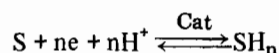
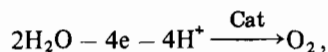


transition metal complexes according to the scheme:



These processes as well as the oxidation, *i.e.*



may proceed in coordination sphere of a polynuclear metal complex as multi-electronic reactions.

Thus  $N_2$  can be reduced to  $N_2H_4$  (without free  $N_2H_2$  as an intermediate) and directly to  $NH_3$ . CO is reduced to  $CH_3OH$  (without intermediate formation of  $CH_2O$ ).  $H_2O$  can be oxidized to  $O_2$  (without  $H_2O_2$  as an intermediate).

The mechanism can be regulated by changing of flow of electrons, pH of the solution or composition of a solvent, *e.g.* four-electron reduction of  $N_2$  to  $N_2H_4$  can be replaced by six-electron reduction of  $N_2$  to  $NH_3$ .

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### Use of Electron Spin Resonance Spectroscopy to Study the Interaction between Cobalt Schiff Base Complexes and Phosphines or Phosphites in Solution

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E.s.r. measurements on frozen solutions of a wide range of phosphine or phosphite adducts of Co(II) Schiff base complexes have given well resolved spectra exhibiting cobalt and phosphorus hyperfine structure. From analysis of the  $^{31}P$  hyperfine tensor, the R-P-R bond angle can be deduced in the phosphine or phosphite,  $PR_3$ . The calculated spin densities in the cobalt and phosphorus orbitals allows a determination of the relative contributions of  $\sigma$ - and  $\pi$ -bonding in the Co-P bond and their influence upon the phosphine or phosphite bond angle. From a full analysis of the  $^{31}P$  polarisation tensor, a correlation is found between its magnitude and the magnitude of the splitting of the cobalt  $d_{xz}$  and  $d_{yz}$  orbitals. In analysing the  $^{59}Co$  spin Hamiltonian parameters, used is made of the theory of McGarvey and the approximations of Attanasio.

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### Nuclear ( $^1H$ , $^{13}C$ ) Magnetic Resonance Studies of the Proton Transfer Processes in Hydrogen Bonded Complexes in Aprotic Solvents

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Nuclear ( $^1H$ ,  $^{13}C$ ) magnetic resonance methods have been widely applied to the study of electronic structure of the hydrogen bond, proton transfer phenomena and dynamics of hydrogen bond formation in the phenol-triethylamine complexes in the temperature range of 100–300 K. Phenolic acids with triethylamine form a 1:1 complex whose nature in solution may be a simple hydrogen-bonded molecular complex or a hydrogen-bonded ion-pair depending on the acidic property of phenol.

Thermodynamic and kinetics quantities of this molecular complex/ion pair tautomerism have been evaluated and results obtained will be discussed in relation to the potential energy profile of the hydrogen bonds. In addition the chemical shift of proton directly engaged in the hydrogen bond and the chemical shift of the oxygen bearing carbon of the phenol ring in a molecular complex ( $O-H\cdots N$ ) and in ion-pair ( $O^-\cdots H-N^+$ ) have been estimated. Those NMR parameters will be discussed in relation to the electronic structure of the hydrogen bond.

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### Some Applications of Liquid Crystals in Organic Chemistry

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Some applications of thermotropic liquid crystals (LC) such as anisotropic solvents for stereochemical, spectrochemical and reactivity studies are presented.

The study of cholesteric mesophases induced in a nematic LC by traces of optically active substances having a single asymmetric centre gives information about the configuration and/or the relative size of the groups connected to the chiral carbon or sulphur atom.

Liquid crystalline solvents, transparent in the UV-Visible region, can be used as orientating matrices

in order to obtain linear dichroism spectra of 'guest molecules'.

Finally the problem of a possible influence of LC used as a solvent for chemical reactions will be discussed.

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## Reactions and Behaviour of Organic Anions in Two-Phase Systems

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Two-phase systems are presently widely applied as convenient and versatile media for reactions of inorganic and organic anions with organic molecules. The main feature of this approach is that organic and inorganic reactants are located in two immiscible phases and that reactions proceed in the presence of catalysts – tetraalkyl ammonium or phosphonium salts or crown ethers. Consequently reacting anions are introduced into the organic phase and react with organic reactants in the form of salts with lipophilic cations supplied by the catalysts. Typical reactions and specific behaviour of organic anions generated in two-phase systems and role of the boundary between the two phases will be discussed.

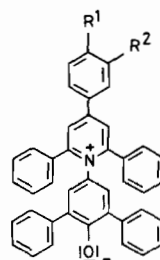
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## Pyridinium-N-Phenoxide Betaine Dyes as Solvent Polarity Indicators. Some New Findings

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The position of the long-wavelength, intramolecular charge-transfer UV/Vis. absorption band of pyridinium-N-phenoxide betaine dyes of the general formula 1 is very sensitive to changes in solvent polarity (negative solvatochromism) [1], temperature (thermo-solvatochromism) [2], external pressure (piezo-solvatochromism) [3], as well as to the introduction of substituents  $R^1$  and  $R^2$  in the 4-phenyl ring [4]. This extreme sensitivity of 1 ( $R^1 = R^2 = H$ ) to small changes in the surrounding medium has been used to establish an empirical scale of solvent polarity, called the  $E_T(30)$ -scale



[1, 5].  $E_T(30)$ -values are simply defined as the transition energy of 1 ( $R^1 = R^2 = H$ ), measured in kcal/mol (or kJ/mol). They are known for more than 150 organic solvents and numerous binary organic solvent/water mixtures, and they have found wide application [5, 6].

It will be shown that empirical parameters of solvent polarity such as the  $E_T(30)$ -values can be understood within the framework of Linear Free-Energy (LFE) Relationships [6].

Examples for the application of  $E_T(30)$ -values to correlate spectral, thermodynamic, and kinetic solvent-dependent data taken from different areas of chemistry will be given.

Finally, the improvement of the LFE-correlations of singular empirical parameters of solvent polarity such as the  $E_T(30)$ -values by means of multi-parametric equations will be described.

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## Solute–Solvent Interactions in Ring Formation

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Physical organic investigations on ring forming reactions from bifunctional substrates over a broad