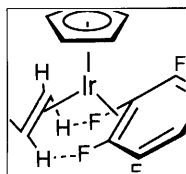


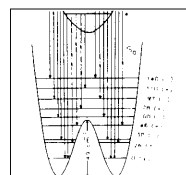
Chemical Society Reviews

Volume 22 Issue 6 Pages 361-442 December 1993



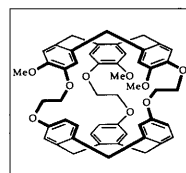
TILDEN LECTURE. Organometallic Intermediates: Ultimate Reagents *By Robin N. Perutz* (pp. 361-369)

Short-lived intermediates play a central role, through their structure and reactivity, in controlling photochemical reactions of organo-transition metal complexes. Molecules such as $\text{Ru}(\text{dmpe})_2$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) can be studied directly by time-resolved spectroscopy and matrix isolation to reveal key features of reaction mechanisms. Photochemical reductive elimination of H_2 may be complete in picoseconds and re-addition of H_2 in tens of nanoseconds. Excited states of organometallics are more elusive, but sometimes emission and excitation spectra are sufficiently well resolved to estimate the change in geometry in the excited state.



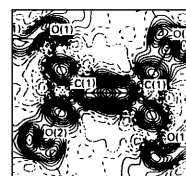
Determination of Molecular Conformation from Large Amplitude Vibrations in Electronic Spectra of Organic Molecules in a Supersonic Jet *By J. Michael Hollas* (pp. 371-382)

Molecules having low wavenumber, large amplitude vibrations are easily distorted in the direction of the corresponding normal mode. Therefore the conformation may be changed appreciably when a molecule is excited from its ground state to another electronic state and there is a tendency for low wavenumber vibrations to have large Franck-Condon factors in electronic transitions. The resulting vibrational progressions can be used to access many levels of what may be inversion, ring-puckering, or torsional vibrations. Fitting these levels to a model potential allows the conformation of the molecule to be obtained.



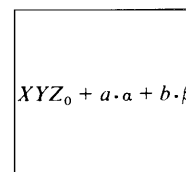
Enantioselective and Diastereoselective Molecular Recognition of Neutral Molecules *By Thomas H. Webb and Craig S. Wilcox* (pp. 383-395)

Biological processes rely upon the specificity of biomolecular interactions. Shape-selective transport and catalysis are facilitated by proteins that show high selectivity for specific carbohydrates, nucleotides, lipids, or peptides. Contemporary chemists are striving to create synthetic receptors that will show similar levels of selectivity. The purpose of these efforts is to illuminate the general mechanisms used by Nature to achieve molecular shape-selectivity, and to provide new synthetic receptors that can be used in separation technologies, drug delivery, or as the basis of new catalytic processes. Recent progress toward this objective is reviewed.



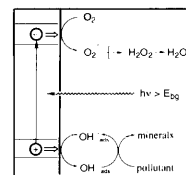
The Hydrogen Bond and Crystal Engineering *By Christer B. Aakeröy and Kenneth R. Seddon* (pp. 397-407)

The hydrogen bond, particularly between ions, is much stronger than commonly acknowledged, and the number of recognized hydrogen-bond donors (such as C-H) and acceptors (such as aromatic π -clouds) is rapidly expanding. We present here an overview of the hydrogen bond, and show how hydrogen-bond patterns in the solid state can be classified using a topological analysis. We conclude by illustrating the use of the hydrogen bond as a synthetic vector for crystal engineering, and consider the problems of polymorphism (a matter of immense current interest, given the multi-billion dollar law suit of Glaxo *versus* Novopharm, which has polymorphism as its cynosure).



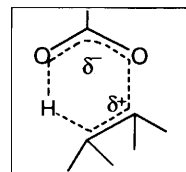
The Properties of Organic Liquids that are Relevant to their Use as Solvating Solvents *By Y. Marcus* (pp. 409-416)

The solvation properties of solvents (solvent effects) depend mainly on their polarity/polarizability (accounting also for dispersion interactions), hydrogen bond donation and acceptance abilities, and cohesive energy density, that are orthogonal to each other. These are best measured by the Kamlet-Taft solvatochromic parameters π^* , α , and β and the square of Hildebrand's solubility parameter, δ_H^2 , respectively. The first three are presented for a large set of solvents, together with several other solvation indices that are correlated with them.



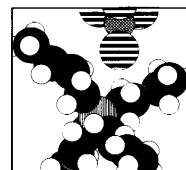
Water Purification by Semiconductor Photocatalysis *By Andrew Mills, Richard H. Davies, and David Worsley* (pp. 417-425)

The basic principles of the photooxidative mineralization of organic pollutants by O_2 , sensitized by TiO_2 , are described. The kinetics of this process as a function of $[\text{TiO}_2]$, [organic pollutant], $[\text{O}_2]$, light intensity, temperature, pH, and the type of anion present are discussed, and a general kinetic model is presented. Standard test and demonstration systems for water purification by TiO_2 photocatalysis are described and other novel applications of semiconductor photocatalysis are outlined.



Mechanisms of Solvolytic Alkene-forming Elimination Reactions *By Alf Thibblin* (pp. 427-433)

Different types of alkene-forming elimination reactions that accompany substitution by the solvent as well as heterolysis reactions in non-nucleophilic solvents are treated. The article discusses kinetic deuterium isotope effects for such reactions and summarizes the use of extreme kinetic deuterium isotope effects as a mechanistic probe of reaction-branching in solvolytic reactions. Mechanistic borderlines are discussed.



Electrochemistry in Media of Low Dielectric Constant *By Andrew Abbott* (pp. 435-440)

This article describes the use of low dielectric constant solvents in electrochemical investigations. It outlines how such solvents can be made conducting, how their solvent properties can be characterized, and how various electroactive solutes can be dissolved in them. Some of the practical applications of these solvents are discussed together with some of the theoretical implications that a low dielectric constant has upon solution chemistry.

1993 Indexes (pp. 441-442)

Articles that will appear in forthcoming issues include

Magnetic Field Gradients in NMR Friend or Foe? **T. J. Norwood**

Helical Poly(isocyanides) **R. J. M. Nolte**

INDUSTRIAL LECTURE Polyelectrolyte Materials—Reflections on a Highly Charged Topic **J. W. Nicholson**

The Kirkwood–Buff Theory of Solutions and its Application **K. E. Newman**

Tetrathiafulvalenes as Building-blocks in Supramolecular Chemistry **T. Jørgensen, T. H. Hansen, and J. Becker**

Solvent Structure and Perturbations in Solutions of Chemical and Biological Importance **J. L. Finney and A. K. Soper**

Thin Film Diamond by Chemical Vapour Deposition Methods **M. N. R. Ashfold, P. W. May, C. A. Rego, and N. M. Everitt**

Thermodynamics of Polar Additives in Surfactant Solutions **R. De Lisi and S. Milioto**

Electrophoresis of Small Particles **C. Boxall**

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