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CHARGE TRANSFER COMPLEXES OF ALUMINUM CHLORIDE[1]

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Abstract—A study has been made of a number of solid charge transfer complex systems employing Aluminum chloride as an electron acceptor with a number of aromatic π-donors. It has been found that a linear relationship exists between the ionization potentials of the methylbenzenes and the energy of the apparent absorption maxima of the complexes. A similar relationship has been found for a number of polycyclic aromatic donors between the energy of the charge transfer band and an energy parameter for the highest occupied molecular orbital of the donor. Stoichiometric evidence is presented that indicates a dimeric aluminum chloride species forms the predominant complex with hexamethylbenzene.

CHARGE transfer theory has been developed in terms of both valence bond[2] and molecular orbital[3] theories. These complexes are postulated to be weakly bound chemical species formed through electronic interaction between two (or more) molecules. Both theories concur in attributing new spectral absorption bands to the molecular complex which results. It has been through analysis of such spectral bands (or some modification of the substrate spectrum) that much of the information about these complexes has been obtained.

Aluminum chloride, a typical Lewis acid, can function quite effectively as an electron acceptor molecule. In view of its importance as a catalyst in many organic reactions there is a paucity of data concerning its complexing characteristics.[4] This has been attributed to the inherent difficulty in handling complexes of this nature. It was observed that when solid aluminum chloride was directly mixed with a number of solid aromatic hydrocarbons an immediate color change occurred. The resulting mixture was usually the yellow or orange color typical of charge transfer complexes between aromatics and other electron acceptors. It is suggested that a solid charge transfer complex formed. In a recent article[5] aluminum bromide was studied with a number of liquid Me-substituted benzenes by use of vapor pressure-composition phase studies and the work in this area reviewed. These authors have found that complexes of the type $ArH{\cdot}Al_2Br_6$ (a 1:2 complex) are formed for all systems with benzene, toluene, *o*-, *m*- and *p*-xylenes and mesitylene, and that $ArH{\cdot}AlBr_3$ (a 1:1 complex) complexes are formed with *m*-xylene and mesitylene. Stability of the complexes was found to increase with increasing methylation corresponding to the increased basicity of the aromatics. By analogy with the $AlBr_3$ work it then appears

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[1] This work was taken in part from the M.S. thesis of S.J.C., Dept. of Chemistry, Boston College, June, 1966. Presented in part at 152nd A.C.S. meeting, New York, 1966.

[2] R. S. Mulliken, *J. Am. Chem. Soc.* **72**, 600 (1950), and subsequent papers in this series.

[3] M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.* **83**, 4560 (1961).

[4] For a review of early work in this area see L. J. Andrews, *Chem. Rev.* **54**, 713 (1954).

[5] S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.* **88**, 930 (1966).

quite reasonable to attribute the observed color changes in the $AlCl_3$ systems to the formation of weak charge transfer complexes between a molecule of aromatic and a molecule of aluminum chloride.

RESULTS AND DISCUSSION

A number of workers have found that aluminum halides occur as the dimeric form in solution[6] or in the vapor.[7,8] There have also been reports that in complexes of the type $ArH{\cdot}AlX_3$ the aluminum species exists as a dimer complexed with a single aromatic molecule[5] or as a dimer complexed with two aromatic molecules[6] resulting in the apparent stoichiometry of 1:1 for $ArH{\cdot}AlX_3$ complexes that would be concluded from any melting point-composition phase studies. Thus from previous work it appeared most probable that the aluminum chloride should be present as a relatively stable dimeric species previous to any complex formation. Since the nature of charge transfer interactions are known to be quite weak[2,3] it was not expected that complex formation with an aromatic donor would alter the pre-existing structure of the Al_2Cl_6 species.

The $AlCl_3$-hexamethylbenzene (HMB) system was chosen to investigate the stoichiometry of the complexes because HMB should be the strongest donor of the methylbenzene series and has been investigated quite extensively in other systems.[9] The molar ratio method was chosen to investigate this aspect. The details of this method are outlined in the Experimental.

In applying the molar ratio method one studies some physical quantity of the system (in this case the spectral absorbance at 246 mμ) as a function of the molar ratio of the components of a binary mixture. The process involves maintaining the concentration of one component constant (HMB) and varying the other ($AlCl_3$). This method is a variation of Job's method of analysis. In this instance the HMB concentration was kept fixed because it was necessary to monitor the amount of HMB extracted by a 100 ml portion of n-hexane. It was found that HMB could be found in the hexane layer in measurable amounts only when insufficient $AlCl_3$ was present, i.e., the $AlCl_3$ phase competed more successfully for the HMB than did the n-hexane phase.

As can be seen in Fig. 1, a sharp break occurs in absorbance at 246 mμ (due to HMB) at a molar ratio of $AlCl_3$:HMB of 2·0. This gives evidence of a specific 2:1 interaction between these two substances. Most probable is the explanation that a single dimeric aluminum chloride species interacts with a single ring to form a weak complex of the apparent 2:1 stoichiometry, $(AlCl_3)_2{\cdot}HMB$. When all the $(AlCl_3)_2$ species is complexed then any remaining HMB can be extracted by the n-hexane layer present. Thus at molar ratios less than 2·0 significant absorbance is measured in the n-hexane phase.

An attempt to determine quantitatively the association constant for this complex was made. No inert solvent could be found that exhibited sufficient solubility for the complex. Only ethyl acetate, an "active solvent" (one that can act as an electron

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[6] R. E. Van Dyke, *J. Am. Chem. Soc.* 72, 3619 (1950).

[7] K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.* 60, 1852 (1938).

[8] L. O. Brockway and N. R. Davidson, *J. Am. Chem. Soc.* 63, 3287 (1941).

[9] L. J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry*, Holden-Day, San Francisco (1964).

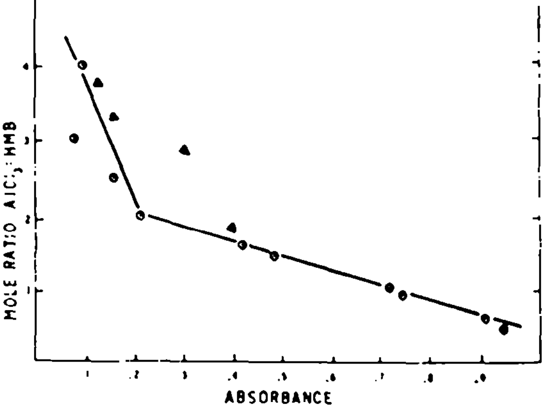

FIG. 1. Stoichiometric determination of the aluminum chloride-hexamethylbenzene system. Absorbance at 246 mμ of n-hexane extracts vs. molar ratio of components. ○ and △ indicate separate runs made using identical weights of HMB.

donor), was found to dissolve enough of the complex to show a measurable absorbance for the complex band but instability in the resulting measurements, probably due to hydration effects, precluded an accurate analysis. Qualitatively it can be said that the extraction method indicates a relatively strong complex interaction since the n-hexane was found to show significant HMB dissolved only when insufficient $AlCl_3$ was present to complex the HMB. When excess $AlCl_3$ was present in the samples, the HMB was found in the complex phase rather than being extracted into the n-hexane phase.

The strength of interaction of $AlCl_3$ with other aromatic donors was investigated by a study of the position of the band maximum of the charge transfer band. From previous work in this area[9] it is known that an increase in the strength of interaction (as measured by the association constants) is accompanied by a shift of the band maximum of the complex to longer wavelengths. It can be seen in Table 1 that this

TABLE 1. $AlCl_3$-AROMATIC COMPLEX SYSTEMS. OBSERVED BAND MAXIMA FOR COMPLEXES, λ_{max}; IONIZATION POTENTIAL OF DONORS, I_p; HÜCKEL PARAMETER, m.

Donor	$\lambda_{max(m\mu)}$[a]	[b] I_p(ev)	[c]	m[d]
p-Xylene	364	8·78		
Mesitylene	365	8·64		
Durene	380	8·50		
Pentamethylbenzene	385	8·30		
Hexamethylbenzene	400	8·14		
Hexaethylbenzene	405	8·03[e]		
Naphthalene	410		8·26	0·618
Phenanthrene	425		8·03	0·605
Chrysene	480		8·01	0·520
Pyrene	520		7·72	0·445
Anthracene	560		7·55	0·414

[a] Estimated from mull spectra or EtOAc soln.

[b] F. Meyer and A. G. Harrison, *Canad. J. Chem.* **42**, 2256 (1964).

[c] M. W. Wacks and V. H. Dibeler, *J. Chem. Phys.* **31**, 1557 (1959); *ibid.* **41**, 1661 (1964).

[d] C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π-Electron Calculations.* Freeman (1965).

[e] Estimated from this work.

trend in band maxima follows the predicted effect of increased alkylation of the aromatic ring.

The trend to longer wavelengths of the complex bands is indicative of a greater degree of association.[9] It is seen from Fig. 2 that this shift in band maxima follows a linear dependence upon the ionization potentials of the donors in question. This relationship is given by the equation: $E_{ct} = 0{\cdot}492I_p - 0{\cdot}890$(ev.). This allows one to make a relatively rapid estimate of the ionization potential of a number of alkyl-substituted benzenes for some of which the data is not readily available in the literature. (The value for hexaethylbenzene in Table 1 was estimated in this manner.) One criterion that must be adhered to is that the structure of the donor must be essentially constant, i.e., a comparison of a series of π-donors and n-donors would be expected to follow different relationships.[10]

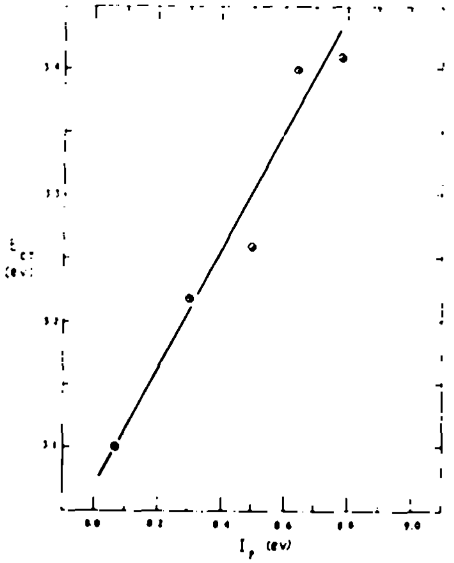

Fig. 2. Correlation of donor ionization potential and the energy of the charge transfer band maxima for alkylbenzenes.

For the series of polycyclic molecules studied the same type of trend in wavelengths of the complex band maxima was observed. It was decided to investigate the correlation of the complex band maxima with the energy level of the highest occupied molecular orbital (HOMO). As suggested[3] the donation of an electron should occur from this orbital and by employing the same acceptor orbital for all systems (by utilizing only one acceptor) a direct correlation should be obtained between the frequency of the charge transfer band maximum and the energy of the HOMO. Since all the orbitals in the aromatic systems studied are carbon p-orbitals, the Coulomb integral, α, and the resonance integral, β, will be identical for all atoms. By use of the Hückel molecular orbital theory it is seen that all the π-orbitals of the aromatics are of the form $E_\pi = \alpha + m\beta$ where m is an energy parameter directly related to the orbital energy. Therefore a correlation should be obtained between the frequency of the charge transfer band maximum and the m-value for the HOMO of the donors. This is shown in Fig. 3.

[10] R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.* 13, 107 (1962).

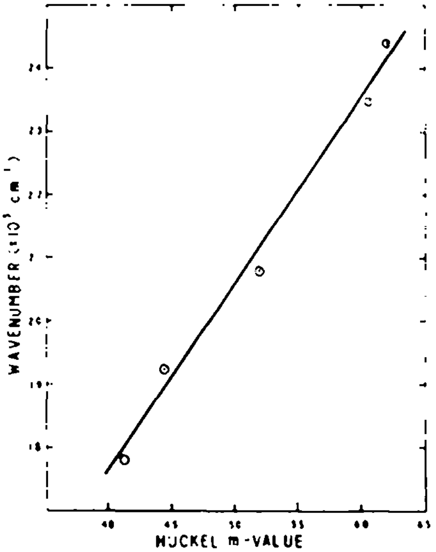

FIG. 3. Correlation of molecular orbital parameter and the frequency of charge transfer bands for polycyclic donors.

The observed relationship has the form $\nu_{ct}' = 30{\cdot}1m + 5{\cdot}53$ ($\times 10^3$ cm^{-1}). These results are consistent with other systems previously reported.[10,11]

The ionization potentials of the polycyclic aromatics were also studied and yield an equation of the form $E_{ct} = 1{\cdot}17I_p - 6{\cdot}62$ (ev). It is noted that changing from the six π-electron donor system to the larger aromatic systems has as profound an effect on the ionization potential relationship as does a change from a π-donor system to an n-donor case. Therefore indiscriminate use of such empirical relationships can lead to sizeable errors.

EXPERIMENTAL

Spectral measurements. Spectral measurements were made on either a Beckman D.U. (thermostatted at 26·0°C) or on a Perkin-Elmer 202. All work requiring accurate absorbance readings were made on a D.U. that had been calibrated with a standard chromate soln.[12] For work not requiring intensity accuracy, measurement of spectra were recorded on the PE-202. The wavelength accuracy of this instrument was estimated to be approximately ±1·0 mμ.

The original components were all solid materials with the exceptions of *p*-xylene and mesitylene. The complexes formed were solids (in the case of the stronger donors) or oily phases (with those donors weaker than pentamethylbenzene). The oily phases normally separated out on standing for several hr. Evidence of interaction could normally be seen immediately on mixing by the appearance of a yellow color. Presence of Kadol oil or n-hexane normally speeded the appearance of the oily phases, presumably by facilitating the process of mixing.

The complexes could easily be formed by mixing the donor with dry $AlCl_3$ to produce a yellow colored mixture. For purposes of recording spectra the components were mixed in the presence of Kadol oil to prevent hydrolysis of the $AlCl_3$. The oily product was then studied on the Perkin-Elmer 202 by spreading on a NaCl plate. Identical handling of $AlCl_3$ in the absence of any aromatic showed no comparable visual absorbance indicating the observed spectra were not due to hydrolysis products of the $AlCl_3$ used.

An attempt was made to obtain soln spectra for the complexes in AcOEt. It was seen that the

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[11] Y. Nakayama, Y. Ichikawa and T. Matsuo, *Bull. Chem. Soc. Japan* **38**, 2110 (1965).

[12] National Bureau of Standards, Letter Circular LC-1017, January 1955.

complex band maximum was shifted approximately 10 mμ toward longer wavelengths relative to the mull spectra. This correction factor was applied to obtain band maxima for the complexes with the weaker donors in which the complex band was overlapped by the aromatic. In some cases a preferential shift of the complex band allowed a determination of the band maximum in solution that could not be obtained from the mull.

Materials. $AlCl_3$ used in this study was Baker reagent grade. Attempts were made to prevent hydrolysis by storage in a desiccator and using fresh bottles of $AlCl_3$ at frequent intervals. Fisher Spectrograde n-hexane was employed for extraction work. Fisher reagent grade AcOEt was dried by storage over a molecular sieve and then normal distillation. Aromatic donors were checked for purity of the commercially available materials by comparison with literature values for refractive index (liquids) or m.p. (solids).

Extraction studies

Molar ratio method. The stoichiometry of the hexamethylbenzene (HMB) – $AlCl_3$ system was studied by the molar ratio method. A fixed weight of HMB was mixed with various weights of $AlCl_3$. After mixing, a fixed volume of n-hexane was added to each sample and the mixtures were allowed to stand for a day to reach equilibrium. Portions of each hexane layer were then removed and the spectral absorbance at 246 mμ was measured. At this wavelength the only species with significant absorbance was the HMB. Results of this study are shown in Fig. 1. Results of two separate runs are indicated in this Fig. 1. Both sets of data were obtained using the same amount of HMB. The difference in these sets is thought to be negligible and may be attributed to a slight difference in room humidity at the time of measurement. Points indicated by ▽ appear to show higher background absorbance.