

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	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.

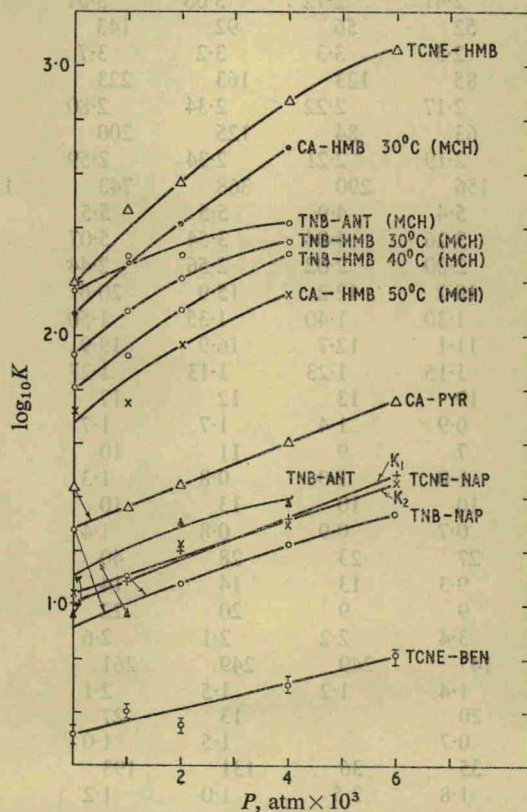


Fig. 2.—Log (stability constant) as a function of pressure. Methylene chloride solvent except where marked (MCH).

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