

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.

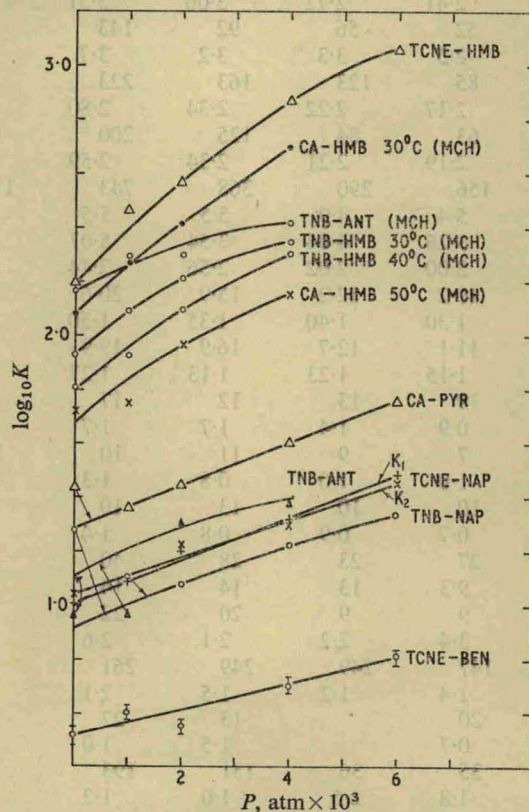


Fig. 2.—Log (stability constant) as a function of pressure. Methylene chloride solvent except where marked (MCH).

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