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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. Ham⁴ 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 Orgel⁹ 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,



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 type¹⁵ $\frac{1}{2}$ in. thick

sapphire windows. It was connected to a pressure intensifier by stainless steel capillary tubing and could be used to 8000 atm with petroleum ether containing 10 % paraffin oil as pressure medium. The pressure in the optical cell was measured in terms of the primary pressure on the intensifier which was calibrated to 6000 atm with a Bourdon gauge. The temperature of the cell was measured with a mercury thermometer sitting in a 2 in. deep hole and was controlled manually to $\pm 0.1^\circ\text{C}$. The solutions were contained in a small stainless steel cell.¹⁶ For some solutions fresh polythene O rings and a fresh polythene plug were used for each measurement in order to avoid contamination.

Blank corrections were determined at each wave length and at each pressure, and, to allow for possible irreproducibility in assembling the cell, all measurements were taken relative to some wavelength at which the CT complex does not absorb (usually 600 $m\mu$, sometimes 750 $m\mu$). This procedure was facilitated by using as a reference an optical path of the same geometry as the high-pressure path but empty and fitted with an iris diaphragm. Corrections for the absorption by the acceptor, when this overlapped the CT band, were determined at each pressure in separate experiments.

Neither CH_2Cl_2 nor MCH freeze under the conditions used but some of the solutions containing relatively high concentrations of the heavier hydrocarbon donors sometimes solidified at the highest pressure. With MCH solutions the solubility of the CT-complex was sometimes exceeded at the higher pressure and the coloured complex crystallized out.

EVALUATION OF DATA

A first approximation to the mole fraction equilibrium constant *K and the absorption coefficient ϵ of the complex was obtained by the method of Benesi and Hildebrand.¹⁷ A further approximation was found by using the exact equation,

$$\frac{x_a^0 x_d^0}{D} + \frac{DV}{\epsilon^2} = \frac{1}{{}^*K\epsilon} + \frac{1}{\epsilon}(x_a^0 + x_d^0), \quad (2)$$

in which x_a^0 and x_d^0 are the initial mole fraction of acceptor and donor respectively, D is the optical density at ν_{max} corrected for the absorption by the pure components, *K and ϵ are the unknown mole fraction equilibrium constant and the absorption coefficient multiplied by the optical path length in cm. The molar volume V of the solution is assumed to be equal to that of the solvent. This equation was fitted to experimental data by a least-square method in which it is assumed that the second term on the left hand side is constant.¹⁸ The difference between using this method and curve fitting the Benesi-Hildebrand equation was generally negligible.

The final adjustment of the constants was made by comparing calculated and observed values of the optical density directly¹⁰ and minimizing $\Sigma(D_{\text{calc.}} - D_{\text{obs.}})^2$ by a Simplex method.¹⁹ This method was more reliable than the method of steepest descent which for these "noisy" data gave results which depended on the starting values of *K and ϵ .*

Only 1 : 1 complexes are formed in our solutions according to published work.¹ CT-bands are characteristically broad and the ν_{max} were estimated by taking the mean of the maxima of all the measurements on a particular system. The accuracy is usually greater at higher pressure due to the greater intensity of the bands. In systems involving CA, TNB, and PIC, the absorption by the acceptor overlaps the CT band and the optical density was corrected for this in order to find the ν_{max} (see fig. 1).

The oscillator strength f of the CT-absorption could be evaluated directly, by graphical integration of the area under the absorption curve plotted on a wave number scale, only for a few systems (TCNE+NAP, CA+NAP, TCNE+BEN) because of the overlap of the absorption bands. In the other case, f was estimated from $\epsilon_{\text{max}} \Delta\nu_{\frac{1}{2}}$, where $\Delta\nu_{\frac{1}{2}}$ is the band width at $\epsilon = \frac{1}{2}\epsilon_{\text{max}}$. If $\Delta\nu_{\frac{1}{2}}$ could not be measured we used the empirical formula of

*I acknowledge the help of Dr. R. Leslie and Mr. D. Shaw of C.S.I.R.O., Division of Mathematical Statistics in evaluating these methods and in computing the answers.

Briegleb (ref. (1), p. 46) which takes account of the dissymmetry of the CT bands. The oscillator strength is then given by²⁰

$$f = 4.319 \times 10^{-9} \int \epsilon dv = 10.36 \times 10^{-9} \epsilon_{\max}(v_{\max} - v_{\frac{1}{2}L}), \quad (3)$$

where $v_{\frac{1}{2}L}$ is the half-height frequency at the red side of the maximum of the CT-band. Some values are shown as a function of pressure in fig. (4).

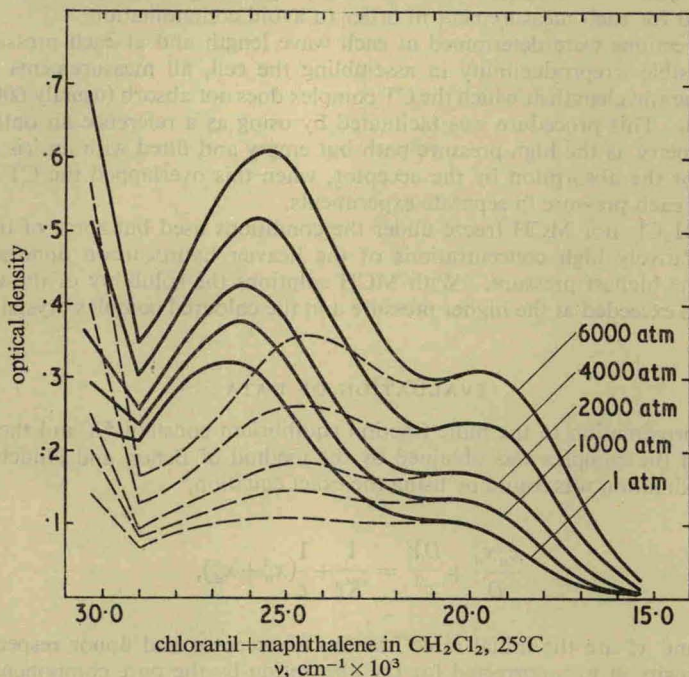


FIG. 1.—Absorption spectrum of CA+NAP complex in methylene chloride at various pressures. The dashed curves are corrected for CA absorption.

ERRORS IN K AND ϵ

The reliability of the best values of K and ϵ can be calculated directly only if they are obtained by fitting a linear equation. Conrow *et al.*¹⁰ devised one measure of the reliability of K derived from non-linear equation; instead, we calculated the standard deviation of the values obtained by fitting the Benesi-Hildebrand equation and these are given (expressed as %) in table 1. These deviations overestimate the uncertainty of the final values in the tables. A large uncertainty in *K and ϵ is, however, inherent in the method of finding both quantities simultaneously from optical density data. In many cases, limited solubility made it impossible to use the optimum experimental conditions¹⁰ for the measurements.

The error in ϵ directly enters into the estimate of the oscillator strength and adds to the uncertainty introduced by use of eqn. (3). For donors which form complexes with two CT-bands, the higher energy band is often completely hidden in the acceptor absorption and still further uncertainty is introduced, even into relative values of f , by possible changes in the relative intensities of the two bands.

The volume changes ΔV associated with the formation of the CT complexes from their components can be calculated from the equilibrium constants by the equation

$$d \ln K/dP = -\Delta V/RT, \quad (4)$$

and are given by the slopes of curves such as shown in fig. 2. The uncertainty in ΔV varies between $\pm 0.5 \text{ cm}^3 \text{ mole}^{-1}$ to several $\text{cm}^3 \text{ mole}^{-1}$ for the systems which gave less satisfactory K values.

TABLE 1.—EQUILIBRIUM CONSTANTS AND ABSORPTION COEFFICIENTS OF CHARGE TRANSFER COMPLEXES

The first line at each temperature gives the value of K in mole fraction units, the second the values of $\epsilon \times 10^{-3}$ l. mole⁻¹ cm⁻¹.

complex (solvent)	temp.	1 atm	1000	2000	4000	6000	average s.d. %
CA+HMB (MCH)	30	121	184	262	502		20
		2.41	2.72	3.06	3.51		5
	50	52	56	92	143		37
TNB+HMB (MCH)	30	2.5	3.3	3.2	3.7		11
		85	123	163	223		10
	40	2.17	2.22	2.34	2.80		5
TCNE+HMB (CH ₂ Cl ₂)	30	63	84	125	200		7
		2.19	2.21	2.34	2.59		8
	30	156	290	368	743	1151	19
TCNE+BEN (CH ₂ Cl ₂)	30	5.4	4.9	5.5	5.5	5.2	16
		3.26	4.04	3.54	5.07	6.5	10
	30	2.00	2.02	2.56	2.44	2.4	9
TCNE+NAP (CH ₂ Cl ₂)	30(I)	10.2	12.2	15.9	20.6	30.5	8
		1.30	1.40	1.35	1.50	1.43	5
	30(II)	11.1	12.7	16.9	19.9	28.5	7
TNB+NAP (CH ₂ Cl ₂)	25	1.15	1.23	1.13	1.27	1.19	5
		19	13	12	17	22	20
	25(I)	0.9	1.4	1.7	1.7	1.7	12
CA+NAP (CH ₂ Cl ₂)	25(I)	7	9	11	10	12	18
		1.0	1.0	0.8	1.3	1.0	16
	25(II)	10	10	13	10	17	28
CA+PYR (CH ₂ Cl ₂)	30	0.7	0.9	0.8	1.4	1.3	21
		27	23	28	40	58	14
	30	9.3	13	14	14	15	10
TNB+ANT (CH ₂ Cl ₂)	30	9	9	20	22		47
		3.4	2.2	2.1	2.6		47
	30	147	249	249	261		25
PIC+ANT (CH ₂ Cl ₂)	30	1.4	1.2	1.5	2.1		25
		20		13	27		30
	30	0.7		1.5	1.0		31
PIC+ANT (MCH)	30	35	36	131	193		
		1.8	2.5	1.0	1.2		

(I) and (II) refer to the lower and higher energy absorption band respectively.

TABLE 2.—ABSORPTION MAXIMA AND ΔV OF FORMATION OF CHARGE TRANSFER COMPLEXES

complex	temp. °C	λ_{\max} m μ	$-\Delta V$ 1 atm cm ³ mole ⁻¹	$-\Delta V$ 4000 atm cm ³ mole ⁻¹
CA+HMB	30	509	11	8
	50	509	8	6
TNB+HMB	30	387	10	4
	40	387	10	6
TCNE+HMB	30	540	12	9
TCNE+BEN	30	388	3	(a)
TCNE+NAP	30	500-428	4	(a)
TNB+NAP	25	365	3	(a)
CA+NAP	25	480-397	5	(a)
CA+PYR	30	609	5	(a)
TNB+ANT (CH ₂ Cl ₂)		448	5	(b)
TNB+ANT (MCH)		444	5	(b)
PIC+ANT (CH ₂ Cl ₂)		431	8	(b)
PIC+ANT (MCH)		444	12	(b)

(a) The volume changes are constant within the experimental accuracy over the whole pressure range.

(b) approximate values.

RESULTS AND DISCUSSION

The equilibrium constants in mole fraction units and absorption coefficients are summarized in table 1 and the volume changes associated with the formation of the CT complexes and the absorption maxima of these are given in table 2. The shifts of absorption maxima observed at various pressures are shown in fig. 3, while the change in oscillator strength is shown in fig. 4.

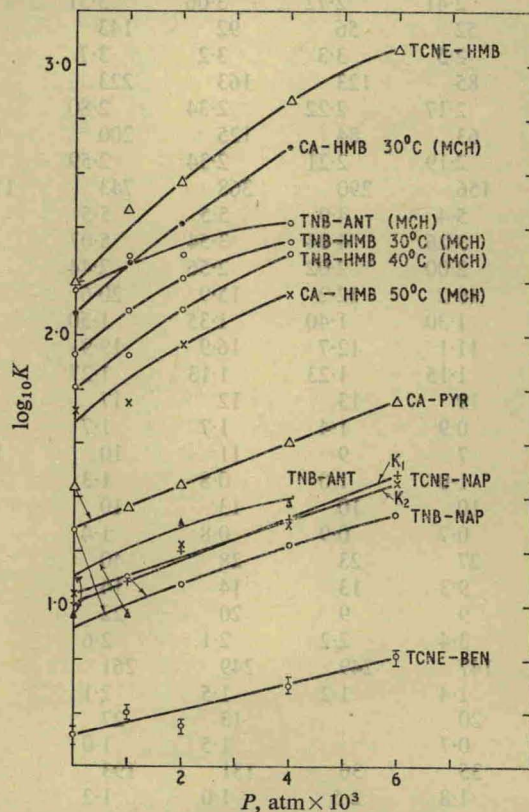


Fig. 2.—Log (stability constant) as a function of pressure. Methylene chloride solvent except where marked (MCH).

We discuss first the individual systems.

CA+HMB. This system was measured at 30 and 50°C and values of ΔH and ΔS calculated from the equilibrium constants are given in table 3. Although the accuracy of the data is not great they show a definite increase of $-\Delta H$ and $-\Delta S$ with pressure. There is an increase of 45% in oscillator strength at 4000 atm which is paralleled by the increased in ϵ_{\max} . There is thus no increase in bandwidths.

TABLE 3.—THERMODYNAMIC FUNCTIONS FOR CA+HMB COMPLEXES IN MCH AT 30°C
kcal/mole OR cal mole⁻¹ deg.⁻¹

P atm	1	1000	2000	4000
ΔG	-2.9	-3.2	-3.4	-3.8
ΔH	-8.2	-9.3	-10.2	-12.3
ΔS	-17	-20	-22	-28

TNB+HMB. There is an overlap between the CT-band and the absorption by TNB and this had to be corrected for in determining the band maximum. The absorption coefficients found at 30 and 40°C are not significantly different and

mean values were used in calculating f ; this increased 20% without increase in bandwidth. ΔH was between 2 and 7 kcal/mole at various pressures but the values are too approximate to establish any trends.

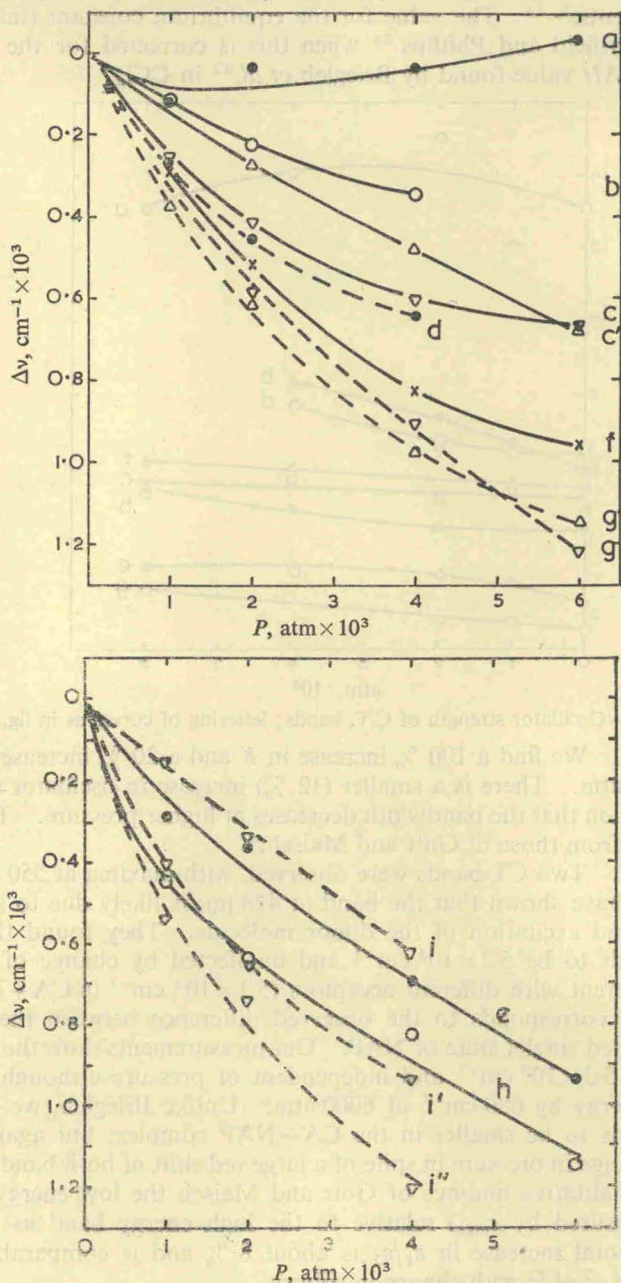


FIG. 3.—Pressure shift of C.T. absorption maxima. In methylene chloride except where indicated. (a) TCNE+HMB; (b) CA+HMB, (MCH); (c) and (c'), first and second max. of TCNE+NAP; (d) TNB+HMB (MCH); (e) CA+PYR; (f) TCNE+BEN; (g) and (g'), first and second max. of CA+NAP; (h), TNB+NAP, (i), (i'), (i'') TNB+ANT in CH_2Cl_2 , MCH, EtOH respectively.

TCNE+HMB. This system could not be measured in MCH because of the low solubility of TCNE in this solvent. The pressure shift of the CT-maximum in CH_2Cl_2 is unusual in going through a minimum and our observations confirm earlier measurements.^{5, 11} The value for the equilibrium constant (table 1) agrees with that of Merrifield and Phillips²¹ when this is corrected for the temperature difference by the ΔH value found by Briegleb *et al.*²² in CCl_4 .

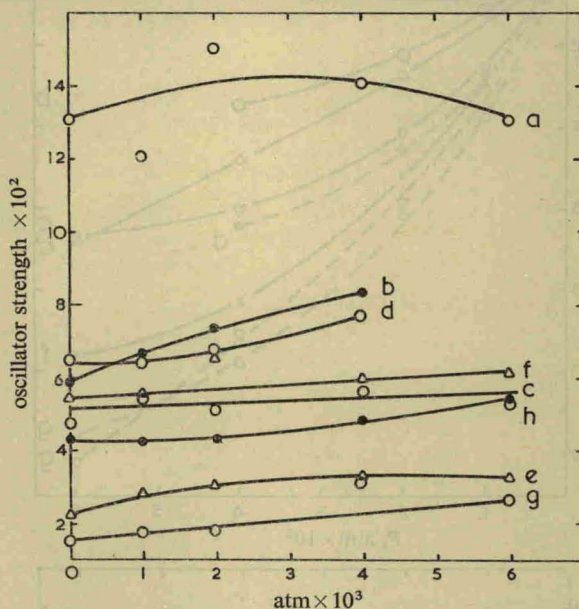


FIG. 4.—Oscillator strength of C.T. bands; lettering of curves as in fig. 3.

TCNE+BEN. We find a 100 % increase in K and a 20 % increase in ϵ for this complex at 6000 atm. There is a smaller (12 %) increase in oscillator strength and thus some indication that the bandwidth decreases at higher pressure. The quantitative results differ from those of Gott and Maisch.⁵

TCNE+NAP. Two CT-bands were observed, with maxima at 550 and 428 $m\mu$. Briegleb *et al.*²² have shown that the band at 428 $m\mu$ is likely due to simultaneous CT absorption and excitation of the donor molecule. They found the difference between the bands to be $5.2 \times 10^3 \text{ cm}^{-1}$ and unaffected by change of solvent and only slightly different with different acceptors ($5.1 \times 10^3 \text{ cm}^{-1}$ in CA+NAP). This energy difference corresponds to the observed difference between the lowest and the strongest excited singlet state of NAP. Our measurements show the gap between the bands to be $5.3 \times 10^3 \text{ cm}^{-1}$ and independent of pressure although both bands shift to lower energy by 680 cm^{-1} at 6000 atm. Unlike Briegleb, we find the gap between the bands to be smaller in the CA+NAP complex, but again to remain constant with change in pressure in spite of a large red shift of both bands. In agreement with the qualitative findings of Gott and Maisch the low energy band gains intensity (as measured by ϵ_{max}) relative to the high energy band as the pressure increases. The total increase in ϵ_1/ϵ_2 is about 8 % and is comparable with that found by Briegleb *et al.*²² with change in solvent.

TNB+NAP. The TNB absorption overlaps the CT bands, and even after correction for this only the low energy band could be measured. The correction usually was a large part of the measured optical density and the accuracy of the results, particularly those at low pressure, is low.

CA+NAP. The absorption curves for this system are illustrated by fig. 1. The CA absorption overlaps the high energy band and the dotted lines show the CT absorption after correction for this. The figure shows why only low accuracy can be expected for K values derived from a series of such curves, particularly at low pressure where the absorption due to the CA is large compared with that due to the complex. In this case the high energy band appears to gain intensity relative to the low energy band, in contrast to the TCNE+NAP system. The band separation remains constant within the accuracy of the measurements.

CA+PYR. The absorption coefficient and estimated oscillator strength are much larger than that of the other complexes. There are two overlapping CT bands,²² but only the low energy peak could be observed since the other peak at 438 $m\mu$ overlaps both the PYR and the CA absorption bands.

Briegleb *et al.*²² have shown that in the TCNE+PYR complex the absorption intensity shift in favour of the low energy band on cooling to -180°C and similar intensity shifts with change of pressure were found by us and by Offen and Kadhim¹¹ for TCNE+NAP and by Gott and Maisch⁵ for TCNE+diphenyl. Offen and Eliason²³ have also shown that PYR alone shows an abnormally large pressure induced red shift coupled with an increase in the oscillator strength of its lowest energy band. Hence the large increase in the oscillator strength found for CA+PYR is probably due to a similar shift in the relative intensity of the two CT bands, since the oscillator strength was estimated from $\Delta\nu_{\pm L}$ of the low energy band.

TNB+ANT. This system was measured in CH_2Cl_2 and in MCH in order to compare the volume effects in the two solvents. Particularly at 1 atm, there is a large overlap between the TNB absorption and the CT band. In spite of the large difference in equilibrium constant between the two solvents similar values of ΔV were found. The pressure induced shift of the CT band was measured for this system also in ethanol. The complex is much less stable in this solvent and shows a large $\Delta\nu$ (fig. 3b).

PIC+ANT. This complex was also measured in CH_2Cl_2 and in MCH as solvents and the results again indicate a much lower value of K in MCH than in CH_2Cl_2 . The weak complex formed in CH_2Cl_2 and the large band overlap make the determination of ΔV at 1 atm uncertain, but extrapolation from the high pressure values of $\log K$ indicate a value of $-\Delta V > 9 \text{ cm}^3/\text{mole}$. In MCH the value is about $16 \text{ cm}^3/\text{mole}$. Comparison of these values with those for the previous system show a slightly larger pressure effect for this system in which steric crowding of the acceptor molecule might be expected to hinder the formation of the complex. Apparently the application of pressure helps to overcome this hindrance and enhances the complex formation.

GENERAL

The three effects of pressure are clearly shown by the results. The red shift of the CT band due to increased interaction with the solvent occurs for every complex except TCNE+HMB, for which the shift changes sign above 1000 atm. In every case, $\Delta\nu$ is nearly a linear function of the density of the solvent. Other properties of the solvent such as refractive index or Lorentz-Lorenz function, would probably give equally linear plots. The red shift of the CT band is usually about twice as great as the shift of the acceptor band which overlaps with it.

The oscillator strength increases with pressure in all cases except for TCNE+HMB in which it goes through a maximum at about 2000 atm. The increase in f appears to be the same in CH_2Cl_2 and MCH. For the three systems for which f could be estimated by integrating over the CT bands, the increase is smaller than

for the others for which the approximate eqn. (3) was used. Since all these systems involve two CT bands, this may indicate that the shift in the relative intensity of bands observed for TCNE+NAP is fairly general.

These pressure effects can be understood in terms of the model of Prochorow and Tramer²⁴ to explain the vapour-phase→solution shift of the CT band of CO(CN)₂ complexes. The characteristic broadness of the CT bands and the small energy of formation of the complexes suggest that their ground state has a shallow and broad potential energy curve. Their excited state, with its strong component of Coulombic interaction, should have a much deeper potential energy curve and a smaller equilibrium separation. This model can account for the sensitivity of the CT band maximum to pressure changes and for the absence of broadening. The greater the value of K , the deeper should be the potential energy minimum of the ground state and the less the red shift for a given pressure. This is in agreement with the observed results (see fig. 5). The results also indicate that the rate of red-shift with $\log K$ for any one complex decreases as K increases. An extreme example is the TCNE+HMB complex for which the shift reverses sign at high K .

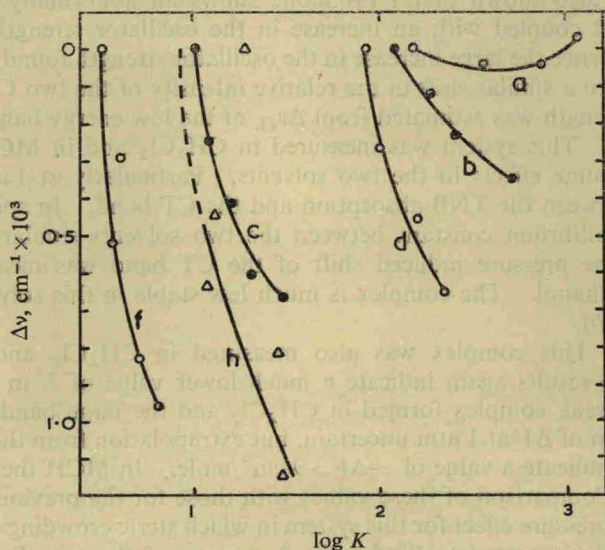


FIG. 5.—Relation between Δv and $\log K$; lettering of curves as in fig. 3.

Apparently, the observed shift is a balance between the red shift due to decreased separation in the ground state, and a blue shift due to the lowering of the ground state energy by increased resonance between the no-bond and the dative-bond structure, as suggested by Offen.¹² The exceptional blue shift observed for complexes with large K at high pressure^{5, 11} could also indicate that the difference between the equilibrium separation of the ground and excited state is so small that under compression excitation raises the complex to the repulsive part of the excited state energy curve.

The decrease in component separation caused by compression will be small compared with the difference between the sum of the van der Waals radii and the CT bond length and will not be reflected in the observed ΔV . The measured values of ΔV represent the change in volume when the complex is formed from its components.

The structures of some complexes are known in the solid state from the X-ray diffraction work of Wallwork.²⁵ In the TNB+NAP complex the two components

are parallel to each other in a more or less symmetrical arrangement and the distance between the planes of the molecules is 3.45 Å. In CA+HMB the molecular planes are also parallel and the distance between them is 3.51 Å, but there is only incomplete overlap between the components. One can calculate the volume change associated with the formation of the complexes from their components by using Wallwork's distances and van der Waals radii²⁶ to calculate the van der Waals volumes of the separate components and the complexes. Using projected areas of the component molecules multiplied by the thickness of the molecules (thickness of HMB 4.0 Å, CA 3.6 Å, TNB and ANT 3.4 Å) one finds for TNB+ANT, $\Delta V = -3 \text{ cm}^3 \text{ mole}^{-1}$ and for CA+HMB, $\Delta V = -13 \text{ cm}^3 \text{ mole}^{-1}$. The first is in exact agreement with the value found from the pressure dependence of the equilibrium constant, while the second is slightly more negative; this difference may be due to neglecting the incomplete overlap of CA and HMB in calculating the volume of the complex. The general agreement of ΔV calculated from the structure of the solid complex and the measurements in solution is consistent with the assumption that similar complexes are formed in the two cases. The magnitude of ΔV is connected with the magnitude of K , but exceptionally large values of ΔV can occur where steric effects prevent the formation of a strong complex (see PIC+ANT above).

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