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 mμ 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 Kadhim [11] for TCNE+NAP and by Gott and Maisch [5] for TCNE+diphenyl. Offen and Eliason [23] 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 $\Delta\nu_{\frac{1}{2}L}$ 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. 3*b*).

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 $-\Delta V > 9$ cm^3/mole. In MCH the value is about 16 cm^3/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~~ suggested by Prochorow and Tramer [24] 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.

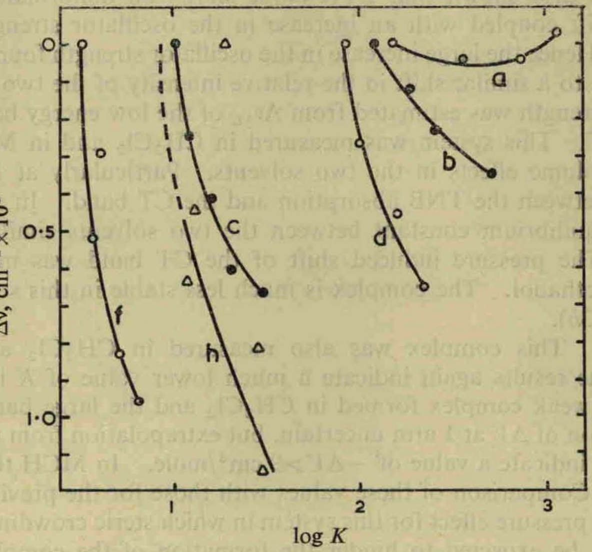

FIG. 5.—Relation between Δν and log K; lettering of curves as in fig. 3.

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