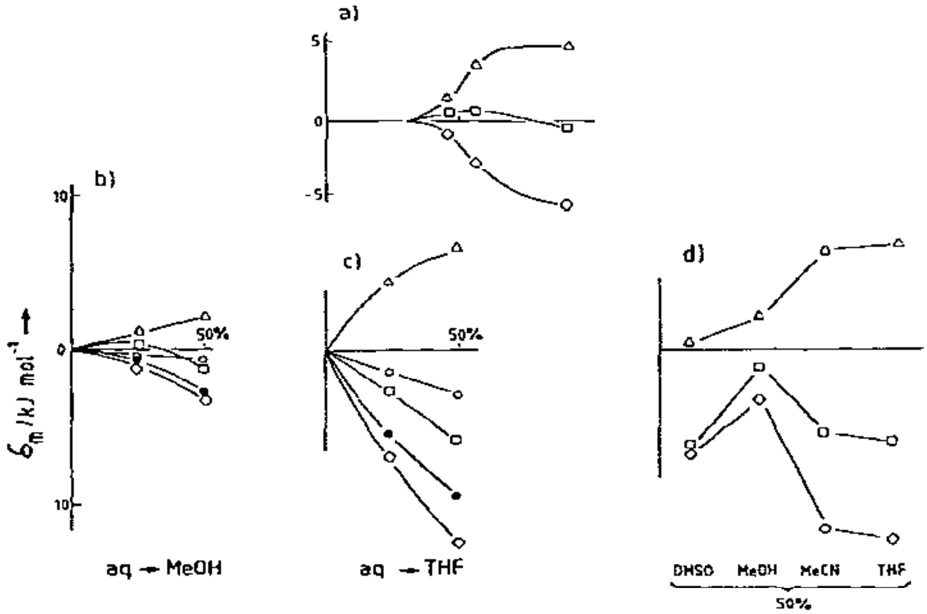


Fig. 6. Comparison of initial state and transition state solvation effects in the reactions of *cis*-[Pt(4CN-py)$_2$Cl$_2$] ((b), (c), and (d)) and of [Pt(bipy)Cl$_2$] (a) with thiourea, at 298 K; effect of added tetrahydrofuran ((a) and (c)), added methanol (b), and various organic co-solvents (d) on $\delta_m\Delta G^{\ddagger}$ (△) and on the chemical potentials of thiourea, $\delta_m\mu^{\ominus}$(tu) (○), of the platinum complexes, $\delta_m\mu^{\ominus}$(complex) (●), of the total initial state (◇), and of the transition state (□).

activation drops quite rapidly because the enthalpies of the reactants move strongly endothermic. This trend continues as more water is added but when $x(H_2O) > 0.2$, the enthalpy of the transition state dramatically increases with the overall result that $\Delta H^{\ddagger}$ becomes less sensitive to changes in $x(H_2O)$. Abraham has analysed in a similar fashion the kinetic and thermodynamic data for Menschutkin reactions [25], for the iododemetallation of tetra-alkyl leads [26] and for reaction (10) in terms of $\delta_m\Delta G^{\ddagger}$ and $\delta_m\mu^{\ominus}$ quantities [27]. In these examples where transfer functions were calculated for reaction in a range of pure solvent systems, the overall pattern is complex. The dominant effect for the Menschutkin reaction of p-nitrobenzyl chloride with trimethylamine in non-aqueous media is assigned to the dependence on solvent of the chemical potential of the transition state, but for the reaction of methyl iodide with trimethylamine in aqueous media, initial state effects dominate [25].

There is a paucity of data in the literature concerning the complete analysis of solvent effects on reactions involving neutral inorganic solutes. This state of affairs arises quite simply because the number of neutral inorganic species is relatively small. The majority of inorganic complexes are charged and many important nucleophiles too are charged. Consequently any general treatment

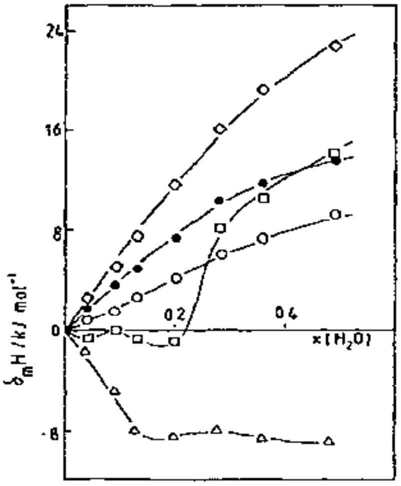


Fig. 7. Reaction between tetraethyltin and mercury(II) chloride in methyl alcohol at 298 K; effect of added water on the enthalpy of activation, $\delta_m \Delta H^{\ddagger}$, (△), and the partial molar enthalpies of tetraethyltin, $\delta_m H^{\ominus}(\mathrm{Et_4Sn})$, (○), mercury(II) chloride, $\delta_m H^{\ominus}(\mathrm{HgCl_2})$, (●) and the transition state, $\delta_m H^{\ddagger}$, (□). Also shown (◇) is the dependence on solvent composition of the sum $\delta_m H^{\ominus}(\mathrm{HgCl_2}) + \delta_m H^{\ominus}(\mathrm{Et_4Sn})$.

of inorganic reactions demands a treatment of reactions involving ions. Moreover the interaction energies involving charged particles are larger than those for neutral/dipolar species, and so we anticipate that ionic solvation energies may be more affected by changes in solvent composition than solvation energies for neutral solutes. Thus solvent effects on initial states, transition states, and their differences (viz. rate constants) may be more marked. Our next step must therefore be to deal with reactions involving charged species. However this step involves the introduction of a large stumbling block, namely the estimation of transfer properties for ions [22,28]. Such estimation involves assumptions and uncertainties, and at the moment there is still argument and controversy over methods used in calculating single ion solvation parameters. We shall therefore deal briefly with this problem before using single ion values in the subsequent discussion of solvent effects on initial and transition states of reactions involving ionic reactants.

D. SINGLE ION PROPERTIES

Consider a reaction involving an ion and a neutral molecule (eqn. (11)) in a given solvent at fixed temperature and pressure.

$$\mathrm{X^- + Y \rightarrow (XY^-)^{\ddagger} \rightarrow products} \tag{11}$$

The dependence of $\Delta G^{\ddagger}$ on solvent is expressed using eqn. (12)

$$\delta_m \Delta G^{\ddagger} = \delta_m \mu^{\ddagger} - \{\delta_m \mu^{\ominus}(\mathrm{X^-}) + \delta_m \mu^{\ominus}(\mathrm{Y})\} \tag{12}$$

Here $\delta_m\mu^\ominus(X^-)$ expresses the solvent dependence of the single ion chemical potential for X^-. Unfortunately this single ion transfer function has no practical meaning because one cannot transfer one mole of ions from one solvent to another without at the same time transferring ions of opposite charge, thus preserving the electric neutrality of the system. The experimental quantity is the transfer parameter for the salt, $\delta_m\mu^\ominus(MX)$. This can be determined in a number of ways. Possibly the most precise method uses the appropriate electrochemical cell where $\delta_m\mu^\ominus(MX)$ is determined from the dependence of standard e.m.f. on solvent. A variety of electrochemical techniques have been used including amalgam cells [29] and cation sensitive glass electrodes [30], as well as the more conventional hydrogen/silver halide electrode systems (e.g. ref. 31). Alternatively, $\delta_m\mu^\ominus(MX)$ may be calculated from solubility data (e.g. ref. 32) or from the effect of salt on the vapour pressure of a mixture (e.g. ref. 33). In the next stage $\delta_m\mu^\ominus(\text{salt})$ is expressed as the sum of the transfer parameters for cation and anion, e.g. eqn. (13) for a 1 : 1 salt.

$$\delta_m\mu^\ominus(MX) = \delta_m\mu^\ominus(M^+) + \delta_m\mu^\ominus(X^-) \qquad (13)$$

If only one absolute ionic transfer function were known, the values for all other ions could be calculated. This is not the case. Consequently a variety of methods for estimating single ion solvation and single ion thermodynamic transfer parameters have been proposed and used [34]. These methods generally fall into one of two categories alternately based either on the analysis of electrical interactions between ion and solvent (i.e. $\delta_m\mu^\ominus(\text{ion}) = f(\Delta\epsilon_r)$, where ϵ_r is the relative permittivity of the solvent) or on the idea that sufficiently large ions are lightly enough solvated for an anion and cation of similar size and similar exterior to have equal transfer parameters (i.e. $\delta_m\mu^\ominus(M^+) = \delta_m\mu^\ominus(X^-) = \frac{1}{2}\,\delta_m\mu^\ominus(MX)$). In describing the electrical interactions between an ion and solvent some modification of the Born model can be used. Thus Wells has used this model in part of his analysis [35] to calculate single ion transfer parameters for simple cations and for anions into binary aqueous mixtures, with data available for such co-solvents as methyl alcohol [35,36], acetone [36], ethylene glycol [37], glycerol [36], and tert-butyl alcohol [38]. De Ligny and co-workers have analysed ion—solvent interactions taking account of quadrupole interactions and derived ion transfer parameters from water to mixed solvents and to non-aqueous solvents, e.g. ref. 39. At present the most commonly used 'large ion' assumption is with respect to the pair of ions, tetraphenylarsonium, Ph_4As^+, and tetraphenylboronate, BPh_4^-, [40] i.e. $\delta_m\mu^\ominus(Ph_4As^+) = \delta_m\mu^\ominus(BPh_4^-)$. Ion transfer parameters have been calculated for a large number of ions from water to a variety of non-aqueous solvents [41]. Recently this assumption has been used to calculate these parameters for binary aqueous mixtures containing either acetonitrile or dimethylsulphoxide [42]. Similar, though less widely used, versions of this approach include the assumption that $\delta_m\mu^\ominus(Am^i_3Bu^nN^+) = \delta_m\mu^\ominus(BPh_4^-)$ for transfer of ions to ethyl alcohol and water mixtures [43]. Abraham's convention [44] that $\delta_m\mu^\ominus(Me_4N^+) = \delta_m H^\ominus(Me_4N^+) = \delta_m S^\ominus(Me_4N^+) = 0$ is closely related to this approach. There are also redox-linked assumptions based for example on the ferrocene—ferrocinium cation [2,45] and on the bisbiphenylchromium couples [46].

Unfortunately, where results for a given ion—solvent system are available from more than one of the analytical approaches, agreement is often rather (and, occasionally, wildly) unsatisfactory. Also at times the variation of chemical potential with solvent composition for an ion is at odds with expectation from other sources, for example the increasingly negative $\mu^{\ominus}(K^+)$ on going from water to aqueous acetone and to pure acetone is astonishing in the light of NMR and other evidence on the relative cation solvating powers of acetone and water [47]. The initial state—transition state analyses of inorganic ionic reactions will improve as estimates of single ion values improve. Meanwhile we will review selected systems, bearing in mind the uncertainties in the ion transfer parameter used and, where possible, using transfer parameters with compatible backgrounds for reactants in a given system.

E. SUBSTITUTION REACTIONS

(i) Aquation of chloro-cobalt(III) complexes

The transfer parameters, $\delta_m\mu^{\ominus}$, for the initial state and for a model dissociative transition state for the aquation of the *cis*[Co(en)$_2$Cl$_2$]$^+$ cation have been estimated [48a], Table 2, for a limited number of systems. The presentation of these results in diagrammatic form (Fig. 8) shows how closely the transition state transfer parameters parallel the initial state parameters. It is also interesting to observe (Fig. 8) how closely both of these parameters follow the transfer property for the leaving group, $\delta_m\mu^{\ominus}(Cl^-)$. Thus it seems that this anion, bound, leaving, or free, plays a dominant role in aquation here, a conclusion also reached from considerations of the temperature variation of the activation enthalpies for aquation of closely related complexes [48b].

More recently Wells has examined the aquation reactions of a range of halo-cobalt(III) complexes from a slightly different standpoint [49]. It is assumed that in the transition state there is considerable charge separation in and extension of the M—X bond, where X = halogen. Wells therefore sets

TABLE 2

Values of $\delta_m\mu^{\ominus}$(*cis*-Co(en)$_2$Cl$_2^+$) and of $\delta_m\mu^{\ddagger}$, i.e. of the transition state, for dissociative aquation of *cis*-Co(en)$_2$Cl$_2^+$, from water into various non-aqueous solvents, at 298 K

Solvent	$\delta_m\mu^{\ominus}$(*cis*-Co(en)$_2$Cl$_2^+$) (kJ mol^{-1})	$\delta_m\mu^{\ddagger}$ (kJ mol^{-1})
Methanol	+12.5	+19.3
TMS	−8.8	+15.9
DMF	−14.8	−9.1
DMSO	−19.9	−9.7

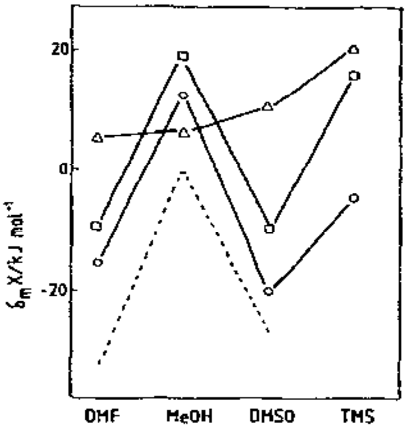
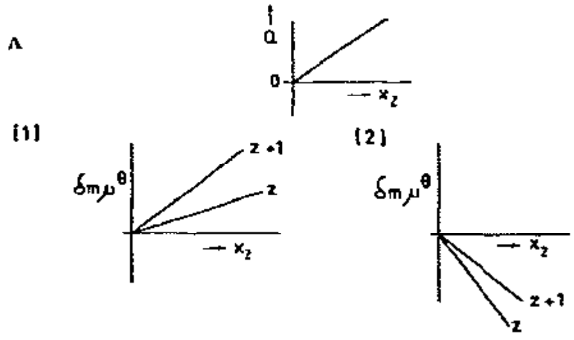


Fig. 8. Solvolysis of *cis*[Co(en)$_2$Cl$_2$]$^+$; effect on activation Gibbs function, $\delta_m\Delta G^{\ddagger}$ (△) and chemical potentials of initial $\delta_m\mu^{\ominus}$(complex) (○) and transition states $\delta_m\mu^{\ddagger}$ (□) of transfer from water to solutions in four non-aqueous solvents. For comparison, the dotted line indicates the dependence of $\delta_m\mu^{\ominus}(\mathrm{Cl}^-)$.

$\delta_m\mu^{\ddagger}(M^{z+1}\cdots X^-) = \delta_m\mu^{\ddagger}(M^{z+1}) + \delta_m\mu^{\ominus}(X^-)$ where z is the charge on the initial state complex. Therefore it is possible to write eqn. (14) which summarises the effect of solvent on initial and transition states and on the measured quantity $\delta_m\Delta G^{\ddagger}$.

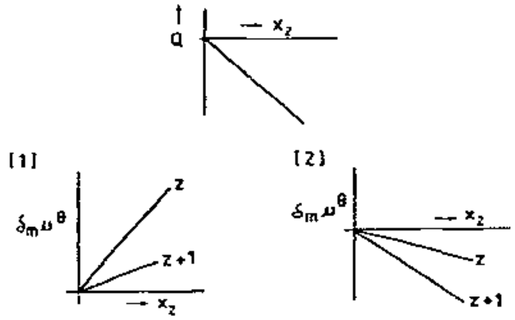
$$\delta_m\Delta G^{\ddagger} - \delta_m\mu^{\ominus}(X^-) = \delta_m\mu^{\ddagger}(M^{z+1}) - \delta_m\mu^{\ominus}(M^z) \quad (14)$$

Wells uses the kinetic data and his previously estimated single ion values for $\delta_m\mu^{\ominus}(X^-)$, thereby calculating the dependence of the left hand side of eqn. (14) on mole fraction of added co-solvent in binary aqueous mixtures. If we designate this calculated quantity as $Q(= \delta_m\Delta G^{\ddagger} - \delta_m\mu^{\ominus}(X^-))$ then we can consider, as shown in the scheme below, two different types of behaviour. In scheme A, Q increases with increase in x_2, and so, according to eqn. (14), $\delta_m\mu^{\ddagger}(M^{z+1}) > \delta_m\mu^{\ominus}(M^z)$. We show in the scheme how this can arise in at least



two ways. In A1, the transition state (i.e. curve $Z + 1$) is destabilised to a greater extent than the initial state (i.e. curve Z) as the mole fraction of co-solvent increases. In contrast the same trend in Q may arise if as shown in A2 the initial state is stabilised more than the transition state. On the other hand Q may decrease; this behaviour may be attributed to at least two different underlying trends even though, according to eqn. (14), $\delta_m\mu^{\ominus}(M^z)$ is now larger than $\delta_m\mu^{\ominus}(M^{z+1})$. Thus the initial state may be destabilised more than the transition state (i.e. B1 in the scheme), or stabilised less (B2). Wells [49] shows

B



that for water-rich mixtures the value of Q decreases with increase in x_2 for a range of halo-cobalt(III) complexes where z is positive. In these cases, Wells interprets the data using scheme B2, concluding that the transition state is stabilised to a greater extent than the initial state. This choice is supported by his previous calculations which show that at a given value of x_2, $\delta_m\mu^{\ominus}(M^z)$ for a cation becomes more negative as z increases.

The range of complexes and solvent mixtures examined by Wells is impressive as is the observation that the pattern of behaviour for the quantity Q is strikingly similar. This wide-ranging analysis lends support to his claim that the solvation of the transition state is dominant for these reactions. Nevertheless one should not lose sight of the assumption made in the analysis. Thus it seems somewhat extreme to model the transition state in the manner described. Indeed one might anticipate that the extent of charge development in the transition state would depend on solvent. It would be interesting also to examine the extent to which the conclusions depend on the particular set of single ion transfer functions bearing in mind that three such quantities appear in eqn. (14) and that the value of Q is initially dependent on $\delta_m\mu^{\ominus}(X^-)$; also that any error in the cation—anion split is cumulative, not compensatory, here. Q, by incorporating $\delta_m\mu^{\ominus}(X^-)$, is a complicated function containing kinetic information and a part description of the transition state. However our major reservation concerns the basis for linking a decrease in Q with the trend depicted in scheme B2. Although Wells argues that $-\delta_m\mu^{\ominus}(M^{z+1})$ is greater than $-\delta_m\mu^{\ominus}(M^z)$, this conclusion is not completely supported by other workers nor by NMR studies of preferential solvation of cations [47]. Indeed on simple electrostatic arguments one might anticipate that cations would be destabilised when an organic co-solvent is added to water with divalent cations destabilised to a greater extent than univalent (e.g. scheme A1). However these simple arguments do not take account of other factors such as solvent-sorting, specific solvation and solvent—solvent interactions. These considerations may lead to the pattern shown in scheme B2 as used by Wells. Nonetheless, comparison between observations and predictions by this method in the area of organic chemistry, specifically for solvolysis of tert-butyl halides in methanol— — water and in ethanol — water mixtures, are not encouraging. Predictions that transition state effects should dominate in about half the situations for which kinetic data are available have to be set against the fact that initial state solvation is in fact always dominant here.

(ii) Tris-(2,2′-bipyridyl)iron(II) plus either cyanide or hydroxide ions

Low-spin tris-diimine complexes of iron(II) react with cyanide (e.g. eqn. (15)) or with hydroxide following a rate law of the type shown in eqn. (16).

$$\mathrm{Fe(bipy)_3^{2+}} + 2\,\mathrm{CN^-} = \mathrm{Fe(bipy)_2(CN)_2} + \mathrm{bipy} \tag{15}$$

$$-\mathrm{d}[\mathrm{Fe(bipy)_3^{2+}}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{CN^-}]\}\,[\mathrm{Fe(bipy)_3^{2+}}] \tag{16}$$

The k_2 term in this equation, which is dominant except at very low cyanide (or hydroxide) concentrations, corresponds to bimolecular nucleophilic attack at the complex. Extensive sets of k_2 values exist for the reaction of the Fe-$\mathrm{(bipy)_3^{2+}}$ cation with cyanide ion [50,51] or hydroxide ion [40] in various binary aqueous solvent mixtures.

We have recently determined the solubility of potassium cyanide in a variety of binary aqueous mixtures, and have thence estimated values for transfer of the cyanide ion, $\delta_m\mu^{\ominus}(\mathrm{CN^-})$ [52]. Unfortunately, values of $\delta_m\mu^{\ominus}(\mathrm{K^+})$ come from several sources employing different assumptions for obtaining single ion values, but, as we shall see below, this is not too important in this system as other transfer parameters dominate. Transfer parameters for the $\mathrm{Fe(bipy)_3^{2+}}$ cation can be derived from two sources, either from Born-based calculations of $\delta_m\mu^{\ominus}(\mathrm{Fe(phen)_3^{2+}})$ [53] or via solubilities of the tetraphenylboronate salt of $\mathrm{Fe(bipy)_3^{2+}}$ [52]. The two sources lead to markedly different values for $\delta_m\mu^{\ominus}(\mathrm{Fe(bipy)_3^{2+}})$ for aqueous methanol (which is the only solvent series where direct comparison is possible). However, despite these difficulties, examination of Fig. 9 [52] shows clearly the predominant role of the iron(II) complex solvation changes in determining the initial state transfer parameters. The closeness of the initial state and transition state plots suggests strongly that this complex moiety also dominates transition state solvation. Its hydrophobic periphery appears to be much more important than the presence of the cyanide in the transition state, or the charge decrease on transition state formation. It is interesting to compare solvent effects on hydroxide attack at a range of organic and inorganic substrates. This can be done for dimethyl sulphoxide plus water mixtures, as shown in Fig. 10. Here it has been assumed that the rate trends are dominated by $\delta_m\mu^{\ominus}(\mathrm{OH^-})$, whose variation will reflect solvation changes at this small hydrophilic anion. The fact that the curves

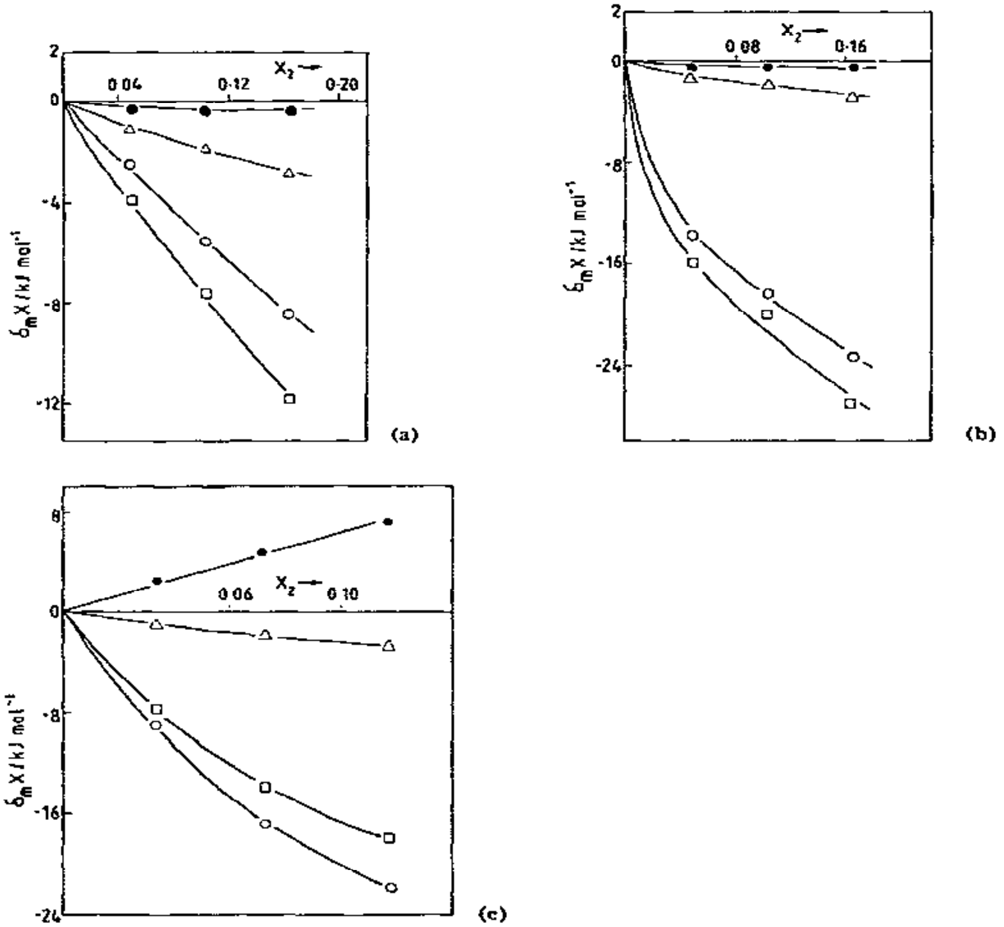


Fig. 9. Reaction of tris-(2,2′-bipyridyl) iron(II) with cyanide ions in aqueous solution; effect of added co-solvent on the activation Gibbs function, $\delta_m \Delta G^{\ddagger}$, (△), and on the chemical potentials of complex, $\delta_m \mu^{\ominus}$(complex), (○), cyanide ion [35,36] $\delta_m \mu^{\ominus}(\mathrm{CN}^-)$, (●), and transition state, $\delta_m \mu^{\ddagger}$(□); effect of added methyl alcohol using (a) calculated values [53] and (b) values obtained from solubilities of the tetraphenylboronate salt [51] for $\delta_m \mu^{\ominus}$(complex); (c) effect of added acetone using calculated values [53] for $\delta_m \mu^{\ominus}$-(complex).

cover a wide area of scatter shows that this assumption cannot in general be valid. However it could be valid for the reaction of $\mathrm{Fe(bipy)_3^{2+}}$ with hydroxide, though the known sensitivity of $\delta_m \mu^{\ominus}(\mathrm{Fe(bipy)_3^{2+}})$ to solvent composition (cf. previous paragraph) indicates that the solvation of this species in the initial and transition states is large and comparable rather than negligible. In the other reactions of transition metal complexes included in Fig. 10, base hydrolysis of $\mathrm{Co(NH_3)_5Cl^{2+}}$ and of $\mathrm{Co(NH_3)_5(dmso)^{3+}}$, the effect of changing chemical potential of the hydroxide ion presumably affects reactivity trends

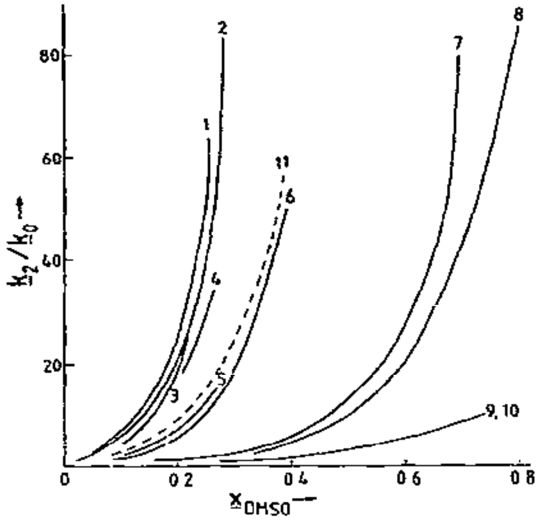


Fig. 10. Variation of the ratio of the second order rate constants for the reaction of various substrates with hydroxide ions in aqueous dimethylsulphoxide (k_2; mole fraction x_{DMSO}) to that in water (k_0). Substrates: (1) $[Co(NH_3)_5(dmso)]^{3+}$; (2) MeI; (3) dinitrofluorobenzene; (4) $[Co(NH_3)_5Br]^{2+}$; (5) $[Co(NH_3)_5Cl]^{2+}$; (6) $[Fe(bipy)_3]^{2+}$; (7) benzyl chloride; (8) $NMe_3 \cdot SO_3$; (9) ethyl acetate; (10) ethyl benzoate. The broken line (11) shows the variation of k_2/k_0 predicted from $\delta_m\mu^{\ominus}(OH^-)$ (cf. text).

through its effect on the conjugate base pre-equilibrium (eqn. (17)) rather than on the dissociative step (eqn. (18)) [51].

$$Co(NH_3)_5(dmso)^{3+} + OH^- \overset{fast}{\rightleftharpoons} Co(NH_3)_4(NH_2)(dmso)^{2+} + H_2O \qquad (17)$$

$$Co(NH_3)_4(NH_2)(dmso)^{2+} \xrightarrow[slow]{k} products \qquad (18)$$

Our conclusions for the $[Fe(bipy)_3]^{2+} + CN^-$ reaction in water-rich mixtures (above) may be contrasted with those for the reaction of $[Mo(CO)_4(bipy)]$ with CN^- in non-aqueous media [54]. In the former case reactivity trends are dominated by the hydrophobic iron(II) complex, as the chemical potential of cyanide $\mu^{\ominus}(CN^-)$ is affected relatively little in going from water to a water-rich mixture. However the chemical potential of cyanide increases greatly on transfer to a pure organic solvent, and depends greatly on the nature of that solvent [52]. As the chemical potential of $Mo(CO)_4(bipy)$ is rather similar in several organic solvents (i.e. $\delta_m\mu^{\ominus} \simeq 0$) the change in the rate of reaction with cyanide is in fact dominated by the cyanide ion transfer properties.

The transfer parameters $\delta_m\mu^{\ominus}(Re(CO)_5I)$ and $\delta_m\mu^{\ominus}(CN^-)$, 50% to 70% methanol, are -3.3 kJ mol^{-1} and $+4.1$ kJ mol^{-1} respectively. The marked decrease in rate constant for the bimolecular reaction between rhenium pentacarbonyl iodide and cyanide [55] ($\delta_m\Delta G^{\ddagger} = +5.2$ kJ mol^{-1}) indicates a marked destabilisation of the transition state ($\delta_m\mu^{\ddagger} = +6.0$ kJ mol^{-1}). This pattern is surprising, and may reflect a poor estimate of $\delta_m\mu^{\ominus}(CN^-)$, and thus of $\delta_m\mu^{\ddagger}$, rather than the actual state of affairs.

F. METAL ION CATALYSED REACTIONS

(i) Mercury(II) catalysed aquation

Metal ion catalysed aquation of transition metal complexes, of which the mercury(II) catalysed aquation of chloro- or bromo-complexes is a well-known case, provides another useful example of a second-order reaction of octahedral transition metal complexes. The interesting feature of these reactions is the variation in charge type, e.g. from 2+/2+ for the $[Co(NH_3)_5Cl]^{2+}$ plus Hg^{2+} reaction to the 2−/2+ of the $[ReCl_6]^{2-}$ plus Hg^{2+} reaction, and the dramatic difference between the rate constant changes with solvent. Thus on going from water to 40% ethanol, the rate constant for the latter reaction increases by thirty times, for the former by only a factor less than 1.2 (at 298.2 K) [56]. The dissection of solvent effects on reactivity into initial state and transition state contributions (Fig. 11) reflects the importance of charge cancellation on transition state formation for $[ReCl_6]^{2-}$, and the relatively minor effect of assembling a large transition state of charge +4 from two smaller complexes each of charge +2.

(ii) Other reactions

Progress on other reactions in this category, for example thallium(III) catalysed aquation of halide complexes and metal ion catalysed aquation of car-

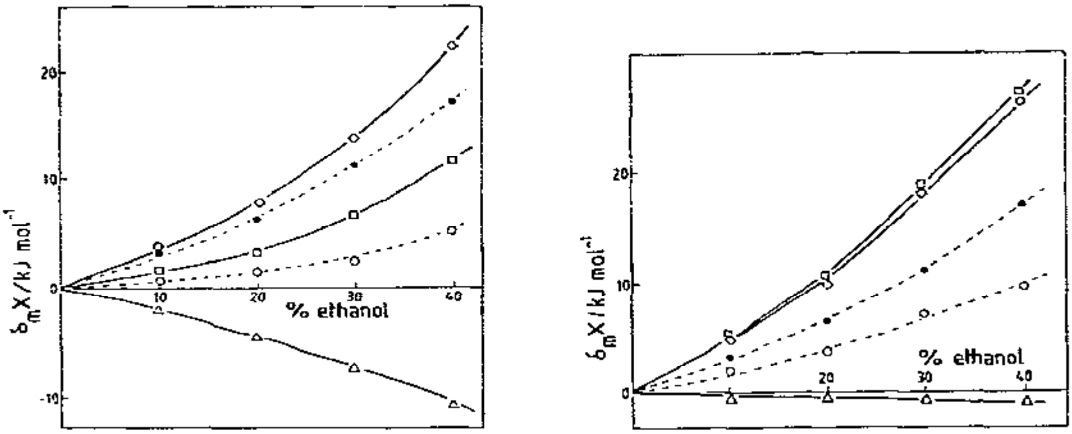


Fig. 11. Mercury(II) catalysed aquation of (a) $[ReCl_6]^{2-}$ and (b) $[Co(NH_3)_5Cl]^{2+}$; effect of added ethyl alcohol on the activation Gibbs function, $\delta_m\Delta G^{\ddagger}$, (△), and the chemical potentials of either $[ReCl_6]^{2-}$ or $[Co(NH_3)_5Cl]^{2+}$, $\delta_m\mu^{\ominus}$(complex) (○), and Hg^{2+}, $\delta_m\mu^{\ominus}(Hg^{2+})$ (●) and the transition state, $\delta_m\mu^{\ddagger}$ (□). For comparison the points (◇) represent $\delta_m\mu^{\ominus}$(complex) + $\delta_m\mu^{\ominus}(Hg^{2+})$.

boxylate complexes, can only be slow due to lack of data for estimating transfer functions not only for the complexes but also for the simple metal ions. As so often in physical chemistry, attention has been concentrated very much on the alkali metal cations, to the virtual neglect of other metal cations.

G. REDOX REACTIONS

(i) General

In principle these are more complicated to deal with than substitution as electron (atom) transfer takes place and oxidation states change. But it should be possible to analyse solvent effects on reactivities into initial state and transition state components, as above, and to use this information to gain further insight into the actual oxidation process. Two main mechanisms are recognised for redox reactions of inorganic complexes, inner-sphere and outer-sphere [57]. Reactions in the former category involve substitution as an essential component of the overall reaction. The classical example of inner-sphere substitution, Taube's (eqn. (19)), is formally analogous to the mercury(II) catalysed aquation, particularly that of this same $[Co(NH_3)_5Cl]^{2+}$ cation, discussed above. However it is the latter class, of outer-sphere redox reactions, that provides the currently available information on the dissection of solvent effects on reactivity into initial state and transition state components. The advantage of the outer-sphere mechanism is, of course, its chemical simplicity — electron transfer without substitution or change of coordination of the metal centre involved.

$$[Co(NH_3)_5Cl]^{2+} + Cr^{2+}aq \xrightarrow{5\,H^+} CrCl^{2+}_{aq} + Co^{2+}_{aq} + 5\ NH_4^+ \tag{19}$$

(ii) Hexachloroiridate(IV) oxidations

Kinetic data are available for the outer-sphere hexachloroiridate(IV) oxidation of iodide (eqn. (20)) in several series of binary aqueous mixtures, in which the co-solvents include monohydric alcohols, ethylene glycol, glycerol, acetone, acetonitrile, and dimethyl sulphoxide [58]. Values of $\delta_m\mu^{\ominus}(I^-)$ are available, from a variety of sources, for many of these solvent mixtures; values of $\delta_m\mu^{\ominus}(IrCl_6^{2-})$, from solubility measurements on K_2IrCl_6, for several mixtures. The initial state—transition state analysis for this redox reaction, in aqueous methanol, is illustrated in Fig. 12(a). The reactants follow the expected trends for ions; the interesting feature here is that the transition state is more sensitive than the initial state. The $[IrCl_nI^{3-}]^{\ddagger}$ solvation seems to vary more than that of the two reactants separately, presumably because of its net 3— charge (cf. estimated values for $\delta_m\mu^{\ominus}(IrCl_6^{3-})$, Fig. 12(a)).

$$IrCl_6^{2-} + I^- \rightarrow IrCl_6^{3-} + \tfrac{1}{2}I_2 \tag{20}$$

The pattern for hexachloroiridate (IV) oxidation of catechol (*o*-dihydroxy-

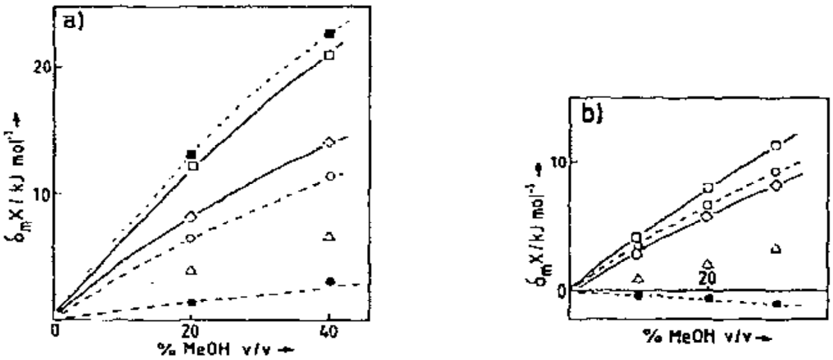


Fig. 12. Hexachloroiridate(IV) oxidation of (a) iodide ions and (b) catechol in water; effect of added methyl alcohol on the activation Gibbs function, $\delta_m \Delta G^{\ddagger}$, (△) and the chemical potentials of iodide ions, $\delta_m \mu^{\ominus}(I^-)$, or catechol, $\delta_m \mu^{\ominus}$(catechol), (●), the ion $[IrCl_6]^{2-}$, $\delta_m \mu^{\ominus}([IrCl_6]^{2-})$, (○) and the transition state, $\delta_m \mu^{\ddagger}$, (□). The graphs include dependences of the sum (a) $\delta_m \mu^{\ominus}(I^-) + \delta_m \mu^{\ominus}([IrCl_6]^{2-})$, (◇) or, (b) $\delta_m \mu^{\ominus}$(catechol) + $\delta_m \mu^{\ominus}([IrCl_6]^{2-})$, (◇) and, in (a) the estimated variation of the chemical potential for the $[IrCl_6]^{3-}$ anion, $\delta_m \mu^{\ominus}([IrCl_6]^{3-})$, (■), the model for the transition state of the $[IrCl_6]^{2-}/I^-$ reaction.

benzene) is similar (Fig. 12(b)) to that for oxidation of iodide, with again the transition state more sensitive than the initial state to solvent variation. Such differences as there are between the catechol and iodide plots arise from the different trends of $\delta_m \mu^{\ominus}$ for these two reactants, with the iodide increasingly destabilised, the catechol increasingly stabilised, as methanol is added.

(iii) Peroxodisulphate oxidations

Such oxidations, for example of low-spin iron(II) complexes, are outer-sphere in mechanism. They are not quite as straightforward as the simple electron transfer reactions first discussed, as oxygen—oxygen bond breaking in the peroxodisulphate is an integral aspect of the redox process. This is indicated for an arbitrary one-electron reductant in eqn. (21). Nonetheless an initial state—transition state analysis can be conducted as above.

$$M^{n+} + S_2O_8^{2-} \rightarrow M^{(n+1)+} + SO_4^{2-} + SO_4^{-\bullet} \qquad (21)$$

The peroxodisulphate oxidation of the complex $Fe(bipy)_2(CN)_2$ is unique in that the transition state solvation effects far outweigh initial state effects (Fig. 13) [59]. This conclusion comes from the usual analysis of kinetic data [60] and solubility data for the iron complex [59] and for potassium peroxodisulphate [61]. Peroxodisulphate oxidation of tris-diimineiron(II) complexes presents a less clear-cut picture [62]. There is a lower variation of reactivity with solvent, perhaps connected with charge cancellation in transition state generation here, and the issue is clouded by uncertainties in $\delta_m \mu^{\ominus}(Fe^{II}$ complex) (cf. substitution section above).

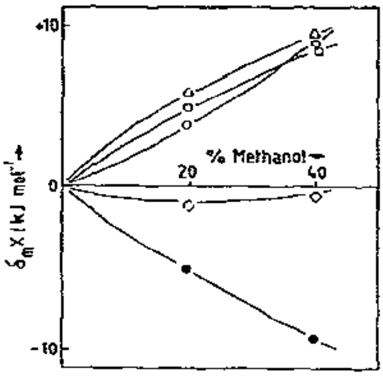


Fig. 13. Peroxodisulphate oxidation of bis-2,2'-bipyridylbiscyanoiron(II) in water; effect of added methyl alcohol on the activation Gibbs function, $\delta_m \Delta G^{\ddagger}$, (△) and the chemical potentials of [Fe(bipy)$_2$(CN)$_2$], $\delta_m \mu^{\ominus}$([Fe(bipy)$_2$(CN)$_2$]), (○), the peroxodisulphate ion, $\delta_m \mu^{\ominus}(S_2O_8^{2-})$, (●) and the transition state, $\delta_m \mu^{\ddagger}$(□). The graph also includes a plot (◇) of the sum, $\delta_m \mu^{\ominus}$([Fe(bipy)$_2$(CN)$_2$]) + $\delta_m \mu^{\ominus}(S_2O_8^{2-})$.

H. TRANSITION STATE MODELS

Thus far we have concentrated on deriving $\delta_m \mu^{\ddagger}$ algebraically from kinetic and initial state data. Although obviously it will never be possible to measure $\delta_m \mu^{\ddagger}$ values directly, it seems likely that for several systems a useful check on analyses of the sort set out in the foregoing review might be provided by the determination of $\delta_m \mu^{\ominus}$(model) values for a suitable transition state model. This has been briefly mentioned in the introduction. In the outer-sphere redox area, the establishment of $\delta_m \mu^{\ominus}(IrCl_6^{3-})$ values for comparison with $\delta_m \mu$-([$IrCl_6I^{3-}$]‡) is in hand [58]. Other examples include the use of naphthalene in transition state modelling for Fe(phen)$_3^{2+}$ aquation and solvolysis [53], and 2-naphthol for the reaction of Fe(bipy)$_3^{2+}$ with hydroxide [63].

I. TWO-STAGE REACTIONS

Our analysis has been applied only to reactions which we feel able to assume are one-step processes — simple bimolecular or unimolecular. However there are many inorganic reactions in which what at first sight (e.g. from a rate law determination over a limited concentration range) seems to be a simple bimolecular process turns out to be a two-stage reaction sequence, often of a rapid reversible pre-equilibrium followed by a rate-determining reaction (eqn. (22)). In fact one important case, base hydrolysis of cobalt(III) complexes by the

$$\mathrm{A{-}B + C \overset{\text{fast}}{\rightleftharpoons} A{-}B{-}C \xrightarrow{\text{slow}} A + B{-}C} \tag{22}$$

normal S_N1CB mechanism, has already been mentioned in Section E. Another important case, complex formation from solvento-metal cations by the Eigen-

Wilkins (dissociative interchange) mechanism [64], seems not to have been fully treated as an initial state—transition state/intermediate problem yet, though the importance of solvent effects on the initial pre-association equilibrium in determining reactivity variation has been established [65].

In many reactions it is not clear whether the proposed transition state is indeed that, or may rather be a transient intermediate. There are several examples in redox reactions involving simple organic and inorganic species [66]. This point is also relevant to two of the reactions discussed in the substitution section above. The fairly convincing evidence for intermediates in the reactions of $Fe(5NO_2phen)_3^{2+}$ with hydroxide and with cyanide [67], and the firm kinetic evidence for binuclear intermediates in some mercury(II) catalysed aquation of chloro- and thiocyanato-transition metal complexes [56,68] means that we cannot be sure that our related reactions are not in fact two-stage reactions with very short-lived intermediates. Such questions do not affect the main features of our treatment of these reactions; their resolution will affect details of interpretation and may well provide further insight into solvent effects in such systems.

J. CONCLUSIONS AND DISCUSSION

The main features of the reactions discussed in this review are summarised in Table 3. This shows the relative importance of initial state and transition state solvation changes, indicates noteworthy influences, covers substitution and redox reactions and puts inorganic complexes in the context of the chemistry of *sp*-block elements and organic chemistry, cf. ref. 2. Some reactions in Table 3 fit into the general pattern for organic reactions established by Ingold [1] (cf. Table 1), but others do not. Thus, for example, the mercury(II) catalysed aquation of $Co(NH_3)_5Cl^{2+}$ or of $ReCl_6^{2-}$ exhibits the reactivity characteristics expected for charge augmentation and charge cancellation in transition state formation. However several of the other inorganic reactions included in Table 3 cannot be accommodated within Ingold's scheme, admittedly based on simple electrostatic considerations. This failure of course is due to the wide variety of ligands and therefore modes of solute—solvent interaction for these inorganic solutes.

In view of the complexity of the chemistry of water and of binary aqueous mixtures [22], solvent effects on reactivity and the associated initial and transition state components may show more dramatic variation with solvent in these media, than in organic solvents. The hydrophobic/hydrophilic character of the solute is a more important consideration in aqueous media than in organic solvents. The kinetic consequences are likely to be particularly striking when water is used as the reference solvent, as is the case for most of the systems cited in this review.

A word of caution must again be introduced at this stage concerning the systems in Table 3 which involve ionic reactants. As stressed above, the transfer parameters for ionic reactants are dependent on the assumptions used in

TABLE 3

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

Reaction type			
Substitution	tert-BuCl solvolysis (also ΔH)	is > ts	is, ts trends opposed
	$C_6H_5CH_2Cl$ solvolysis (ΔV)	is > ts	
	Finkelstein $CH_3I + Cl^-$	is > ts	Chloride ion transfer dominant
	Menschutkin $Me_3N + MeI$	is < ts	But is >> ts for transfer from water
	Me_3N + *p*-$O_2NC_6H_4CH_2Cl$	is < ts	
	$Et_4Sn + HgCl_2$ (also ΔH)	is > ts	Reactants and ts trends parallel
	$R_4Pb + I_2$	is ~ ts	
	$Pt(bipy)Cl_2$ + tu	is >> ts	Reactants (and ts) trends parallel
	cis-$(Pt(4CNpy)_2Cl_2$ + tu	is > ts	
	$Fe(bipy)_3^{2+} + CN^-$	is ~ ts	bipy solvation dominates is and ts
	$Co(NH_3)_5Cl^{2+} + Hg^{2+}$	is ~ ts	All reactant trends parallel; cf. charges is → ts
	$ReCl_6^{2-} + Hg^{2+}$	is > ts	
Redox	$IrCl_6^{2-} + I^-$, catechol	is < ts	
	$Fe(phen)_3^{2+} + S_2O_8^{2-}$	is > ts	Reactant solvation trends opposed; $Fe^{II} > S_2O_8^{2-}$
	$Fe(bipy)_2(CN)_2 + S_2O_6^{2-}$	is << ts	Reactant solvation trends equal and opposite

their derivation. Some assumptions seem better than others; the improvement of single ion values consequent on improvements in the derivation of these quantities will make some difference to $\delta_m\mu^{\ominus}$(reactants) and thus to $\delta_m\mu^{\ddagger}$. There are particular instances where a dramatic improvement in the analysis is clearly possible. For example in relation to the reaction between cyanide ion and $Mn(CO)_5X$, the value for $\delta_m\mu^{\ominus}(CN^-)$ for transfer between methyl alcohol and DMSO may be either +2.5 or +14.5 kJ mol^{-1} [52]! However in most cases we are of the opinion that future adjustments to single ion values will make a difference to the actual values for $\delta_m\mu^{\ominus}$(reactants) and $\delta_m\mu^{\ddagger}$, but not to the overall pattern (cf. the $Fe(bipy)_3^{2+}$ plus CN^- reaction discussed above).

Our treatment in this review is based on the postulates of transition state theory [3]. Consequently values for $\delta_m\mu^{\ddagger}$ are algebraically valid in the sense that they are obtained from $\delta_m\Delta G^{\ddagger}$ and initial state values for $\delta_m\mu^{\ominus}$(reactants). However careful consideration of the assumptions implicit in the transition state approach to kinetics of reaction is needed when one attempts to interpret $\delta_m\mu^{\ddagger}$ values and their dependence on solvent. The theory requires that the transition state and reactants are in thermodynamic equilibrium. The activation process is an equilibrium transformation (i.e. a reversible process) and so the organisation of solvent in the co-spheres around the solute [11] changes reversibly from that determined by the initial state to that determined by the transition state. In addition, the solvent in the co-sphere is in equilibrium with the bulk solvent [2] so we have the following interesting equality [69], eqn. (23).

$$\mu(\text{solvent in co-sphere of reactants}) = \mu(\text{solvent in co-sphere of transition state}) = \mu(\text{bulk solvent}) \quad (23)$$

Thus we assume that the activation process is sufficiently slow to allow this equilibrium to be established at all stages [70]. We also note that an equality similar to eqn. (23) does not apply to other partial molar properties (e.g. enthalpy, entropy and partial molar heat capacity) because the temperature and pressure derivatives of the three chemical potentials in eqn. (23) are not necessarily equal. In addition eqn. (23) does not rule out the possibility that the organisation in the co-sphere changes on going from the initial to the transition state. Nonetheless it is this underlying emphasis on equilibrium and reversible change which allows one to characterise the transition state in the manner described in the previous reactions. If we adopt the concept of reversible transformation when applied to the activation process as one limiting case, we can formulate the other extreme. This is encountered in the analysis of solvent effects on the energy of absorption band maximum of a solute in the UV/visible range [71]. Thus the Franck-Condon principle requires that electronic excitation is much faster than the rate at which nuclei of both solvent and solute change position. Consequently in the electronic excited state, the organisation of solvent in the co-sphere is precisely that in the ground (cf. initial) state. In the context of chemical kinetics, it is not difficult to imagine that the key process for reaction (e.g. bond initiation, charge separation and electron transfer) is sufficiently rapid for the reorganisation of solvent in the co-sphere to lag the equilibrium structure. It may be therefore that the solvent reorganisation 'catches up' with the solute on the product side of the energy maximum. However, assumption of this type of irreversible activation carries with it a heavy penalty, namely that it is no longer correct to characterise the transition state by the use of a chemical potential, $\mu^{\ddagger}$. This suggested lag in solvent reorganisation contravenes the principle of microscopic reversibility. If one adopts this irreversible lag model, then transition state theory is inapplicable, and quantities such as $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are not meaningful [72]. It is obvious from the central role that transition state theory has played in this review that we are not advocating its abandonment in this area of kinetics. There may well exist cases in which transition state theory is not applicable, but at the present time we do not have compelling evidence in this direction.

Another factor ignored in our analysis concerns the position of the transition state along the reaction co-ordinate. We have not considered the possibility that this position is dependent on solvent. Evidence that this position does vary stems from the observation that solvent variation can cause a change in the mechanism of reaction. Thus polar solvents favour ionic intermediates both in catalysed isomerisation of certain platinum(II) complexes, PtL_2X_2 [73], and in ethene loss from the $PtCl(bipy)(C_2H_4)^+$ cation [74]; both reactions have different, non-ionic, reaction mechanisms in non-polar solvents.

There is one further aspect of the properties of solutes in solution which we have not considered in detail. We refer to the role of repulsive forces, i.e. size effects. This is an important omission. Our evidence for the latter comes from another series of studies with which we have been concerned. Thus we have examined the effects of added salts on the kinetics of reactions in aqueous solutions [75]. The patterns which emerge are often complex and, in order to probe these more closely, we have used [76] the Friedman pair potential for solutes in solution [77] in conjunction with the hyper-netted chain integral equation as a basis for the analysis of a relatively simple problem, the effect of added salt on the rate constant for the hydrolysis of tert-butyl chloride in water. It turns out that the size effect, as accounted for in the core-potential term [77], is extremely important. This prompts the suspicion that these forces play an important part in determining the effect of solvent on inorganic reactions. Clearly the detailed quantitative analysis of solvent effects presents a formidable challenge. The ultimate aim is to obtain molecular models for the whole reaction sequence, initial state → transition state → products, including changes in both solute and solvent structures. Perhaps this might be achieved using molecular dynamic calculations. We have in mind the models obtained [78] for $Li^+ F^- + 20$ water molecules at different ion—ion distances but now extended to the approach of two reactant molecules to form a transition state. A pre-requisite to these calculations will, we are sure, be a detailed consideration of the effects of solvent on initial and transition states along the lines discussed in this review.

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