

## 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<sup>1</sup> 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  $\pi$  donors and  $\pi$  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  $\lambda_{CT}$ .

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<sup>2</sup> 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.*,<sup>4</sup> and was obtained in good yields, mp 482-483°K; (ref 4 gives 483°K); nmr in  $CH_3CN$ : singlet at 556 cps *ex* TMS (ref 5 = 552 cps); uv  $\lambda_{max}(CH_3CN)$  273.7 nm ( $\log \epsilon = 3.7$ ) (ref 4  $\lambda_{max}(CH_3CN) = 273.5$  nm ( $\log \epsilon = 3.64$ )). Potassium pentamethoxycarbonylcyclopentadienylide (KMCP) was prepared by the method of Le Goff and LaCount,<sup>6</sup> mp 492-493°K (ref 6 = 493°K); nmr in  $CH_3CN$ : singlet at 219 cps *ex* TMS; uv  $\lambda_{max}(MeOH)$  265 and 294 nm (ref 7 = 265 and 295 nm). Acetone and 2-

(1) A. H. Ewald, *Trans. Faraday Soc.*, **64**, 733 (1968); referred to as part I.

(2) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958); **83**, 3147 (1961).

(3) A. H. Ewald and J. A. Scudder, *Aust. J. Chem.*, **23**, 1939 (1970).

(4) H. P. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(5) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

(6) E. Le Goff and R. B. LaCount, *J. Org. Chem.*, **29**, 423 (1964); *J. Amer. Chem. Soc.*, **85**, 1354 (1963).

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<sup>8</sup> and Bridgman.<sup>9</sup> Acetonitrile was distilled from CaH<sub>2</sub>, stored in brown bottles and handled under dry nitrogen. The normal density was obtained from Timmermans<sup>8</sup> 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,<sup>1</sup> and the results were evaluated by the methods described there,<sup>10</sup> except that we used Liptay's<sup>11</sup> 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.<sup>12</sup> 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

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

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

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

where  $V$  = molar volume and  $D$  = optical density of the solution,  ${}^x K_s$  and  $\epsilon$  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  $\bar{a} = 5 \text{ \AA}$  as in the evaluation of the conductivity measurements.<sup>3</sup> This may not be the best choice for this parameter when evaluating spectroscopic measurements as was discussed at length by Davies, Otter, and Prue<sup>13</sup> and by Matheson;<sup>14</sup> small variations in  $\bar{a}$ , however, do not alter the values of  $K$  and  $\epsilon$  greatly.<sup>14</sup>

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.

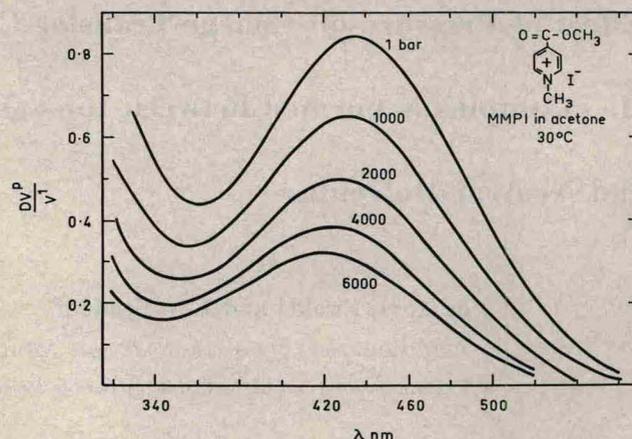


Figure 1. Charge-transfer absorption band of MMPI in acetone at 30° and various pressures. Concentration,  $72.3 \times 10^{-5}$  mole fraction; path length, 1.91 mm.

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

## 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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(8) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950.

(9) P. W. Bridgman, "The Physics of High Pressure," 2nd ed, Bell, London, 1949.

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

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

(11) W. Liptay, *Z. Elektrochem.*, **65**, 375 (1961).

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(14) R. A. Matheson, *J. Phys. Chem.*, **69**, 1537 (1965); **70**, 3368 (1966).

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(16) W. B. Person, *ibid.*, **87**, 167 (1965).

(17) R. A. LaBuddle and M. Tamres, *J. Phys. Chem.*, **74**, 4009 (1970).

(18) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London, 1969, p 158.

it is necessary to allow for the change in density of the solution. For the very dilute solutions used in the present work, adequate correction is obtained by multiplying the optical density by the relative volume of the solvent referred to some standard condition. Such a correction has been applied to the measurements shown in Figure 1.

Table I gives the wavelength of the CT maximum,  $\lambda_{CT}$ , and the energy shift of it at 3040 bars ( $\delta\nu$  in  $\text{cm}^{-1}$ ), as well as the equilibrium constants and absorption coefficients found at 1 bar and the volume change derived from the pressure variation of  $K$ , for the different complexes we have examined.

**Table I:** Equilibrium Constants, Absorption Coefficients, and CT Maxima of EDAC in Solution

Complex (solvent)	Temp, °K	$\lambda_{CT}$ , nm	$\delta\nu$ (3040 bars), $\text{cm}^{-1}$	$K$ , (mole fraction) $^{-1}$	$\epsilon$ , $\text{mol l.}^{-1} \text{cm}^{-1}$	$\Delta V$ , $\text{cm}^3 \text{mol}^{-1}$
MMPI (acetone)	265.2			2680 <sup>a</sup>		
	275.2			4180 <sup>a</sup>		
	293.2	427	416	3600	1060	
	303.2	429	590	3200	930	+16
	313.2	434	660	3000	1710	
MMPI ( <i>i</i> -BuOH)	303.2	372	220	43000	910	+17
	298.2	360	0	87	390	0
I <sup>-</sup> -TNB (MeOH)	318.2		0	27	940	
	298.2	365	0	1540	575	
I <sup>-</sup> -TNB ( <i>i</i> -BuOH)	308.2		0	550	340	
	303.2	417 ± 3	0	165	455	0
TRP <sup>+</sup> -HMB (CH <sub>3</sub> CN)	313.2	413 ± 2	0	52	1180	
	303.2	382	0	194	1260	0
MCP <sup>-</sup> -TNB (MeOH)	313.2	385	0	73	2620	

<sup>a</sup> From ref 3.

Figure 2 is a plot of the values of  $\log K^p/K^1$  as a function of pressure and includes<sup>1</sup> the neutral complex TNB-HMB for comparison. Figure 3 shows the values of  $\delta\nu$  found for the complexes at various pressures. Values for TNB-HMB are again included. The pressure shift is zero within the accuracy of the measurements for all the ion-neutral EDAC and only the TRP<sup>+</sup>-HMB complex is shown.

We shall discuss the individual systems first and then draw some general conclusions.

**MMPI.** The spectra of this salt were measured in acetone at three temperatures, and in *i*-BuOH at one temperature, at five pressures between 1 and 3040 bars. The concentration range was 5 to 80 × 10<sup>-5</sup> mole fraction MMPI.<sup>12</sup> The absorption band in *i*-BuOH was found at a shorter wavelength and showed less pressure shift than the band in acetone. The great sensitivity of the MMPI/CT band to solvent polarity has been attributed by Kosower<sup>2</sup> to a "dipole flip" of the complex during excitation which, due to the Franck-Condon

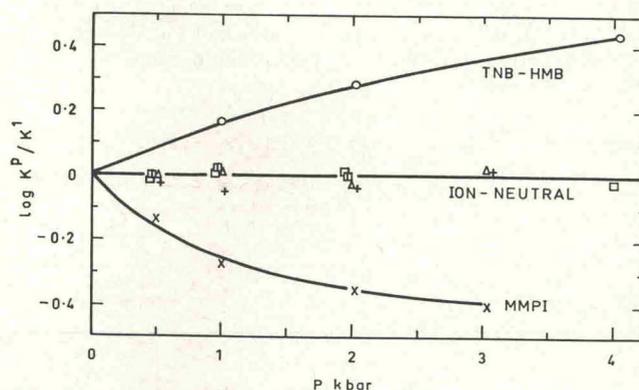


Figure 2. Effect of pressure on the relative stability of various EDAC.

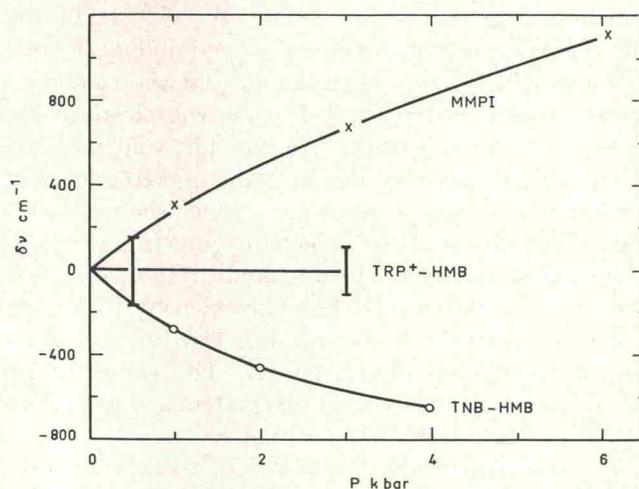


Figure 3. Effect of pressure on the energy of the CT transition of various EDAC.

effect, leads to a mismatch between the dipole field of the excited complex and the reaction field of the solvent around it. This destabilizes the excited state relative to the ground state and leads to a blue shift of the absorption band when the solvent interaction is increased by increase of pressure.

The system has been the subject of a detailed conductometric investigation<sup>3</sup> and this led to association constants which were rather different (Table II) from those found spectroscopically and given in Table I. According to Prue's "optical marker" argument<sup>19</sup> the two methods could give the same association constant even if not all the associated species give a CT absorption; the  $\epsilon$  derived from spectroscopic measurements on such systems, on the other hand, is a weighted average of the absorption coefficient of the different associated species. We therefore carefully analyzed our present results to see whether the difference between them and the earlier results is significant.

(19) J. E. Prue in "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barradas, Ed., Wiley, New York, N. Y., 1966, p 170.

**Table II:** MMPI Association Constants at 1 bar Found Conductometrically (from Ref 3 Converted to (mole fraction)<sup>-1</sup> Units)

Temp, °K	265.2	275.2	293.2	303.2	313.2
	—In acetone—				
$K_\gamma \times 10^{-3}$	2.68	4.18	8.11	8.56	13.3
	—In <i>i</i> -BuOH—				
$K_\gamma \times 10^{-3}$	...	...	...	52.1	...

We used a computer to map out the standard deviation in the fit of eq 2 as a function of  $K$  and  $\epsilon$ . This showed the minimum to lie in a long, narrow, approximately hyperbolic valley, along which the value of the standard deviation varies little. We calculated the 90% confidence limits for  $K$  and  $\epsilon$  by applying a  $\chi^2$  test to the residual variance and found that the conductometric association constant  $K_\gamma$  was contained within these limits in every case. We therefore conclude that the difference between  $K_\gamma$  and the spectroscopically determined  $K_s$  is *not significant*. Since the conductometric measurements are inherently much more accurate ( $\pm 10\%$ ),<sup>3</sup>  $K_\gamma$  is the best estimate of the association constant in this system. For convenience we quote in Table II the values from ref 3, converted to mole fraction units as used in this paper. The values of  $\log K^p/K^1$  shown in Figure 2 for this system and the values of  $\Delta V$  in Table I are derived from  $K_\gamma$ .

The positive values of  $\Delta V$  are in marked contrast with the contractions found for the EDAC formed from neutral molecules and indicate the important role of desolvation when the EDAC is formed from the component ions. The magnitude of  $\Delta V$  is not as great as one would expect for completed desolvation of a pair of ions (30–40 cm<sup>3</sup>/mol, from kinetic measurements<sup>20</sup>) and this, together with the solvent sensitivity of the CT energy, indicates that the EDAC is still solvated.

*I<sup>-</sup>-TNB.* The color produced when iodide solutions are added to TNB solutions has been attributed to the formation of EDAC.<sup>21–23</sup> Briegleb, *et al.*,<sup>21</sup> found the absorption maximum to be solvent dependent and measured the formation constant and absorption coefficient in a series of solvents using different salts as sources of I<sup>-</sup> ions. He showed by infrared studies that the complexes differed from "Meisenheimer" complexes, and we confirmed this by nmr measurements.

In our measurements NaI was used as the source of I<sup>-</sup> and for the measurements in methanol the concentrations ranged from 250 to 1000  $\times 10^{-5}$  mole fraction I<sup>-</sup>, and from 5 to 9  $\times 10^{-5}$  mole fraction TNB. In *i*-BuOH the solutions darken in the course of a few hours,<sup>21</sup> but this effect can be suppressed by the addition of a small amount (*ca.* 10<sup>-4</sup> M) of glacial acetic acid. The concentration of I<sup>-</sup> in this solvent was 15 to 300  $\times 10^{-5}$  mole fraction and that of TNB 3 to 30  $\times$

10<sup>-5</sup> mole fraction. The CT band was observed as a shoulder on the TNB absorption and the spectra had to be corrected for this absorption.

NaI is known to be almost completely dissociated in MeOH<sup>24,25</sup> and the EDAC formation is therefore not complicated by any ion pair equilibrium. Our results show the CT energy and the equilibrium constant to be unchanged by pressure, but  $\epsilon_{\max}$  was found to increase slightly with pressure.

In *i*-BuOH only 75% of NaI is dissociated<sup>3</sup> and two different complexes can be formed, one between free I<sup>-</sup> and TNB and therefore carrying a negative charge, and the other from an ion pair and TNB and carrying no charge. These cannot be distinguished in the present experiments. The results in this solvent are similar to those in MeOH except for larger values of  $K$  and a decrease of  $\epsilon$  with rising temperature. This last effect could occur if the charged EDAC had a larger  $\epsilon$  than the uncharged complex, since with rising temperature the ion pairing in *i*-BuOH increases<sup>3</sup> and the observed average  $\epsilon$  would thus decrease.

In both solvents  $K$  is independent of pressure and  $\Delta V = 0$ . Comparison between the negative  $\Delta V$  found for neutral complexes<sup>1</sup> and the positive value for MMPI suggests that the contraction due to the formation of the CT bond is just balanced by the reduced electrostriction of the solvent due to the spreading of the ionic charge.

*TRP<sup>+</sup>-HMB.* The tropylium halides do not give stable solutions and are therefore not suitable for lengthy measurements. The tetrafluoroborate is stable in acetonitrile and was used in these measurements at concentrations between 15 and 150  $\times 10^{-5}$  mole fraction. The  $\pi$ - $\pi$  complex formed by TRP<sup>+</sup> with mesitylene<sup>26</sup> has  $K = 13$  and in order to measure a larger  $K$  we used HMB as the donor at concentrations between 25 and 140  $\times 10^{-5}$  mole fraction. The solid brown complex could be obtained by evaporating the solutions and gave an ir spectrum equal to an intimate mixture of the components and a uv spectrum, as a mull, similar to the EDAC in solution.

The EDAC has a very broad CT band at 417 nm and the position has been found to be solvent independent.<sup>27</sup> The pressure measurements showed that  $K$  is independent of  $P$  ( $\Delta V = 0$ ), but  $\epsilon$  increases slightly with increasing pressure. A rise in temperature caused a decrease in  $K$  and an increase in  $\epsilon$ .

(20) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

(21) G. Briegleb, W. Liptay, and R. Fick, *Z. Elektrochem.*, **66**, 851 (1962).

(22) K. M. C. Davis, *J. Chem. Soc., B*, 1128 (1967).

(23) K. M. C. Davis, *ibid.*, 1020 (1969).

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(25) R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *ibid.*, **75**, 2855 (1953).

(26) M. Feldman and S. Winstein, *ibid.*, **83**, 3338 (1961).

(27) T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc., B*, 1010 (1968).

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

**MCP<sup>-</sup>-TNB.** In contrast to the cyclopentadiene anion, the pentacarbonyl-methoxy substituted anion is stable, and its EDAC with charged acceptors<sup>6</sup> and the unstable complex formed with TCNE have been studied.<sup>27</sup> We found the complex formed between the potassium salt of MCP<sup>-</sup> 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  $\times 10^{-5}$  mole fraction, and for KMCP from 4 to 170  $\times 10^{-5}$  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  $\epsilon$  are independent of pressure ( $\Delta V = 0$ ), but that with rising temperature  $K$  decreases and  $\epsilon$  increases.

### General Discussion

Within the accuracy of our measurements,  $K$  and  $\lambda_{CT}$  for EDAC formed between ions and neutral molecules are pressure independent, but our present and earlier<sup>3</sup> measurements indicate a pressure dependence for the ion-ion complex MMPI. Briegleb and his co-workers<sup>21</sup> found  $\lambda_{CT}$  to be solvent dependent for I<sup>-</sup>-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,<sup>27</sup> on the other hand, agree with our results in finding  $\lambda_{CT}$  to be constant for TRP<sup>+</sup>-HMB in most solvents, but to be strongly solvent dependent for TRP<sup>+</sup>-I<sup>-</sup> and TRP<sup>+</sup>-MCP<sup>-</sup>.

The average thermodynamic quantities for ion-neutral complexes are given in Table III; detailed values for MMPI were reported earlier.<sup>3</sup> The values of  $\Delta H$  and  $\Delta S$  are very uncertain but indicate rather large negative values, contrary to Briegleb's finding<sup>21</sup> that  $\Delta H \approx 0$  and  $\Delta S$  is positive for I<sup>-</sup>-TNB. Our  $\Delta H$  and  $\Delta S$  values for the ion-neutral complexes have the same sign as those found for neutral-neutral complexes<sup>1</sup> 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 observed<sup>28</sup> for the formation of "Meisenheimer" complexes between TNB and anions such as CN<sup>-</sup> and EtO<sup>-</sup>. Although the bond formed in these complexes is differ-

**Table III:** Values of Thermodynamic Quantities Averaged over All Pressures for Ion-Neutral Complexes<sup>a</sup>

	I <sup>-</sup> -TNB in MeOH (308°K)	I <sup>-</sup> -TNB in <i>i</i> -BuOH (303°K)	TRP <sup>+</sup> -HMB in MeCN (308°K)	MCP <sup>-</sup> -TNB in MeOH (308°K)
$-\Delta G$	9.9 $\pm$ 0.6	17.3 $\pm$ 0.6	11.8 $\pm$ 0.7	12.2 $\pm$ 0.4
$-\Delta S$	130 $\pm$ 30	190 $\pm$ 80	220 $\pm$ 70	200 $\pm$ 40
$-\Delta H$	50 $\pm$ 10	80 $\pm$ 30	80 $\pm$ 20	70 $\pm$ 10

<sup>a</sup>  $\Delta G$ ,  $\Delta H$  in kJ mol<sup>-1</sup>,  $\Delta S$  in J mol<sup>-1</sup> °K<sup>-1</sup>.

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 earlier<sup>29</sup> 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

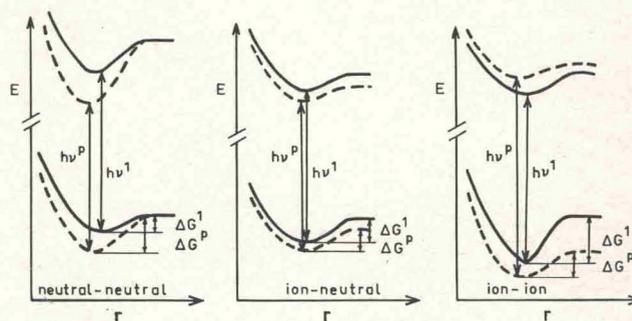


Figure 4. Schematic energy diagrams for three types of EDAC in solution, showing the effect of pressure on the stability ( $-\Delta G$ ) and on the energy of the CT transition ( $h\nu$ ) of the complexes. Key: —, ordinary pressure; ----, high pressure.

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(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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