Evaluation of Solvation Energies of Reagents and Transition States

Initial State and Transition State Solvent Effects: Reactions in Protic and Dipolar Aprotic Media

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Interpretation of the variation in reaction rates brought about by solvent changes has traditionally utilized relationships based on absolute rate theory. Thus the Laidler–Eyring equation satisfactorily correlates rate data for the Menschutkin reaction in a number of binary solvents. However solvent parameters such as the dielectric constant are limited as measures of solvent influence since correlation is attempted with a quantity ($\Delta G^{\neq}$ or ΔG_o) which represents a difference of two states and these may be affected differentially by the solvent change. Direct information about the nature of solvent involvement requires dissection of the solvent effects into initial and transition state (final state) contributions. This dissection is possible using the thermodynamic transfer function appoach [1–5].

In this presentation we utilize the relationship $\delta\Delta^{T}_{tr} = \delta\Delta G^{R}_{tr} + \delta\Delta G^{\neq}$ for the free energy of transfer of the transition state ($\delta\Delta G^{T}_{tr}$) on solvent change, from the experimentally determined free energies of transfer of the reactants ($\delta\Delta G^{R}_{tr}$) and the kinetic activation parameters ($\delta\Delta G^{\neq}$), and correspondingly for the equilibrium process $\delta\Delta G_{tr} = \delta G^{P}_{tr} - \delta G^{R}_{tr}$, to discuss solvent effects on various rate and equilibrium processes. The discussion emphasizes dipolar aprotic solvents such as dimethyl sulfoxide for which dramatic medium effects have been observed in a number of systems. Specific reactions considered include solvent effects on S_N2 and S_NAr processes; the competing σ-complex formation and proton abstraction in nitroaromatics-base interactions; and the hydroxide ion catalyzed isotopic exchange of D_2. Some future directions in this area are indicated, as for example synergistic and antagonistic effects as probes of changing transition states.

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Solvent Effects on Solvolysis of Alkyl Halides

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The separation of solvent effects on reaction rates into initial-state and transition-state contributions will be discussed with reference to the solvolysis of alkyl halides and to the Menschutkin reaction of triethylamine with ethyl iodide. In both of these cases, gas-chromatographic head-space analysis has been used to determine the effect of solvents on the free energy of the reactants, and solution calorimetry to determine the corresponding effect on the enthalpy (and hence the entropy) of the reactants. Combination of these measurements with the activation parameters ΔG, ΔH, and ΔS enables the solvent effect on the free energy, enthalpy and entropy of the transition states to be obtained.

It is shown that initial-state solvent effects on the various reactants are usually not very large, except when water or aqueous–organic mixtures are used as solvents, unless there are specific solute–solvent interactions, for example in the triethylamine–chloroform system.

Determinations have also been made of solvent effects on the standard free energies, enthalpies and entropies of a number of compounds that might be useful as models for transition states. In terms of free energy, ion-pairs ($R_4N^+X^-$) and α-aminoacids are shown to be suitable models for highly polar but electrically neutral transition states, especially if corrections are made for the 'size' or 'cavity' effect on introducing a solute into a solvent. It is more difficult to select highly polar model compounds for which enthalpy and entropy data can be obtained. It is shown that pairs of dissociated ions ($R_4N^+ + X^-$) are usually not very suitable, but that α-aminoacids can be used, again provided that size or cavity corrections are made.

It is suggested that measurements and calculations on model compounds and transition states enable deductions to be made as to the polarity of the transition states and their position along the reaction coordinate.

Solvation Energies in Acid Catalyzed Processes

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Rates of acid catalyzed reactions have been correlated with various parameters, such H_0 or log

c_{H^+} (Zucker–Hammett hypothesis), or log a_{H_2O} (Bunnett's w and w* values and Yates's *r* parameter), in order to clarify whether the reaction mechanism may be classified as A-1 or A-2, or A_{SE}-2.

If one considers the general equations for acid-catalyzed processes:

$$S + H^+ \rightleftarrows SH^+ \rightleftarrows \neq \rightarrow \text{products} \qquad (1)$$

$$v = k_\psi [S]_{st} = k_o [SH^+] f_{SH^+}/f_{\neq} \qquad (2)$$

$$\log k_\psi - \log([SH^+]/[S]_{st}) = \log k_o + \log(f_{SH^+}/f_{\neq}) \qquad (3)$$

it becomes apparent that, after correction for the amount of protonated substrate ($[SH^+]/[S]_{st}$), the variation in rates is caused only by variation in the activity coefficient ratios of the protonated substrate and the transition state. Therefore, this, rather than the classification into a defined mechanistic scheme, is the only information that can be obtained by studying the rate *vs.* acidity profiles.

This piece of information is however of paramount importance since activity coefficients of the type reported in eqn. (3) represent the free energy of transfer of the indicated species from the reference aqueous state to the acid solutions, *i.e.* their solvation requirements. Since solvation of charged species in aqueous acid media depends on structural factors, such as the site protonation, the charge localization, *etc.*, a knowledge of the solvation requirements of the transition state offers several hints on its structure, and hence on the reaction mechanism.

Derivation of the analytic expression for the ratio $f_{SH^+}/f_{\neq}$ and the results obtained in perchloric and sulphuric acid will be discussed for some exemplicative reactions.

References

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