Some properties, including frequencies and intensities of spectral transitions, may suffer profound changes on a change of solvent, thereby providing a means of adapting the property to various needs. And some properties result entirely from the interaction of the molecules – for example, the dipole moment of a pair of unlike inert-gas atoms, or the circular dichroism of an achiral compound in the presence of a chiral species –.

In the general theory of the effects of long-range intermolecular forces on molecular properties, the change in the property with distance between two molecules is expressed in terms of properties of the free molecules. The limitations of such a description will be discussed, and the role of short-range forces considered.

Progress in understanding intermolecular forces, and solvent effects, will depend upon a combination of experiment and *ab initio* computation.

The Nature of 'Solvent Effects'

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The coordination model for nonaqueous solvent chemistry was the first attempt to offer a unified presentation of those interactions essential to the understanding of the behavior of solutes in nonaqueous solvents. The model focused on two distinct aspects of the problem; specific interactions of the Lewis acid base type and non-specific interactions in which coordinate bond formation is not involved. As in any classification, there are gray areas in which it is difficult to assign the interaction to one category or another. However, in many instances the assessment is straightforward. Though the original publication of this work met with considerable resistance, it is now quite generally accepted that the Coordination model accurately represents the behavior of solutes in a wide variety of solvents including many of the oxyhalides.

In recent years the problem has become one of ascertaining coordination strengths and solvation energies. With the wide publicity given to the class A and B concept, HSAB theory and the E and C model, it should be obvious to all that there is no single scale of donor strength that permits an estimate of solvent coordinating abilities. However, one still finds in the literature attempts to correlate all sorts of phenomena with single scale models; for example, pK_B data or donor numbers. In this talk the pitfalls associated with such procedures will be discussed. In their place an approach will be described that enables one to determine if observed phenomena are being dominated by sigma bond, donor strengths. A set of experiments will also be discussed which permits one to detect when coordination involves contributions other than a normal sigma bond type of interaction. Procedures for ascertaining the source of these additional effects will be discussed.

A second and independent contribution to reactions in non-aqueous solvents involves the solvating ability of the solvent. This was demonstrated earlier by showing that solvents with similar donor properties behaved quite differently toward the solute iron(III) chloride in terms of chloride ion dissociation. Models have been developed which enable one to work in polar solvents and correct the enthalpies obtained back to the solvent minimized type of data that one measures in carbon tetrachloride or in alkanes. These studies provide insight regarding some subtle solute–solvent interactions and permit one to obtain data that can be interpreted in terms of bond strength considerations for systems in which it is necessary to work in more polar solvents because of solubility limitations.

Cycloaddition Mechanism and the Solvent Dependence of Rate

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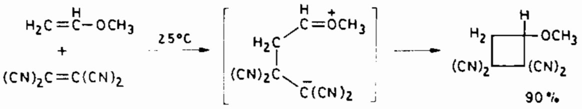
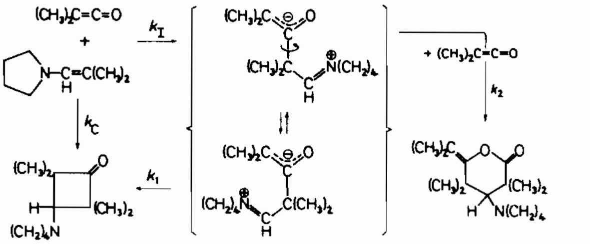
The dependence of the rate constant on solvent polarity is an important mechanistic criterion which should always be used in conjunction with other diagnostic tools. The slow step of 2 + 2 cycloadditions of tetracyanoethylene (TCNE) with enol ethers [1], thioenol ethers [2] and *trans*-fixed 1,3-dienes [3] is the formation of a zwitterionic intermediate. The log k_2 values are linear functions of the Dimroth–Reichardt parameter E_T. The rate accelerations of TCNE cycloadditions in going from cyclohexane to acetonitrile amount to 29,000 for anethole, 10,800 for 1-ethoxyisobutene, 2,600 for butyl vinyl ether, 17,000 for ethyl 1-propenyl sulfide and 54,000 for verbenene. The violation of stereospecificity becomes greater with increasing solvent polarity.



In contrast, the additions of TCNE to anthracene [4] and related Diels–Alder reactions show only a minute solvent dependence. The same is true for 1,3-dipolar cycloadditions of diazoalkanes [5], phenyl azide [6], C-phenyl–n-methylnitrone and azomethine imines to various dipolarophiles. These concerted cycloadditions are characterized by early transition states, *i.e.*, there is hardly any change of solvation energy during the activation process.

A dichotomy of reaction paths was found for diazocarbonyl compounds and enamines. Whereas dialkylaminocyclohexenes produce cycloadducts, the corresponding enamines containing the cyclopentene ring undergo azo coupling which furnishes enaminohydrazones *via* a zwitterionic intermediate. The contrasting dependence of rate on solvent polarity supports different mechanisms [7].



Dimethylketene combines with N-isobutenylpyrrolidine to give a 3-pyrrolidinocyclobutanone as 1:1 adduct and a δ-methylene-δ-lactone as 2:1 adduct. The dependence of the product ratio on the concentration of dimethylketene allows to disent angle a concerted pathway and a rection *via* a zwitterionic intermediate which can be intercepted by a second molecule of dimethylketene (see formula Scheme) [8]. The different solvent dependencies of the two reaction branches confirm the mechanistic divergence.

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Cryptate Inclusion Complexes and the Regulation of Solute–Solvent Interactions

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The uptake of an ion into the intramolecular cavity of a hollow cryptand molecule may greatly affect the properties of *both* the cryptated ion and its counterion.

The resulting *lipophilisation* of one of the ions renders salts soluble in media in which they are otherwise insoluble.

Protection of the cryptated species modifies its physicochemical properties and its chemical reactivity.

Activation of the uncomplexed ion may be produced, which strongly affects its chemical reactivity.

These three major effects, lipophilisation, protection, activation, all result from/in a modification of the solute–solvent interactions experienced by the ionic species subjected to cryptation.

This talk will survey the results of some of the numerous studies which have demonstrated and made use of these effects, covering *inter alia*:

(*a*) physico-chemical properties of cation cryptates;

(*b*) the use of cryptate cations as counterions in X rays studies, solutions of metal anions and clusters *etc.*;

(*c*) cation participation in reaction mechanisms;

(*d*) anion activation in strongly basic systems, in rate and orientation of anionic reactions, in molecular rearrangements, in anionic polymerisation *etc.*

A further consequence of lipophilisation is the use of cryptands as *carriers* in membrane transport phenomena.

When available, comparisons with corresponding crown type or other complexes will be made.