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COMPLEXES OF DICHLOROMALEIC ANHYDRIDE WITH SOME METHYLBENZENES AND THE ELECTRON AFFINITIES OF MALEIC ANHYDRIDE AND DICHLOROMALEIC ANHYDRIDE

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Abstract—Isomeric 1 : 1 complexes and higher order complexes are formed between dichloromaleic anhydride and either durene, pentamethylbenzene or hexamethylbenzene in carbon tetrachloride solution. The electron affinities of dichloromaleic anhydride and maleic anhydride as calculated from the charge transfer transition energies of the corresponding complexes are $0{\cdot}5_8$ and $0{\cdot}1_1$ ev respectively.

ACCEPTOR properties of anhydrides are well established from studies of their charge transfer complexes with aromatic hydrocarbons.[1] The association constants and the molar absorptivities of the complexes have been computed by means of the Benesi-Hildebrand equation or one of its many variations.[2] However Johnson and Bowen[3] have recently shown that association constants derived by means of the Benesi-Hildebrand equation are only meaningful if the value of the association constant is independent of the wavelength of measurement. In view of this and the fact that there are no reports on the electron acceptor properties of dichloromaleic anhydride, the charge transfer interaction between dichloromaleic anhydride and some methylbenzenes has been investigated and the variation of the association constant with wavelength reported.

The absorption spectra of mixtures of dichloromaleic anhydride with durene, pentamethylbenzene and hexamethylbenzene in carbon tetrachloride gave broad featureless bands in the region 355–430 mμ which were not observable in the spectra of the individual components. These bands were ascribed to the formation of a charge transfer complex or complexes since good straight line plots were obtained for the Benesi-Hildebrand relation:

$$\frac{1}{D} = \frac{1}{K\varepsilon a} \cdot \frac{1}{b} + \frac{1}{\varepsilon a} \tag{1}$$

where a is the constant acceptor concentration, b the varied donor concentration ($b \gg a$), ε the molar absorbance of the complex, D the optical density for a 1 cm light path and K (l. mole^{-1} units) is the association constant for complex formation.

The positions of the band maxima, the values of the association constants and molar absorptivities (calculated for $\lambda_{\max}$) at 20·2 and 40·1° are given in Table 1, while

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[1] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* **75**, 3776 (1953); W. G. Barb, *Trans. Faraday Soc.* **49**, 143 (1953); M. Chowdhury and S. Basu, *Ibid.* **56**, 335 (1960); L. L. Ferstandig, W. G. Toland and C. D. Heaton, *J. Amer. Chem. Soc.* **83**, 1151 (1961).

[2] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* **71**, 2703 (1949); R. L. Scott, *Rec. Trav. Chim.* **75**, 787 (1956); N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.* **81**, 6138 (1959).

[3] G. D. Johnson and R. E. Bowen, *J. Amer. Chem. Soc.* **87**, 1655 (1965).

the corresponding values at 20·2° over the wavelength range 355–430 mμ are given in Table 2.

Although the association constants are reasonably invariant in the region of the band maxima the values increase in each case at longer wavelengths. Jurinski,[4] Hayman[5] and Johnson and Bowen[3] have shown that this would be expected for the case where higher order complexes are formed simultaneously with 1 : 1 species. It is thus apparent that higher order complexes and 1 : 1 complexes are present in the dichloromaleic anhydride–methylbenzene systems studied. Jurinski and de Maine[6] have also observed an increase in association constant with increasing wavelength in the case of aromatic hydrocarbon–aromatic nitro compound complexes and attributed this to the formation of higher order complexes.

Table 1. Association constants (K) and molar absorptivities (ε) for complexes of dichloromaleic anhydride with methylbenzenes in carbon tetrachloride at λ_{max} of charge transfer absorption

Donor	λ_{max} mμ	K(l. mole^{-1}) 20·2°	40·1°	ε 20·2°	40·1°
Durene	360	1·08	0·67	1792	894
Pentamethylbenzene	372	2·40	1·67	2029	1670
Hexamethylbenzene	390	4·64	2·60	2042	1816

Table 2. Association constants[a] (in l. mole^{-1}) at 20·2° for dichloromaleic anhydride–methylbenzine complexes for all wavelengths studied (numbers in parenthesis are 95% probability limits)

mμ	Durene	PMB[b]	HMB[c]
355	1·10(0·10)	2·08(0·09)	4·98(0·16)
360	1·08(0·15)	2·35(0·11)	4·53(0·15)
365	1·12(0·12)	2·44(0·13)	4·01(0·22)
370	1·19(0·12)	2·32(0·19)	4·46(0·19)
372	—	2·40(0·20)	—
375	1·09(0·09)	2·40(0·26)	4·40(0·15)
380	1·11(0·15)	2·32(0·13)	4·58(0·12)
385	1·09(0·10)	2·35(0·14)	4·68(0·20)
390	1·00(0·13)	2·38(0·09)	4·64(0·10)
395	0·98(0·12)	2·46(0·12)	4·69(0·20)
400	1·49(0·21)	2·58(0·18)	4·70(0·16)
405	1·50(0·09)	2·55(0·21)	5·20(0·25)
410	1·62(0·14)	2·58(0·17)	5·41(0·21)
415	1·69(0·20)	2·67(0·18)	5·53(0·18)
420	—	2·90(0·21)	5·77(0·10)
425	—	—	6·01(0·18)
430	—	—	6·01(0·28)

[a] The mean value of five determinations. [b] Pentamethylbenzene
[c] Hexamethylbenzene

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[4] N. B. Jurinski, *J. Miss. Acad. Sci.* **10**, 74 (1964).

[5] H. J. G. Hayman, *J. Chem. Phys.* **37**, 2290 (1962).

[6] N. B. Jurinski and P.A.D. de Maine, *J. Amer. Chem. Soc.* **86**, 3217 (1964).

The decrease in the molar absorptivities of the complexes with increasing temperature (Table 1) can be explained by the presence of "isomeric" or orientational complexes. The molar absorptivities of the complexes decreased with temperature over the complete range of the complex absorption band and comparison of the plots (not shown) of the molar absorptivity against wavelength at 20·2 and 40·1° did not reveal any significant change in the position of the band maxima or shape of the absorption band with increased temperature. Thus it would appear that the most stable species and hence the relatively more abundant at a higher temperature does not absorb at a different energy from any other complex.

The molar absorptivities of the complexes increase slightly with increasing complex stability (Table 1). As the electron donor becomes more effective and the association constant increases the transition moment increases and an increase in the molar absorptivity is observed. The contribution of contact charge transfer absorption to the total absorption intensity must be small, if any, as this would be reflected by a decrease in the absorptivity of the complex with increasing stability.[7]

According to Mulliken's theory of intermolecular interaction between electron-acceptor and electron-donor molecules the energy $h\nu_{CT}$ of electron transfer from donor to acceptor is related to the ionization potential I of the donor and the electron affinity EA of the acceptor by the expression:[8]

$$h\nu_{CT} = I - (EA - E) + \frac{c_1}{I - (EA - E)} \tag{2}$$

where E is mainly the energy of the coulomb attraction between D^+ and A^- after the transfer of one electron from the donor D to the acceptor A and c_1 is a constant. At sufficiently large ionization potentials ($I > 7{\cdot}5$ ev) the last term in the above expression may be neglected and the equation reduces to:

$$h\nu_{CT} = I - (EA - E) \tag{3}$$

For charge transfer complexes of the same bond type and configuration E may be considered constant, and for two acceptors of similar structure and one and the same donor the following relationship will apply:

$$(h\nu_{CT})_1 - (h\nu_{CT})_2 = EA_2 - EA_1 \tag{4}$$

The electron affinity of an acceptor 1 can be calculated from the charge transfer transition energies of complexes of acceptor 1 and acceptor 2 with the same donor if the electron affinity of acceptor 2 is known. The $h\nu_{CT}$ values for complexes of various aromatic hydrocarbons with *p*-chloranil, maleic anhydride and dichloromaleic anhydride in carbon tetrachloride are listed in Table 3 alongwith the values of the electron affinities of maleic anhydride and dichloromaleic anhydride calculated relative to the electron affinity of *p*-chloranil.

The mean values of the electron affinities of maleic anhydride and dichloromaleic anhydride are 0·11 and 0·53 ev respectively. Owing to the assumptions made in the derivation of Eq. 4 the accuracy in these values is probably not greater than about 0·1 ev. Briegleb[9] has previously calculated the electron affinity of maleic anhydride

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[7] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* **79**, 4839 (1957).

[8] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 600 (1950); **74**, 811 (1952); *J. Chem. Phys.* **19**, 514 (1951).

[9] G. Briegleb, *Angew. Chem.* (Inter. Ed.) **3**, 617 (1964).

from Eq. 4 to be $0{\cdot}5_7$ ev while Batley and Lyons,[10] using the same method, have given values of $2{\cdot}0_1$ and $1{\cdot}5_3$ ev. These results cannot be considered reliable since the $0{\cdot}5_7$ and $2{\cdot}0_1$ ev values were determined from data on a single complex only, viz. the perylene–maleic anhydride complex, while the $1{\cdot}5_3$ ev value was calculated relative to the electron affinity of iodine. Iodine is a σ type acceptor and will form complexes of different configuration from those formed with maleic anhydride which is a π type acceptor. Consequently it is not valid to assume that the E term of Eq. 3 will be the same for the different types of complex. The $1{\cdot}5_3$ ev value will therefore be in error by an amount equal to the difference between the E terms for π, σ and π, π complexes. From the above results this difference would appear to be about 1·4 ev.

TABLE 3. ELECTRON AFFINITIES (EA) OF DICHLOROMALEIC ANHYDRIDE AND MALEIC ANHYDRIDE CALCULATED FROM ENERGIES OF COMPLEX ABSORPTION BAND MAXIMA.[a] REFERENCE-*p*-CHLORANIL, EA = 1·37 ev[b]

	p-Chloranil	DCMA[c]		MA[d]	
Donor	$h\nu_{CT}$(ev)	$h\nu_{CT}$(ev)	EA(ev)	$h\nu_{CT}$(ev)	EA(ev)
Toluene	3·34	4·16	0·55	—	—
m-Xylene	3·08	3·95	0·50	4·39	0·06
Mesitylene	2·89	3·70	0·56	4·12	0·14
Durene	2·56	3·45	0·48	3·97	−0·04
Pentamethylbenzene	2·53	3·34	0·56	3·74	0·16
Hexamethylbenzene	2·40	3·19	0·58	3·62	0·15
1,2,4 Trimethoxybenzene	2·19	2·98	0·56	—	—
Naphthalene	2·59	3·48	0·48	3·82	0·14

[a] Solvent-carbon tetrachloride,
[b] Ref. 9.
[c] Dichloromaleic anhydride,
[d] Maleic anhydride.

The electron affinities of the anhydrides reflect their relative electron acceptor properties. Substitution of chlorine into the anhydride ring enhances the electron acceptor ability and increases the electron affinity by about 0·4 ev. This value is comparable to the difference in electron affinity between *p*-benzoquinone ($0{\cdot}7_7$ ev) and 2,3 dichlorobenzoquinone (1·1 ev)[9].

EXPERIMENTAL

Materials. Carbon tetrachloride, Hopkins and Williams "Spectrosil" grade was used without further purification. Toluene, mesitylene and *m*-xylene, B.D.H. were distilled before use and respective fractions boiling 110–111°, 163–164°, 138–139° collected. Durene, pentamethylbenzene and hexamethylbenzene, B. Newton Maine Ltd., were recrystallized 3 times from EtOH, resp. m.ps 79°, 53°, 162°. Naphthalene, B.D.H., was recrystallized from EtOH, m.p. 80°. 1,2,4 Trimethoxybenzene, B. Newton Maine Ltd., was distilled and the fraction boiling 86–90° collected. Dichloromaleic anhydride, L. Light and Co., was recrystallized 3 times from pet. ether (60–80°) and stored under vacuum, m.p. 120°. Maleic anhydride, B.D.H., was recrystallized from $CHCl_3$, vacuum sublimed, and stored under vacuum, m.p. 60°.

Spectrophotometric determinations. The absorption spectra and optical density measurements were recorded on a Unicam S.P. 500 spectrophotometer using 1 cm silica cells sited in a thermostated cell holder. Stock solutions of dichloromaleic anhydride and the particular hydrocarbon under study were prepared just prior to use. For each hydrocarbon–dichloromaleic anhydride system 5 sets of solutions were prepared. In each set the dichloromaleic anhydride concn. was kept constant in the

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[10] M. Batley and L. E. Lyons, *Nature, Lond.* **196**, 573 (1962).

range 1 × 10^{-3} to 3 × 10^{-3} M for durene and pentamethylbenzene and 3 × 10^{-4} to 7 × 10^{-4} M for hexamethylbenzene while the hydrocarbon concn. was varied over the range 3 × 10^{-2} to 1·5 × 10^{-1} M for durene and pentamethylbenzene and 3 × 10^{-3} to 1 × 10^{-2} M for hexamethylbenzene. A hydrocarbon solution of the same concn. as the hydrocarbon in the solution under study was used as the reference. Where necessary the measured optical densities were corrected for the absorbance of dichloromaleic anhydride using Klaboe's procedure.[11] All solutions were prepared at room temp using CCl_4 as solvent, and concns were corrected to the temp of measurement.

The λ_{max} for complex absorption bands in hydrocarbon–maleic anhydride and hydrocarbon–dichloromaleic anhydride systems were determined by making up solutions of known concn. in CCl_4 and plotting the absorption spectra of these solutions with a hydrocarbon solution of the same concentration as reference.

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[11] P. Klaboe, *J. Amer. Chem. Soc.* **84**, 3458 (1962).