CHAPTER I

INTRODUCTION

Introduction

The theory of complexes of charge-transfer is still little developed, but interest in it has increased of late in connection with the production of similar complexes through the interaction of two organic components, one of which is the donor and the other is the acceptor of electrons. Molecules of chloranil, tetracyanoethylene, $C_2(CN)_4$ and others can function as acceptors; while hydrocarbons of the type of naphthalene, various amines etc... behave as electron donors.

Complexes formed with charge-gransfer are usually strongly coloured, and in addition possess semiconductor properties. To clarify the structure of the electron shells of such complexes it is necessary to know the ionization potential of the donor and the electron affinity of the acceptor. Between these extremes are many interactions which are conventionally termed " Complexes " such as the weak electron-donor-acceptor (EDA) complexes and hydrogen-bonded complexes.

Indeed the term "Complex " has assumed a variety of meanings in the language of chemistry, it has been used to describe the products of certain reactions in which. beyond argument electrons have been redistributed in such a way that one should really describe the product as a new compound. For the chemist, the term " Complex " also has the suggestion of a stoichiometry. Weiss(1) proposed that all molecular complexes have an essentially ionic structure $(D^+....A\ )$ and painted out that a low ionization potential for the Lewis base "D" and a high electron affinity for the lewis acid "A" should then favour a stable complex. He attributed the colour of the molecular complexes to intense charge resonance spectra arising within the ions of the complex.

Brackmann$^{(2)}$ attributed molecular complex formation to "Complex resonance" meaning quantum mechanical resonance between a no-bond structure and a structure with a bond between the two partners A and D, but made no clear statement about the ionic character in the latter structure.

Mulliken$^{(3)}$, discussed the structure of the complexes formed by halogen molecules (X_2 or Xy) with aromatic (Ar) and other solvents interms of resonance between a predominant no-bond structure ($Ar-X_2$) and small admixtures of structures of the type ($Ar^+ - X_2^-$). It was shawn by Benesi, Hildebrand and others$^{(4-7)}$, that the spectra of the $Ar-Z_2$ complexes, in addition to the visible absorption attributable to the I_2 in the complex, display an intense characteristic ultraviol - peak near   = 300 nm. This band was at first attributed to a modified Ar absorption to an $Ar-I_2$ electron transfer process$^{(7)}$ In harmaony with Brackmann's$^{(2,7)}$ idea that any complex should have a characteristic absorption of its own.

Contrast of solution and solid - state complexes:-

Solutions of electron donors (D) and acceptors (A) exhibit absorption spectra not associated with either individual molecule(8). Mulliken(9) proposed that the new absorption involves an electron tronsfer from D to A as indicated by:-

$$\Psi_{\text{complex}}(DA) \xrightarrow{h\nu\, CT} \Psi_{\text{complex}}\ (D^{+}A^{-}) \qquad (1)$$

Here $h\nu_{CT}$ is the charge - transfer (CT) excitation energy, and the CT band is explicity assaciated with the molecular complex formed between D and A molecules.

The nature of such DA complexes has been the subject of extensive experimental and theoritical studies(10-12). The energetic of dimer formation, the geometry of the complex, the systematics of varying D,A, and solvents; the nature of CT absorption have been explored. The CT excitation is greatly enhanced(10,11,13), as suggested by Mulliken(9) via small admixtures of the excited singlet configuration $(D^{+}A^{-})$ into the ground state (DA). However, the additional configuration interaction stabilization due to this small admixture(13,14) does not usually dominats the binding energy or the geometry of the complex. It is now evident that aromatic donors and acceptors usually crystallize in molecular stacks(15,16). All intermolecular separations are normal vander waals distances. The π-overlap of D and A molecules along the stacks then bead to a CT band in addition to the molecular excitations expected in molecular crystals.

Classification of Electron Donors, Acceptors and Complexes:-

Donars and acceptars are classified according to theit structure and function. Tablulated shows a classification of donors and acceptors according to major types. A donor of any type can in general form a compound or a complex with an acceptor of any type, but some types of DA pairs are more stable than others. If D and A are odd free radicals (R and A), their combination is an ordinary valence compounds R-Q, usually more or less polar due to ionic resonance structure D^+A^-, such molecules (e.g; Hcl, I_2, CH_3Br) possess. Intermolecular (ineratomic or interradical) CT spectra. The CT action is nearly is nearly completely one-way, just as in typical molecular complexes. Increvalent donors lone-pair (n) donors which can be described in terms of the donation of one electron from a lone pair located on a key atom (e.g N in R_3N). Leaving D^+ with an odd electron which can form an additional valence bond (hence the term increvalent). Similarly, increvalent acceptors (ν) whose interaction can be described in terms of the acceptance of an electron into vacant orbital of a key atom (e.g B in BR_3), so that this atom can form an additional valence bond. Combination between neutral n-donors and π -acceptors yields the familiar dative compound. In sacrificial donation takes place from a bonding molecular orbital (b), so that when such a donor enters into a complex; the bonding with the donor is weakened resulting in an increase in the bond lengths and a decrease in the corresponding vibrational frequencies within the donor. However, a decrease in the energy of course results for the complex as a whole. Similarly in sacrificial acceptors, acceptation of an electron occurs into an antibonding level within the acceptor. Sacrificial donors and acceptors each fall into two classes (σ and π) with respect to the type of molecular orbital inolved in donation or acceptation. Among sacrificial donors (b σ or b π) and acceptors, both σ- and π- acceptors are important; but σ donors (b π) are weak and only π-donors, (b π) are usually encounted. Although it is convenient to electron donor and acceptors one should realize that these names do not refer to fixed absolute types of molecules, but rather modes of interaction. The same atom or molecule may function sometimes as a donor, sometimes as an acceptor depending on its behaviour. For example; in the C_2H_4 functions as a π -donor to Ag^+ as a ν -acceptor, and simultaneously as a π-acceptor to Ag^+ as an n-donor. On the other hand, pyridine (C_6H_5N) in two - way complexes functions as an n-donor with the donor action focused at the N-atom and as a π -acceptor with the acceptor action spread over the entire ring. For example in C_6H_5 OCH_3, the O-atom is acceptor in its σ- bonds, but is π-donor, so that there is mutually reinforcing two - way action in the C_6H_5 - Q link. Complexes formed between donors and acceptors classified on this basis can be dessignated by two symbols, the first of these symbols indicates the type of the donor action while the secand symbol indicates the type of the acceptor action. Thus, a complex between R_3N and I_2 would be called an (n- a σ) complex, while the benzene halogen complexes are celled (bπ- a σ) complexes.

Classification of electron Donors and Acceptors

Donor types

No of electrons	Functional type	Structure type	Examples
Odd	Free Radical	R	Na,C_2H_s, H, NO NO_2
Even	Increvalent	n	R_3N, R_3N oxide py (pyridine), R_3p, PYN-oxide, R_2O, dioxane, R_2S, Rx, RCN, R_2CO, CO, R_3 po_4 RNO_2, X^-S_1, OR^-S_1, $-NR_2$, OR,- X (intermolecular n- π donor island groups).
	Sacrificial	σ	A(aliphatic hydrocarbons), especially if cyclic (very weak), often Rx, etc.
		π	Ar (aromatic) and (unsaturated) hydrocarbons, especially if forti-field by electron releasing groups C_6H_5 etc, intermolecular donor island groups.

Acceptor types

No of electrons	Functional type	Structure type	Examples
Odd	free Radical	Q	X, OH, NH_2, H, NO_2
Even	Increvalent	v	BR_3, AlR_3, BX_3, ALX_3, $Sncl_4$ $Ag^+ClO_4^-$, Ag^+S_1, etc., NO_2^+ S_1.
		σ	X_2, Xy, HX, HQ, RQ, CoI_4, etc
	Sacrificial	π	Ar and Cln, especially if polycyclic or heterocyclic, orif fortifield by electron with-drowing group (X, NO_2, CooR, CN) as e.g in trinitro benzene, quinones, $-C_6H_5$, NO_2, COR, - COOR, (intermolecular π -acceptor island gfroups.)

R may be (H or an alkyl) or other groups, R_2 and R_3 may include two or three different R's.

X,Y mean F, Cl, Br or I

S_1 mean solvated.

Literature survey on charge transfer complexes.

Hetero aromatics represent a very important class of compounds in that their π- and n- electrons can give at least in principle, two different types of charge tranafer complexes. It has been shown that pyridine derivatives are predominantly n- donors(17). The combination of the inductive and mesomeric interactions between the lone pair and the n - electrons of the aromatic ring, which have electron releasing influence on the base strength of the nitrogen atom (K_{CT} decreases about fifty times on going from ethyl(18)- to phenyl amine(19)), have however a small overall effect in this case. Charge transfer complexes of substituted thiophenes as donors with tetracyano ethylene, 2,3 - dichlore - 5.6 - dicyano p-benzoquinone, cheoranil and Iodine have been studied spectrophotometrically to obtain deeper insight into the CT-interactions of sulphur heteroaromatics by Aloisi. etal(20). From the energies of the charge transfer transitions, the ionization potentials of the donors have been the close agreament found between the CT and electron impact (1.e) ionization potential(21), suggests that the orbital of thiophenes involved in the interaction with these four acceptors is the same as that involved in the first ionization process(20). Issa and El-Essawey(22) investigated a series of charge transfer compounds of aniline derivatives with picric acid. They pointed out that a correct idea about the type of bonding in CT complexes is gained from ir-spectra by investigation the N-H stretching region, the asym, and sym. NO_2 bands as well as the γCH bands of both donor and acceptor..From the shift of these bands in comparison to their position in the spectra of the free molecules, the nature of the bonding in the complex can be visualised. The main changes considered are the following:-

a) The shift of γCH bands of the donor to higher wavenumber as a result of lowered electron density on the molecule, while its increase on the acceptor leads to a shift of its γ CH bands to lower values this behaviour is generally considered as an indication for a bonding of the $\pi - \pi^*$ type.

b) The shift of ν_{NH_2} bands to higher wavenumbers due to decrease electron density on the aniline ring if the $\pi - \pi^*$ interaction is the only type of bonding exists.

c) The shift of the ν_{NH_2} bands to lower wavenumbers, if intermolecular hydrogen bonding between the - NH_2 group of the donor and NO_2 groups of the acceptor occurs or when an n- π^* interaction takes place. The latter type involves the transfer of an n- electron of the NH_2 groups to the lowest vacant π^*-orbital of one nitro group of the acceptor.

d) Disappearance of the NH_2 bands within the 3500-3300 cm^{-1}

range and the ν_{OH} bands of picric acid and the appearance of new set of bands within the 2900-2400 cm^{-1} range is a characteristic of the - $\overset{+}{N}H_3$ groups when the charge transfer complex formed is of the salf type.

Issa, et.al(23) studied the charge transfer complexes of some methyl pyridine as donor with tri - and dinitro benzene as acceptors by IR, ^1H NMR and electronic spectroscopy. These outhers showed that acidic acceptors form CT complexes involving $\pi - \pi^*$ and proton transfer interaction while nonacidic were bonded through $\pi - \pi^*$ electronic interaction.

Issa et.al(24) prepared and studied the solid CT complexes of some hydroxy aromatic schiff bases with 23 dichlore -5,6- dicyane -p- benzoquinone and chloranilic acid, using electronic absorption, ir and ^1H-NMR spectroscopy. The formation of molecular complexes between hydrxyy aromatic schiff bases and the acceptors used would be different since the donor molecules display basic properties while acceptor (chloranilic acid) only has the acidic character. Accordingly, it is expected that the molecular compounds formed with the acidic acceptor would be formed through proton and electron transfer.

Issa, et.al(25) investigated the reaction of phenylendiamine and benzene with some aromatic nitro compounds using

IR and ^{1}H.NMR spectrascopy. The reaction yields 1:1 complexes with all donors; benzidine also formed 1:2 compounds. Molecular complexes with acidic acceptors are formed through proton transfer and $\pi - \pi^*$ bonding; n- π^* interaction also takes place with strong acidic acceptors. For the nonacidic acceptors $\pi - \pi^*$, n- π^* and intermolecular mydrogen bonding contribute to complex formation; the formation of 1:2 complexes with benzidine is ascribed to the presence of two rings that can participate in $\pi - \pi^*$ bonding.

Issa, et.al(26) prepared and investigated the molecular complexes of N- dimethylbenzlidine aniline with chloranil, dichloro- dicyano- p - Benzoquinone and chloranilic acid by IR, ^{1}H NMR and electronic absorption spectrascopy. Non acidic acceptors yield complexes having $\pi - \pi^*$ and n- π^* interactions. Chloranilic acid forms complexes through $\pi - \pi^*$ and proton transfer interactions. The ioniaztion potentials of donors were calculated from the electronic absorption spectra.

Abd. El-Mottaleb., et.al(27) studied the charge transfer complexes of some cyanine dyes, the association constant (K) for CT complexes of two cyanine dyes of the type 2-(2^{-}-phenyl -4^{-}-aryl- 1^{-},3^{-}- butadiene) -1- ethyl quinolinium iodide have been determined. The effect of solvent polarity, temperature and nature of substituent on K were studied and discussed on the basis of solvent. separated ion-pair model.

Issa, et.al.(28) prepared and investigated the molecular complexes of six quinoline derivatives (as donors) with some tri- and dinitro benzene (as acceptors) by IR spectroscopy. The spectral changes suggest that the formation of the molecular complex with acceptors deprived of an acidic centre takes place through $\pi - \pi^*$ and n- π^* interaction. With the strong acidic acceptors, the molecular complex is formed through proton transfer and $\pi - \pi^*$ bonding for the weaker acidic acceptors. The type of interaction depends on the basicity of the donor molecule; the reaction with tetrahydro quinoline was discussed separately.

Chandra(29) studied the CT spectra of molecular complexes of chloro- substituted p- benzoquinone (4)- chlorimides with aromatic π- donors in cyclohexane, the interaction of 2,6-dichloro p-benzoquinone with the same set of donors has also been studied. The spectroscapic and thermadynamic data indicated that the complexes are very weak in nature. A comparison of the absorption intensities and formation constants for these complexes shows that the contribution of charge transfer forces are not the only dominant stabilising factors. The charge-transfer energies of each complex are plotted against the ref-active index function and inverse dielectric constant of the solvents separately. The extrapolated values obtained at unit refractive index or dielectric constant are considered to be the corresponding values of the complexes in the gase-phase.

Silber(30) studied the interaction of diethyl, triethyl, n- butyl and tri-n-butyl amines as n-donor with benzonitrile as π - acceptor in n- hexane.

The formation of weak electron donor-acceptor (EDA) complex was proposed to explain the spectroscapic behaviour of the mixtures. An alternative procedure was used to obtain values of stability constonts (K) and extinction coefficients ($\mathcal{E}$), the fact that the new absorption observed for these systems, a value of (K) and finit constant value of ($\mathcal{E}$) could be determined, gives evidence of the existence of EDA complexes.

Dessouki., et.al.(31) studied and investigated the formation of molecular complexes of some schiff bases derived from 2- Amino -4- methyl pyridine as electron donors with tri and dinitrobenzenes as electron acceptors by elemental analysis, IR, H^1 NMR and electronic absorption spectroscopy.

The spectral changes revealed that acidic acceptors form complexes with π - π^* electronic interaction and proton transfer while non acidic or weak acidic acceptors yield complexes having the π - π^* transition.

ABoul. Fetouh(32) studied the charge-transfer molecular complexes of some para cyclophanes with tetracyanoethylene, dichloro dicyano -p- Benzoquinone and chloranil. The stoichiometry and apparent formation constants of the complexes formed were determined by applying the conventional spectrophotometric molar ratio and continuous variation methods. The role of the molcular structure of the electron donor and acceptor compounds as well as the nature of the solvent on the formation and stability of such charge- transfer complexes was elucidated.

Seal.. et.al.(33) rearranged the Bensi- Hildebrand equation and its modified forms to give equations which enable evaluation of K and ε of molecular complexes from spectrophotometric data by graphical procedures. The equations have been tested with data on several 1:1 complexes, the results agreed fairly well with those determined by other well- known procedures.

Nour el-Din.. et.al.(34) studied charge- transfer molecular complexes between some nitrones with different substituents and tetra cyano ethylene, 2,3- dichlore- 5,6- dicyano benzoquinone and chloranil in methylene chloride solution at 25°c. The maximum absorption wavelengths, stoichiometry, apparent formation constants and transition energies confirm the formation of the $\pi - \pi^*$ molecular complexes. The effect of solvent, the formation and stability of these complexes were discussed.

Dessouki..et.al.(35) prepared and studied the solid CT complexes of some indolyldien aniline derivatives with di- and tri- nitrobenzenes by ir, electronic and ^1H NMR spectroscopy. Non-acidic acceptors yield complexes having $\pi - \pi^*$ and $n - \pi^*$ bonding; strong acidic acceptors yielded complexes having $\pi - \pi^*$ and proton transfer interaction. The formation of 1:2 (D:A) complexes was also ascertained. The ionization potential of the donors as well as the electron affinities of the acceptors were determined from the electronic absorption spectra.

Nour-El-Din..et.al.(36) measured the characteristic charge- transfer absorption bands of some nitrones as electron donor with tetracyano ethylene, 2,3- dichloro- 5,6- dicyano benzoquinone and chloranil as electron acceptor in methylene chloride solution. The stoic-hiometry, appearent formation constants and transition energies of the charge-transfer complexes formed as well as the effect of solvent and the stability of these complexes are discussed.

Hindowey..et.al.(37) prepared and investigated charge-transfer complexes of benzylidene anilin containing the P-N$(CH_3)_2$ substituent with some aromatic nitro compounds applying ir- spectroscopy. The shifts in the $_{CH}$ and NO_2 bands were considered to identify the type of banding between the donor and acceptor molecules in the molecular complex being of the $\pi - \pi^*$ or $\pi - \pi^* + n - \pi^*$ types. For acidic acceptors, proton transfer interaction contributed also to complex formation.

Nour-El-Din(38) investigated spectrophotometrically charge-transfer complexes of some hetero-aromatic N-oxides with tetracyano ethylene, 2,3 dichloro- 5,6- dicyano - P - benzoquinone, tetrachloro cyclohexa- 2,5- diene- 1,4- dione and 7,7,8,8- tetracyanoquinadimethane in methylene chloride. The spectral data, molar extinction coefficiemts and transition energies of the complexes formed as well as the ionization of the donors are reported. Bensi-Hildebrand and Job(4) methodes were applied to the determination of formation and apparent formation constants, respectively. The effect of temperature and solvent on the stability of the complexes were as well discussed.

Gaber..et.al.(39) prepared and investigated the CT complexes of some schiff bases of quinaldine -4- phenyl- azomethine derivatives with tri and dinitrobenzenes by elemental analysis, IR, ^{1}H-NMR and electronic absorption spectra. The results of micro analysis revealed the formation of 1:1 and 1:2 CT complexes for strong acidic acceptors, and 1:1 formation in the case of weak acidic acceptors; the formation took place through $\pi - \pi^*$ intermalecular charge-transfer interaction while the n- π^* interaction is either of low contribution to the bonding or even absent.

Dwived.. et.al.(40) examined the interaction of p-Nitraphenol with aliphatic tertiary amines triethyl-amine, tributylamine and triactylamine in a variety of solvents by means of electronic absorption spectroscopy. The acid- base interaction in these systems led to various types of complexes depending upon the dielectric constant of the medium. The equilibrium data for different kinds of equilibria have been evaluated and discussed, the pK- equilibrium constant plots were found to be linear.

Benoy..et.al.(41) studied the thermodyamic and spectrophotometric properties of the charge-transfer (CT) complexes of chloranil with mesitylene and benzene in different solvents such as n-hexane, cyclohexane,n-heptane, carbontetrachloride,$CHCL_3$ and CH_2Cl_2 the results showed that the ascillator strength (f) of the CT absorption bands of these complexes in different solvents increase with the heats of formation ($-\Delta H$), the role of the solvent in changing both thermodynamic as well as spectrophotometric properties of these complexes was assumed to be due to the solvent interaction with chloranil. An attempt has been made to calculate the thermodynamic and spectrophotometric properties of the solvent- chloranil interaction, moreover the CT absorption band positions of chloranil complexes with mesitylene and benzene in the gas phase have been determined from the corresponding values in different solvents.

Azon..et.al.(42) studied the stability constant of the EDA between N,N,N^{-},N^{-}- tetramethyl-p- phenyl diamine and m-dinitrobenzene in acetonitrle by cyclic voltammetry and potentiometric titration at constant finite current. For comparison, spectral measurement were made; this solvent effect is expected for such weak complexes. The electrochemical techniques give a higher value of the stability constant under similar conditions.

Giorgio Tasi.. et.al.(43) analyzed the interactions of 1-hydroxy -2- phenylindole and 2,2^{-}- diphenyl- $\Delta^{3,3^{-}}$ -bi- 3H-indol with common organic acceptors depending on the nature of donor - acceptor partners; the reaction offord molecular complexes, redox product or some kind of adduct. Molecular complexes of Indol derivatives have encountered interest mainly because many biologically active compounds contain the Indol moieties.

Aim of the Present Investigation

From the foregoing literature survey, it is clear that CT complexes of schiff bases studied above are derived from aniline and benzaldehyde derivatives.

Studies dealy with schiff bases containing a heterocyclic nucleus have not been concluded. The present wark is designed to throw more light on the different bonding modes in charge-transfer complexes formed between schiff bases derived for 2-Amino-4-methyl pyridine, 4-Amino quinaldine and indolyl -3-aldehyde with different aryl alcelydes and aniline derivatives to obtain the solid motecular compounds of these schiff bases as donors and p-Binzoquinone derivatives as acceptors are prepared and studied by spectroscopic methods.

The main object of the present study leis in the determination of the type of intermolecular CT interaction between donor and acceptors leading to the complexes in different raties; which are important in relation CT formation. The spectral methads utilised are the electronic absorption in halogenated solvents to calculate physical parameters (K_f, ε_{max}, f, μ and ΔG^*) and their stoichiometeric by spectral and conductometric titration. The electronic absorption being used (in solid stat - Nujol mull) to calculate the ionization potential of donors (I_p) and the eletectronic affinity (E_A) of acceptors.

The IR spectra in the solid state of such compounds are analysed which would aid in discussing the boning between donor and acceptor. ^{1}H-NMR also used to characterise the different types of CT complexes formed.