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Effect of Pressure on Charge Transfer Complexes in Solution

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The stability constants and absorption coefficients of π-π charge transfer complexes were measured in solution at pressures up to 6000 atm. The donors used were hexamethylbenzene, benzene, naphthalene, anthracene, and pyrene, the acceptors tetracyanoethylene, s-trinitrobenzene, 2,4,6-trinitrochlorobenzene, and chloranil. The stability constants increased with pressure in every case and the volumes ΔV of formation of the complexes from their components, varied between -2 and -12 ml mole^{-1}. The pressure changes in K and $h\nu_{CT}$ can be interpreted in terms of shortening of the charge-transfer bond. For complexes of known crystal structure values of ΔV calculated for the solid agree with the values found in solution.

The field of electron donor acceptor complexes has recently been reviewed [1, 2]; the basic theory has changed little since Mulliken's theory.[3] According to this theory the stability of the complexes and the energy of the charge transfer absorption are sensitive to changes in the overlap of the molecular orbitals of the donor and the acceptor molecules and a small change in the separation of the two components should cause large changes in the stability constant K and the charge-transfer (CT) energy ($h\nu_{CT}$). The complexes should thus be sensitive to hydrostatic pressure. Ham [4] for the I_2+benzene system found general agreement with this prediction but analysis of his results was difficult because of the overlap of the CT band and the I_2 absorption band. Gott and Maisch,[5] however, for the TCNE+benzene system obtained results contrary to Mulliken's prediction.

The effect of pressure on solid CT complexes has been investigated by Drickamer and co-workers.[6, 7] Offen,[8] in agreement with all the other measurements on solid CT-complexes found the CT absorption of TNB+ANT complexes to move to lower energies with increase of pressure. CT complexes in solution are sensitive to the solvent properties and different values are found for K and ε (absorption coefficient) and even $h\nu_{CT}$ in different solvents. Early investigations of series of complexes having one component in common indicated an inverse relation between K and ε, and Mulliken and Orgel [9] introduced the notion of contact charge transfer to account for this. These earlier results, however, often included weak complexes and are of doubtful significance.[10]

Increase of pressure can affect the solution spectrum of a given CT-complex by changing the CT energy, the oscillator strength f of the CT transition and the equilibrium constant of complex formation, the two last being observed as an increase in optical density.

The effect of solvent on the energy of the C.T. bands depends on specific solute-solvent interactions.[12] Polar solvents often cause a blue shift relative to non-polar solvents and the effects can not be described by classical solvation theory.[27] As a rule, increased pressure causes a red shift of the absorption in solution as for

solid complexes.[6-8] Exceptional blue shifts have been observed for the same complexes in liquid and in solid solution.[5, 11]

The most marked change with pressure in CT-absorption spectra in solution is the increase in optical density. To ascribe all of this to an increase in the transition moment predicted by Mulliken would, however, neglect the effect of pressure on the association equilibrium,

$$A + D \rightleftharpoons C \qquad (1)$$

between the complex and its component molecules. Only a complete analysis of the optical density observed over a range of donor and acceptor concentrations will allow one to evaluate the two distinct pressure effects on K and on the absorption coefficient ε in liquid solutions.

The effect on K can be due to the volume of the complex being smaller than that of the components, or to the partial polar character of the complex leading to some electrostriction of the solvent around it.[12] Offen and Kadhim,[11] using a solid polymer as solvent for the complexes, consider that all the increase in optical density is due to increase in oscillator strength under those conditions.

In the present work we have examined a number of π-π CT-complexes formed between organic donor and acceptor molecules. We measured the optical densities of their liquid solutions over a range of concentrations and pressures and were able to evaluate K, ε, f and $h\nu_{CT}$. From the change of K with pressure we found the volume change ΔV which accompanies the formation of 1 mole of complex from its components.

EXPERIMENTAL

Hexamethylbenzene (HMB), pyrene (PYR), naphthalene (NAP), anthracene (ANT) were recrystallized from appropriate solvents. Benzene (BEN) was purified by repeated recrystallization and fractional distillation and dried over sodium. Tetrachloro-p-benzoquinone (CA), s-trinitrobenzene (TNB), and 2,4,6,-trinitrochlorobenzene (PIC) were recrystallized from ethanol while tetracyanoethylene (TCNE) was crystallized from chlorobenzene and repeatedly sublimed at 100°C at low pressure immediately before use.

Methylene chloride was dried over KOH and freshly distilled before use. Methylcyclohexane (MCH) was freed from aromatic compounds by long (24 h) stirring with oleum followed by washing, drying and fractional distillation. Fresh solutions were made up each day by weighing the components on a micro-balance. Those containing TCNE were deoxygenated by bubbling solvent-saturated nitrogen through them. TCNE dissolved extremely slowly and prolonged shaking was often necessary.

MCH is a poor solvent for all the acceptors and for the complexes. The solubility of TCNE in it is so low that measurements with it were impossible. MCH was chosen as a solvent for systems containing HMB because this forms complexes with chlorinated solvents.[13]

The concentration of acceptors was *ca.* 10^{-4} mole fraction and that of the donors was between 10^{-3} and 10^{-1} mole fraction and was varied at least five-fold for any one system. Both concentrations were adjusted so as to keep the optical density within suitable limits. The densities of CH_2Cl_2 and MCH over a range of pressure are known from Bridgman's measurements.[14] In some solutions slow reactions took place, consequently fresh samples were used at each pressure.

APPARATUS

The spectra were measured on a UNICAM SP500 spectrophotometer modified to accommodate the high-pressure cell. An additional quartz lens condensed the light beam after it emerged from the monochromator. The cell had two Poulter type[15] $\frac{1}{2}$ in. thick