Effect of Pressure on Charge-Transfer Complexes in Solution.

II. Complexes Formed between Ions and between Ions

and Neutral Molecules

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The effect of pressure on the charge-transfer (CT) absorption of a number of electron donor–acceptor complexes (EDAC) has been measured in solution over a range of 3 kbars and at several temperatures. The EDAC formed between an anion donor and a cation acceptor (4-methoxy-*N*-methylpyridinium iodide) showed a decrease in the stability constant and a blue shift of the CT absorption with increase in pressure. Three EDAC formed between ions and neutral molecules (sodium iodide and trinitrobenzene, tropylium tetrafluoroborate and hexamethylbenzene, and potassium pentamethoxycarbonylcyclopentadienylide and trinitrobenzene) showed little effect of pressure on the stability constant and on the CT maximum. The pressure effects found for these, and for the neutral–neutral complexes investigated earlier, are interpreted qualitatively in terms of the change of solvation of the components and the complexes brought about by the change in pressure.

Introduction

In part I[1] we measured the effect of increased hydrostatic pressure on the formation constant (K) and the charge transfer (CT) absorption energy of electron donor–acceptor complexes (EDAC) formed between π donors and π acceptors in solution and came to the conclusion that a large part of the effect could be explained by changes in the solvation of the donors, acceptors and EDAC with change in pressure. We have now extended our measurements to include EDAC formed between charged donors and acceptors and neutral molecules.

In the case of EDAC formed between ions, the polarities of the ground state and the excited state differ in the opposite sense to those in complexes formed between neutral components; the effect of pressure on these complexes should also be opposite if change in solvation is the predominant factor. For complexes formed between ions and neutral molecules little change in polarity is expected either during formation or on excitation and there should be only small solvent and pressure effects on K and λ_{CT}.

We have measured the absorption spectra of one ion–ion complex, 4-methoxycarbonyl-*N*-methylpyridinium iodide (MMPI), and three ion–neutral complexes, NaI–trinitrobenzene (I⁻–TNB), tropylium tetrafluoroborate–hexamethylbenzene (TRP⁺–HMB), and potassium 1,2,3,4,5-pentamethoxycarbonylcyclopentadienylide–trinitrobenzene(MCP⁻–TNB) over a range of pressures and at several temperatures and have evaluated formation constants and absorption coefficients from them. From the pressure effects we have calculated volume changes of formation.

MMPI was chosen for the measurements because it has been shown that the energy of its CT absorption is strongly solvent dependent[2] and that the CT maximum is well separated from the component absorptions and readily observed. The other systems were chosen to include a variety of ionic donors and acceptors.

Experimental Section

Materials. MMPI and NaI were prepared and recrystallized as in ref 3. 1,3,5-Trinitrobenzene (TNB) was recrystallized twice from ethanol. Hexamethylbenzene (HMB) was recrystallized from methanol. Tropylium tetrafluoroborate (TRP⁺) was prepared by the method of Dauben, *et al.*,[4] and was obtained in good yields, mp 482–483°K; (ref 4 gives 483°K); nmr in CH₃CN: singlet at 556 cps *ex* TMS (ref 5 = 552 cps); uv λ_{max}(CH₃CN) 273.7 nm (log ϵ = 3.7) (ref 4 λ_{max}(CH₃CN) = 273.5 nm (log ϵ = 3.64)). Potassium pentamethoxycarbonylcyclopentadienylide (KMCP) was prepared by the method of Le Goff and LaCount,[6] mp 492–493°K (ref 6 = 493°K); nmr in CH₃CN: singlet at 219 cps *ex* TMS; uv λ_{max}(MeOH) 265 and 294 nm (ref 7 = 265 and 295 nm). Acetone and 2-

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methylpropan-1-ol (i-BuOH) were purified and handled, and their physical properties were evaluated as in ref 3.

Methanol was purified and after distillation was stored and handled under dry nitrogen. Density data were obtained from Timmermans[8] and Bridgman.[9] Acetonitrile was distilled from CaH_2, stored in brown bottles and handled under dry nitrogen. The normal density was obtained from Timmermans[8] and its pressure dependence was measured by a piston displacement method. The results at 303°K were fitted to the Tait equation to give

$$\frac{\Delta V}{V} = 0.229 \log \frac{P + 818}{P + 1}$$

with P in atmospheres.

The spectroscopic measurements were made as described in part I,[1] and the results were evaluated by the methods described there,[10] except that we used Liptay's[11] method to average measurements taken at eight to ten different wavelengths, and an analogous method to select and reject those spectra which showed an anomalous pressure variation at the absorption maximum.[12] By using a criterion of 5% deviation from a mean value, this led to the rejection of 5% of the data.

For equilibria in which ions are involved it is necessary to include an activity coefficient in the definition of the equilibrium constant. For the MMPI system the equilibrium can be defined as

$$^xK_s = \frac{x_c}{(x_0 - x_c)^2 f^2} \quad (1)$$

which assumes unit activity coefficient for the complex of concentration x_c. This leads to the equation for the evaluation of the data

$$\frac{x^{0^2}}{DV} + \frac{DV}{\epsilon^2} = \frac{1}{^xK_s \epsilon f^2} + \frac{1}{\epsilon} 2x^0 \quad (2)$$

where V = molar volume and D = optical density of the solution, ^xK_s and ϵ are the mole fraction formation constant and absorption coefficient of the EDAC, x^0 is the total concentration (in mole fractions) of MMPI, and f is the activity coefficient of MMPI calculated by the Debye–Hückel equation, using $\mathring{a} = 5$ Å as in the evaluation of the conductivity measurements.[3] This may not be the best choice for this parameter when evaluating spectroscopic measurements as was discussed at length by Davies, Otter, and Prue[13] and by Matheson;[14] small variations in $\mathring{a}$, however, do not alter the values of K and ϵ greatly.[14]

For complexes which involve only one ionic component one may assume that the activity coefficients of the complex and the ion are very similar and therefore cancel out in the expression for the equilibrium constant. The equation used for evaluation then takes the form given in footnote 10.
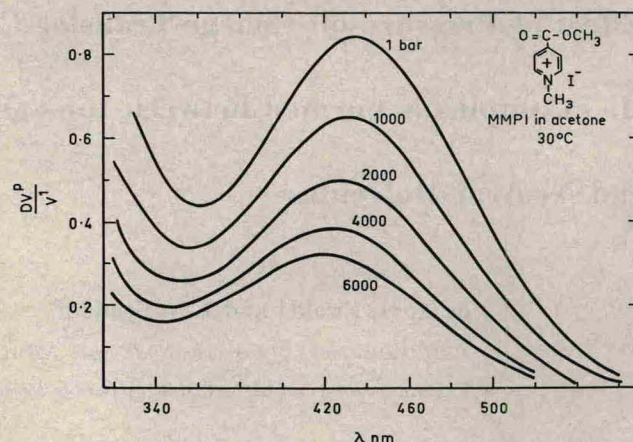
Figure 1. Charge-transfer absorption band of MMPI in acetone at 30° and various pressures. Concentration, 72.3×10^{-5} mole fraction; path length, 1.91 mm.

The evaluation of K and ϵ from spectroscopic measurements has in the last few years been shown to be very uncertain except under rather stringent conditions.[15-17] Owing to the algebraic form of eq 2 it is very difficult to arrive at unique values of K and ϵ, although the product $K\epsilon$ can be determined with greater certainty.[18]

Results and Discussion

A set of spectra of MMPI in acetone at various pressures is shown in Figure 1. The broad absorption bands are typical of EDAC in solution and are one reason why quantitative determination of the absorption maximum is often difficult. In many cases the CT band overlaps the absorption of one of the components (e.g., TNB) and it is necessary to correct for this before the absorption maximum can be found. When comparing spectra at different pressures and temperatures

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(10) The equation given in part I omitted a factor $1/V$ in the first term. It should have read

$$\frac{x_a^0 x_d^0}{D V} + \frac{D V}{\epsilon^2} = \frac{1}{^xK\epsilon} + \frac{1}{\epsilon} (x_a^0 + x_d^0)$$

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