

In contrast to the invariance of the CT maximum with pressure we found that the absorption of the TRP⁺ ion at 275 nm shifted to higher energies by 230 cm⁻¹ at 2026 bars, and showed a slight increase (3%) in ϵ and a larger increase in the oscillator strength calculated from the band width as in ref 1.

MCP⁻-TNB. In contrast to the cyclopentadiene anion, the pentacarbonyl-methoxy substituted anion is stable, and its EDAC with charged acceptors⁶ and the unstable complex formed with TCNE have been studied.²⁷ We found the complex formed between the potassium salt of MCP⁻ and TNB to be sufficiently stable in methanol (less than 5% change in four hours) to make absorption measurements in our usual pressure and temperature range. The concentrations for TNB ranged from 5 to 11 × 10⁻⁵ mole fraction, and for KMCP from 4 to 170 × 10⁻⁵ mole fraction. The CT band was observed as a shoulder on the TNB absorption at ca. 385 nm and the spectrum had to be corrected for the TNB absorption.

The results show that K and ϵ are independent of pressure ($\Delta V = 0$), but that with rising temperature K decreases and ϵ increases.

General Discussion

Within the accuracy of our measurements, K and λ_{CT} for EDAC formed between ions and neutral molecules are pressure independent, but our present and earlier³ measurements indicate a pressure dependence for the ion-ion complex MMPI. Briegleb and his co-workers²¹ found λ_{CT} to be solvent dependent for I⁻-TNB, but were not able to correlate this dependence with any bulk property of the solvent and concluded that specific solvent interactions are important. Beaumont and Davis,²⁷ on the other hand, agree with our results in finding λ_{CT} to be constant for TRP⁺-HMB in most solvents, but to be strongly solvent dependent for TRP⁺-I⁻ and TRP⁺-MCP⁻.

The average thermodynamic quantities for ion-neutral complexes are given in Table III; detailed values for MMPI were reported earlier.³ The values of ΔH and ΔS are very uncertain but indicate rather large negative values, contrary to Briegleb's finding²¹ that $\Delta H \approx 0$ and ΔS is positive for I⁻-TNB. Our ΔH and ΔS values for the ion-neutral complexes have the same sign as those found for neutral-neutral complexes¹ but are about twice as big. It is difficult to account for the large negative entropy, but in the case of the neutral complexes it was found to be highly solvent dependent and, together with the solvent dependence of K for both types of complexes, this indicates the important role solvent interactions play in the stability of EDAC. Similar negative entropies and enthalpies have been observed²⁸ for the formation of "Meisenheimer" complexes between TNB and anions such as CN⁻ and EtO⁻. Although the bond formed in these complexes is differ-

Table III: Values of Thermodynamic Quantities Averaged over All Pressures for Ion-Neutral Complexes^a

	I ⁻ -TNB in MeOH (308°K)	I ⁻ -TNB in <i>i</i> -BuOH (303°K)	TRP ⁺ -HMB in MeCN (308°K)	MCP ⁻ -TNB in MeOH (308°K)
- ΔG	9.9 ± 0.6	17.3 ± 0.6	11.8 ± 0.7	12.2 ± 0.4
- ΔS	130 ± 30	190 ± 80	220 ± 70	200 ± 40
- ΔH	50 ± 10	80 ± 30	80 ± 20	70 ± 10

^a ΔG , ΔH in kJ mol⁻¹, ΔS in J mol⁻¹ °K⁻¹.

ent, their formation involves the desolvation of the anion as for the EDAC.

The effect of pressure on the different types of EDAC is illustrated in the energy diagrams in Figure 4. These diagrams are not quantitative but are given to show the effect of pressure on the CT energy and on the free energy of formation of the EDAC. The molecular dimensions of the complexes are affected only very little by the pressures used in the present experiments and the change will have little effect on the CT energy or the stability of the complex. The solvation of the components and the EDAC is, however, changed by increase in pressure and this in turn changes the stability of the complex if it is either more or less polar than the components from which it is formed. Thus the stability of both neutral-neutral and ion-ion complexes is changed because in one the EDAC is more polar than the components while in the other it is less polar. During the combination of a large ion with a neutral molecule there is not much change in solvation, as was shown earlier²⁹ for the formation of triiodide ions, and it is not surprising that there is no pressure effect on the stability of the ion-neutral EDAC.

The energy of the CT band is affected by the change in solvation brought about by increase in pressure again

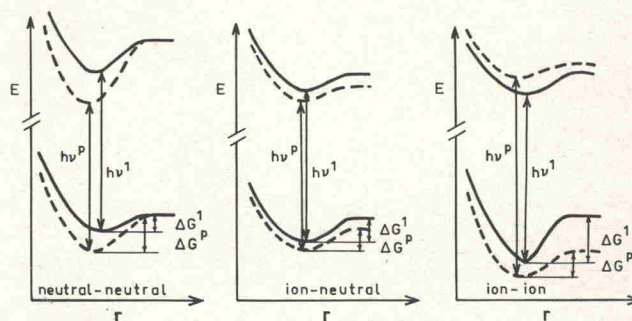


Figure 4. Schematic energy diagrams for three types of EDAC in solution, showing the effect of pressure on the stability ($-\Delta G$) and on the energy of the CT transition ($h\nu$) of the complexes. Key: —, ordinary pressure; ----, high pressure.

(28) E. Bunce, A. R. Norris, W. Proudlock, and K. E. Russell, *Can. J. Chem.*, **47**, 4129 (1969).

(29) A. H. Ewald and S. D. Hamann, *Aust. J. Chem.*, **9**, 54 (1956).

only if there is a change in polarity during excitation. This is the case in the neutral-neutral and the ion-ion complexes and in the case of MMPI it is reinforced by the change in direction of the dipole moment in the excited state. Changes in solvent polarity should on the whole parallel the changes caused by increase in pres-

sure, but the picture is often complicated by specific solvent-solute interactions.

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