

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 pit-

falls 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.

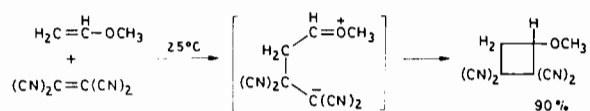
A second and independent contribution to reactions in non-aqueous solvents involves the solvating ability of the solvent. This was demonstrated earlier by showing that solvents with similar donor properties behaved quite differently toward the solute iron(III) chloride in terms of chloride ion dissociation. 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 cycloaddi-



tions 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.