Chapter I

Introduction
1.1 Organic charge transfer (CT) complexes

The term 'electron donor-acceptor' (EDA) or 'charge transfer' (CT) complex in organic chemistry is used to mean loose (van der Waals) adducts of two kinds of molecules, one of which has the capacity of accepting electrons owing to the presence of electronegative groups or atoms and the other has the capacity of donating electrons; practically no transfer of electron (charge) from one component of the adduct to the other occurs in the ground state but absorption of light of suitable frequency (in the UV/VIS range) by the adduct is accompanied with electron transfer. A very well known example is the CT complex between naphthalene and p-chloranil. When a colourless solution of naphthalene in CCl₄ is mixed with faintly yellow solution of p-chloranil in the same solvent, a beautiful red colour develops and experimental evidences¹ are in favour of the existence of the following equilibrium:

\[ \text{Naphthalene (D) + p-chloranil (A) } \rightleftharpoons \text{DA} \]

CT complexes differ from the 'complexes' that occur in co-ordination chemistry in two important aspects: (1) In co-ordination complexes donation of electron pair occurs from ligand to metal ion leading to the formation of covalent bonds; in the ground states of organic CT complexes there is no such bond formation — weak van der Waals forces are responsible for the adduct formation. (2) Formation constants of co-ordination complexes are very high (~10¹⁸ to ~10²⁰) compared to those of CT complexes (usually of the order of 1⁰ to 1⁰¹). The UV/VIS absorption bands of CT complexes are, according to Mulliken², due to the following transition:

\[ \psi_G \rightarrow \psi_{\text{ex}} \; ; \; E = h\nu_{\text{CT}} \]

where \( \psi_G \) and \( \psi_{\text{ex}} \) are respectively the ground and excited state wave functions, given by

\[ \psi_G = a\psi_o(D...A) + b\psi_1(D^+ - A^-), \; a>>b \] ... (1.1)

\[ \psi_{\text{ex}} = b^*\psi_1(D^+ - A^-) - a^*\psi_o(D...A), \; b^*>>a^* \] ... (1.2)

This means that both the ground and excited states of a CT complex are resonance hybrids of a 'no-bond' structure $D\ldots A$ and a 'dative' structure $D^{-}\cdot A^{+}$. In the ground state the former structure predominates while the latter is predominant in the excited state.

1.2 *Unsaturated cyclic anhydrides as electron acceptors*

The ability of unsaturated cyclic anhydrides to form CT complexes is now a well known fact. The unsaturated anhydride acts as a $\pi$-electron acceptor in the formation of molecular complexes. Whether the anhydride group alone or the unsaturated $\pi$-system of the anhydride molecule as a whole is responsible for complex formation has been questioned in the past. That the entire $\pi$-system of the anhydride molecule lies at the root of the acceptor property was experimentally demonstrated by observing that benzene solution of succinic anhydride shows no UV absorption spectrum of the type exhibited by the corresponding unsaturated maleic anhydride (MA). The new UV absorption band of the latter is due to complex formation between benzene and MA. That the entire $\pi$-electron system of the cyclic anhydride is involved in complex formation may be argued as follows:

Para-benzoquinone (PBQ) is a well known $\pi$-acid. The group $-\text{CH} = \text{CH}-$ is bivalent. Its replacement by electronegative bi-covalent oxygen atom, as shown in fig. 1.1, leads to the molecule MA in which the remaining $\pi$-electrons can take part in conjugation.

These substances have been used as a class of electron acceptors in the formation of molecular complexes with various $\pi$- and n-electron donors. Both mono- and poly anhydrides have been used, the former being more extensively used than the latter. In this introductory chapter attention is confined to studies of CT complexes formed by polyanhydrides with various Lewis bases. The polyanhydrides so far investigated and reported in the literature include the following:

(a) *Dianhydride*

(i) Pyromellitic dianhydride has been used as an electron acceptor more extensively than its dichloro- and dibromo- substitution products in spite of higher electron
Fig. 1.1. Correlation between the structures of p-benzoquinone (PBQ) and maleic anhydride (MA).
affinities of the latter substances. The abbreviations of these acceptors are PMDA, DCPMDA and DBPMDA. Their structures are shown in fig. 1.2(a).

(ii) A novel compound p-benzoquinone tetracarboxylic dianhydride embracing both quinonoid and anhydride structures [fig 1.2(b)] has been employed as an electron acceptor. So far, this molecule has been explored only a little with regards to its ability to form CT complexes.

(iii) Naphthalene-1,4,5,8-tetracarboxylic dianhydride and its 2-bromo derivative [fig. 1.2(c)] have been used as electron acceptors.

(b) Trianhydride

Mellitic trianhydride, abbreviated as MTA, has been employed as an electron acceptor. Its structure is shown in fig. 1.3.

In course of searching literature on CT complexes it has been found that works done on CT complexes involving di- and trianhydrides are not so extensive as those carried out with the acceptors iodine, p-chloranil, tetracyanoethylene (TCNE), dichlorodicyano p-benzoquinone (DDQ), tetracyanoquinodimethane (TCNQ) etc. Further, except the one written by Foster, there is practically no systematic review on the complexes formed by polyanhydrides. In the present chapter an attempt has been made to review the works done so far on the CT complexes formed by di- and trianhydrides with various π- and n-electron donors. The chapter is divided into two sections, of which the first is a summary of the works reported so far on stable CT complexes involving polyanhydrides and the second is a brief survey of kinetic studies on unstable CT complexes involving anhydride acceptors.
Fig. 1.2. Structures of some polyanhydrides.

(a) Parabenzquinone tetracarboxylic dianhydride

(b) Naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTCDA)

(c) Naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTCDA)

X = H → PMDA
X = Cl → DCPMDA
X = Br → DBPMDA
X = H → 2-Bromo NTCDA
X = Br → 2-Bromo NTCDA
Fig. 1.3. Mellitic trianhydride (MTA)
Section I

Stable CT complexes involving polyanhydrides as acceptors
1.1.1 Molecular Complexes of PMDA and its substitution products

As early as 1926 Seka and Sedlatschek⁶ studied the formation of molecular complexes between PMDA and aromatic compounds such as anisole, tetraline etc. A systematic investigation of CT interactions between PMDA (a π-acid) and various types of donors (particularly π-bases) was made by Heaton et al.⁷ who concluded that PMDA is a stronger electron acceptor than phthalic anhydride (PA). They determined formation constants and molar extinction coefficients of complexes of PMDA with polymethyl benzenes and other aromatics. The complex of PMDA with o-xylene is stronger than those with meta- and para-xylenes. The results are described in table 1.1. Matsuo et al.⁸ studied interactions between PMDA and several polymethylbenzenes such as hexamethylbenzene (HMB), pentamethylbenzene (PMB), durene and mesitylene in different solvents. Ethyl acetate was found to be the best for complexes of PMDA with a variety of aromatic compounds. The association constants of the complexes are less in ethyl acetate than in carbon tetrachloride. Gorodyskii et al.⁹ studied the spectral features of the complexes of PMDA with benzene, naphthalene, anthracene and tetracene and determined their thermodynamic parameters. The equilibrium constants and molar absorption coefficients of a series of complexes of PMDA with several aromatic hydrocarbons as donors were determined by Kondratov et al.¹⁰ The formation of CT complexes by PMDA with methyl- and dimethyl naphthalenes in different solvents was investigated by Neletova et al.¹¹

Table 1.1. Equilibrium and spectral data for PMDA and some aromatics at 26°C in CCl₄

<table>
<thead>
<tr>
<th>Donor</th>
<th>λ_{max} (nm)</th>
<th>ε_{max} (lit. mol⁻¹)</th>
<th>K_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>330</td>
<td>1030</td>
<td>3.05</td>
</tr>
<tr>
<td>Tolune</td>
<td>346</td>
<td>1670</td>
<td>5.03</td>
</tr>
<tr>
<td>o-xylene</td>
<td>342</td>
<td>1710</td>
<td>10.30</td>
</tr>
<tr>
<td>m-xylene</td>
<td>344</td>
<td>1750</td>
<td>7.60</td>
</tr>
<tr>
<td>p-xylene</td>
<td>354</td>
<td>1210</td>
<td>8.25</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>346</td>
<td>1670</td>
<td>5.68</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>344</td>
<td>1380</td>
<td>3.68</td>
</tr>
<tr>
<td>t-Butylbenzene</td>
<td>348</td>
<td>1260</td>
<td>4.00</td>
</tr>
</tbody>
</table>
**Higher order complexes of PMDA**

Higher order CT complexes are frequently formed in the solid state than in solution where they are, in general, of 1:1 stoichiometry. The existence of multi-order CT complexes has been suspected by noting, in several systems, a dependence of their formation constants on the wavelength of measurement. If the formation constant varies systematically with a change in wavelength, then the existence of higher-order complexes in solution is more likely.\(^{12-15}\) Search for complexes with stoichiometry other than 1:1 has been made much easier with the availability of high speed computers and development of suitable programmes for the purpose.\(^{16,17}\) The formation of higher-order complexes in solution depends on the relative concentrations of donor and acceptor used in the experiment. For example, Naletova et al.\(^{11}\) reported that with excess of biphenyl PMDA forms both 1:1 and 1:2 (PMDA : biphenyl) complexes whose stability constants were measured in several solvents such as acetone, acetic anhydride, ethyl acetate and 1,4-dioxane. When PMDA is used in excess, a 2:1 PMDA-biphenyl complex is formed as reported by the same investigators.

**Solvent effect on charge transfer complexes of PMDA**

It is well established that solvents have a marked influence on the properties of CT complexes. A very good account of various aspects of solvent effect on charge transfer complexes has been given by K.M.C. Davis\(^{18}\). However, a search of literature shows that solvent effect on complexes formed by polyanhydrides with various \(\pi\)- and \(n\)- donors has been very little investigated.

Naletova and Yulbarisova\(^{19}\) studied the formation of CT complexes of PMDA with methyl- and dimethyl naphthalenes in a number of solvents like carbon tetrachloride, chloroform, 1,4-dioxane, acetic anhydride, ethyl acetate, acetone and dimethyl formamide. The shifts of UV absorption of charge transfer complexes increased and the dissociation energy of the excited charge transfer complexes decreased in the same series. It has been stated earlier that using varying ratios of acceptor and donor Naletova et al.\(^{11}\) detected and studied multi-order PMDA-biphenyl complexes in several solvents like acetone, acetic anhydride, ethyl acetate and 1,4-dioxane.
Solvatochromic effects on the charge transfer band maxima of the complexes formed by PMDA with arenes like benzene, naphthalene, anthracene and tetracene were studied and quantitatively accounted for by deriving equations containing solvent dielectric constant and refractive index.

Regarding solvent effect on the thermodynamic properties, Matsuo et al. have observed that PMDA-methylbenzene EDA complexes are less stable in ethyl acetate than in carbon tetrachloride.

**Solid complexes PMDA**

According to Heaton et al. the formation of solid complexes appears to have important steric as well as electronic demands. Benzene and all the methyl substituted benzenes up to durene were shown to form solid complexes. On the other hand, none of the following materials form solid complexes at room temperature: ethylbenzene, cumene, t-butyl benzene, o- and p-ethyl toluene, and a mixture of di-isopropyl benzenes. The fact that compounds containing these electron-donating substituents do not undergo solid complex formation must mean that steric requirements are severe.

Matsuo et al. studied solid complexes of PMDA with polymethyl benzenes by X-ray diffraction and reflectance spectral methods. It was found that PMDA-polymethyl benzene solid complexes have many characteristics which are not found in the complexes in solution. In a later paper Matsuo extended the study to polycyclic aromatics in solution as well as in the solid state. It was noted that PMDA in ethyl acetate behaves as if it is an electron acceptor weaker than that in a solid complex by about 0.2 eV in the zero-order approximation.

Casellato et al. obtained charge transfer type 1:1 solid crystalline complexes by reacting PMDA with dibenzopyrene isomers.

CT complexes from solid state reaction of various donors with PMDA crystal in NaCl matrix were studied by diffuse reflectance spectroscopy.
Crystal structure studies

Very little work on the determination of crystal structures of solid CT complexes of unsaturated cyclic anhydrides has been done. Structural studies on pairs of solid complexes derived from the same electron donor-acceptor pair but with different stoichiometry and in which there is no possibility of H-bonding are considered to be interesting. Although such systems have been described, containing, for example, pyrene and PMDA\textsuperscript{24} or HMB and TCNE, detailed X-ray crystal structures have not been reported. PMDA appears to be somewhat exceptional showing variable stoichiometry in its hydrocarbon complexes. Unusual orientations of the donor and acceptor molecules in the crystal lattice are found in the anthracene-PMDA and the pyrene-PMDA complexes.\textsuperscript{25}

Dipole moments of PMDA complexes with $\pi$- and $n$-donors

A survey of literature reveals that no detailed studies of dielectric properties of CT complexes of anhydrides have so far been made. The great potentiality of dielectric measurements on molecular complex formation by anhydrides with various donors is yet to be utilised. Anhydrides are, in general, polar. When they form complexes with different donors (which may be polar or not) the dipole moment(s) of the resulting complex(es) may be either larger or smaller than the moment of the free acceptor in an inert solvent. Comparison of the dipole moments of phthalic and maleic anhydrides in several aromatic donor solvents, 1,4-dioxane and carbon tetrachloride show these trends (vide Table 1.2). From this table it is seen that the dipole moment of each of maleic and phthalic anhydride is larger in 1,4-dioxane than in benzene while for PMDA complexes\textsuperscript{26} the opposite trend is observed.

The results have been explained by assuming that the permanent dipole of the acceptor induces in the donor a moment which, depending on the geometry of the complex, may either increase or decrease the permanent dipole moment of the acceptor. The total moments of the complexes formed by $\pi$-donors with pi-acceptors will be less than that of the free acceptors because the two components are stacked over each other, and the moments induced in the donors will oppose the permanent dipole moments. On the other hand when the anhydride forms a complex with an n-
donor such as 1,4-dioxane the arrangements of the components and of the induced and permanent moments have the same directions and the dipole moment of the complex will be greater than that of the free acceptor. The reversal noted in the interactions of PMDA with benzene and 1,4-dioxane has been explained by considering the geometry of PMDA and its complexes. The dipole moments of CT complexes of PMDA with benzene, naphthalene, anthracene and tetracene were determined by Gorodyskii et al.20

Table 1.2. Dipolemoments (\(\mu\)) of anhydrides in various solvents

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Solvent</th>
<th>(\mu) (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>CCl4</td>
<td>3.86</td>
</tr>
<tr>
<td>MA</td>
<td>C(_6)H(_6)</td>
<td>3.20-3.55</td>
</tr>
<tr>
<td>MA</td>
<td>p-xylene</td>
<td>3.69</td>
</tr>
<tr>
<td>MA</td>
<td>Mesitylene</td>
<td>3.59</td>
</tr>
<tr>
<td>MA</td>
<td>1,4-dioxane</td>
<td>3.93</td>
</tr>
<tr>
<td>PA</td>
<td>CCl4</td>
<td>5.87</td>
</tr>
<tr>
<td>PA</td>
<td>C(_6)H(_6)</td>
<td>4.71</td>
</tr>
<tr>
<td>PA</td>
<td>p-xylene</td>
<td>4.75</td>
</tr>
<tr>
<td>PA</td>
<td>Mesitylene</td>
<td>4.85</td>
</tr>
<tr>
<td>PA</td>
<td>1,4-dioxane</td>
<td>5.30</td>
</tr>
<tr>
<td>PMDA</td>
<td>C(_6)H(_6)</td>
<td>2.41</td>
</tr>
<tr>
<td>PMDA</td>
<td>1,4-dioxane</td>
<td>1.74</td>
</tr>
</tbody>
</table>

MA = Maleic anhydride, PA = Phthalic anhydride.

Dielectric loss measurements

Measurements of dielectric loss in the microwave region provide some idea of the life time of a complex in solution. For complexes in solution it is clear that the complex will be breaking up and forming at a rate which depends on its life time. The exact frequency of this relaxation depends, of course, on the overall strength of donor-acceptor interaction. For strong complexes relaxation will occur relatively slowly and the species will have a long life time. On the other hand for weak complexes relaxation will occur more quickly due to the complex having a much shorter life time.
A survey of literature on dielectric loss measurements of CT complexes of anhydrides reveals that although some studies of this important property have been carried out with respect to complexes formed by maleic and phthalic anhydrides with aromatic donors, there is practically no work done as yet with polyanhydrides dissolved in various donor solvents.

Photoconductivity of PMDA complexes

The photoconductivity of weak CT complexes is particularly amenable to study since the dark conductivity of these complexes is low and therefore does not swamp the photoconductivity. Photoconductivity of charge transfer complexes of PMDA was studied by Kolninov et al.

Polarography

Polarography as an aid in the study of organic charge transfer complexes has been very little used. In fact, the potentiality of the technique in this area of research is yet to be explored. Polarographic one electron reduction potentials $E_{1\text{red}}$, whilst not directly measuring electron affinity, may nevertheless, provide one of the few independent experimental estimates of electron affinity which are available for a wide range of electron acceptor species. The half wave reduction potentials of a wide range of electron acceptors including unsaturated cyclic anhydrides in aprotic solvents, particularly acetonitrile, have been determined by Peover and his coworkers. The values of $E_{12\text{red}}$ (in volt units) for some anhydrides are shown in Table 1.3.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$E_{1\text{red}}$ (volt)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyromellitic dianhydride</td>
<td>- 0.55</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Dibromopyromellitic dianhydride</td>
<td>- 0.32</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Tetrachlorophthalic anhydride</td>
<td>- 0.86</td>
<td>Acetonitrile</td>
<td>27</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>- 1.31</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>- 0.84</td>
<td></td>
<td>27</td>
</tr>
</tbody>
</table>
Electrophysical properties of PMDA complexes

The temperature dependence of electrical conductivity and thermoelectromotive forces of molecular complexes of PMDA with N,N,N',N'-tetramethyl paraphenylenediamine (TMPD), paraphenylenediamine (PD), pyrene, anthracene and dithiohydroquinone dimethyl ether were measured from room temperature to 78 K.

Thermophysical properties

The heat capacities of naphthalene-PMDA complex have been measured. It shows no anomalies when compared with similar measurements performed on naphthalene complexes of tetracyanobenzene (TCNB) and tetracyanoethylene (TCNE).

Thermal stability of molecular complexes of a number of anhydrides including dichloropyromellitic dianhydride (DCPMDA) with anthracene, phenanthrene, pyrene, fluoranthene and carbazole as donors was studied by differential thermal analysis method. Melting and evaporation of the complexes proceed without decomposition. On heating some crystalline adducts undergo phase transitions caused by re-orientation of the donor and acceptor molecules.

Electron spin resonance studies

Solution of PMDA in tetrahydrofuran (THF) when irradiated with a Hg lamp display intense esr spectrum characteristic of PMDA negative ion. It is particularly interesting that photoproduction of radical ion from PMDA occurs with near-UV light of wavelength close to that at which major absorption of complexes of PMDA with common donors takes place.

Emission from CT complexes of PMDA

Fluorescence emission from CT complexes is generally observed either in crystalline state of the complexes or in complexes dissolved in organic glasses, particularly at low temperatures. The earlier work has been reviewed by Briegleb. The fluorescence band was observed as the mirror image of the CT absorption band and was characterized by a large, solvent-dependent Stokes shift.
Very few intermolecular complexes exhibit CT fluorescence in liquid solution. Only the complexes of the acceptors, tetrachlorophthalic anhydride (TCPA), pyromellitic dianhydride (PMDA) and 1,2,4,5-tetracyanobenzene (TCNB) with aromatic hydrocarbon donors have so far yielded CT fluorescence in liquid solution.\(^{35-43}\)

For a series of complexes with a given acceptor the energy of the CT fluorescence band correlated well with the ionization potentials of the donors. This confirms the assignment of the fluorescence to the \(\psi_{\text{ex}} \rightarrow \psi_{\text{G}}\) transition.\(^{43}\) The general failure to observe CT fluorescence in liquid solution must be ascribed to the efficient quenching of the CT excited state by the various modes of radiationless transition to the ground state.

The effect of viscosity of the medium on the position of fluorescence bands of charge transfer complexes of PMDA with a series of aromatic donors has been studied by Gorodyskii and Sisetskii.\(^{44}\) Prochorow\(^{45}\) measured the quantum yields and decaytimes of fluorescence of CT complexes of PMDA with some methylbenzenes in polar and non-polar solvents. The fluorescent state of PMDA-toluene complex seems\(^{46}\) to be 1:2 complex having the structure \(\text{AD}_2\).

Bright \textit{et al.}\(^{46}\) studied the change in the phosphorescence spectra of naphthalene and phenanthrene when they were complexed with PMDA compared with the uncomplexed donor.

Iwata, Tanaka and Nagakura\(^{48}\) studied phosphorescence emissions from CT complexes of PMDA with mesitylene, durene and hexamethylbenzene and attributed them to transitions from the charge transfer triplet level, rather than to transitions from ‘locally excited’ triplet states of either of the components within the CT complexes. The same investigators measured the life times of phosphorescence emission in a degassed ethyl ether-isopentane glass at \(-196^\circ\text{C}\). The life time of CT phosphorescence decreases with increasing donor ability. G.D. short,\(^{49}\) however, contradicted the above observations by suggesting that the emission spectra are the result of delayed fluorescence.
**Ionic dissociation of CT complexes of PMDA**

The remarkably low quantum yield of fluorescence of CT complexes in polar solvents may be mainly attributed to dissociation of the excited states into ionic forms. Formation of ion radical through excited EDA complexes seems to be important in connection with the primary processes of various kinds of photochemical reactions like photo-induced ionization in solution, photo-oxidation polymerization etc. The photo-induced ionic dissociation has hitherto been studied for several CT complexes in various solvents by recording esr spectra, emission spectra, transient absorption spectra, and transient photo-currents.

Potashnik et al. studied the photo-ionization of CT complex between PMDA and mesitylene in an ether-isopentane mixed solvent at 152 K by measuring the rate of formation of PMDA anion and the decay rate of phosphorescence of the complex. Both rates agree with each other within the limits of experimental error. This indicates that the ionic dissociation of the complex is brought about through its lowest triplet state:

\[ \text{DA} \xrightarrow{h\nu} \text{DA}^* \xrightarrow{~~~~} \text{DA}^* \rightarrow \text{D}^+ + \text{A}^- \]

Achiba and Kimura studied the photo-induced ionization by the flash-photolysis of solutions of PMDA in ether, 1,4-dioxane, tetrahydrofuran, and acetonitrile. They measured transient absorption spectra for these solutions. The results obtained for the degassed 1,4-dioxane and acetonitrile solutions at room temperature show that the concentration of PMDA anion increases with decreasing concentration of the triplet state. This means that the photo-induced ionization of the 1,4-dioxane solution of PMDA occurs via the triplet state of the PMDA-1,4-dioxane complex. This mechanism is supported by the fact that the addition of a triplet quencher such as oxygen or piperylene greatly reduces the yield of the anion. The same mechanism also holds for the ether and tetrahydrofuran solutions. On the other hand, the PMDA anion is formed mainly through the lowest excited singlet state of the complex in the acetonitrile solution. A tendency for the ionic dissociation of PMDA complexes to occur in the CT triplet states in non-polar solvents and mainly in the excited CT singlet states in polar solvents was also observed by Shimada, Masuhara and Mataga.
1.1.2 CT complexes of $p$-benzoquinone tetracarboxylic dianhydride ($C_{10}O_8$)

Hammond studied the CT properties of this acceptor. The acceptor is stable in dry air, although moist air turns it blue within 10 minutes. It can be heated to 140°C without decomposition. It is insoluble in most solvents (ether, petroleum ether, carbon tetrachloride, carbon disulphide etc.) Towards those in which it does dissolve (acetone, ethyl acetate, tetrahydrofuran, ethanol, water) it exhibits remarkable chemical reactivity. It dissolves in the methylbenzenes giving coloured solutions of the charge transfer complexes — benzene, orange; toluene, red; m-xylene, magenta; mesitylene, violet. The colours are associated with the single, broad bands shown in table 1.4 and thus $p$-benzoquinone tetracarboxylic dianhydride is one of the strongest $\pi$-electron acceptors so far known. Approximate half lives of the unstable complexes are also shown in table 1.4. It is found from this table that even the benzene adduct has to be stored at low temperatures in absence of light.

Table 1.4. CT absorptions of complexes of $C_{10}O_8$ with methylbenzenes in dichloromethane at 19°C.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$h\nu_{\text{max}}$ (eV)</th>
<th>Half life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.98</td>
<td>10</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.57</td>
<td>12</td>
</tr>
<tr>
<td>O-xylene</td>
<td>2.53</td>
<td>60</td>
</tr>
<tr>
<td>m-xylene</td>
<td>2.41</td>
<td>6</td>
</tr>
<tr>
<td>p-xylene</td>
<td>2.30</td>
<td>3</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>2.34</td>
<td>0.3</td>
</tr>
<tr>
<td>Pseudocumene</td>
<td>2.10</td>
<td>0.3</td>
</tr>
<tr>
<td>Durene</td>
<td>Blue</td>
<td>0.2</td>
</tr>
<tr>
<td>Pentamethyl benzene</td>
<td>Blue-green</td>
<td>0.1</td>
</tr>
<tr>
<td>Hexamethyl benzene</td>
<td>Green</td>
<td>0.05</td>
</tr>
</tbody>
</table>
1.1.3 **CT complexes of 1,4,5,8-Naphthalenetetrabaxylic dianhydride (NTCDA)**

Jacquignon *et al.*\(^{54}\) studied the CT complexes of the above mentioned anhydride and its 2-bromo derivative with a large number of polycyclic aromatic hydrocarbons with and without substituents and heterocyclic donors. In a large number of cases they isolated solid complexes and described their physical characteristics.

Kolninov *et al.*\(^{28}\) studied the photo-conductivity of CT complexes of NTCDA.

Thermal stability of molecular complexes of NTCDA with aromatic donors was studied by differential thermal analysis method.\(^{12}\)

Ilmet and Berger\(^{55}\) studied the effect of solvent on the absorption spectra of NTCDA dissolved in aromatic solvents. They explained the observed results as due to special effects of the aromatic solvents.

1.1.4 **CT complexes of mellitic trianhydride (MTA)**

Complexes of MTA were first investigated by Mustafin.\(^{56}\) Rosenberg *et al.*\(^{57}\) determined the CT band maxima of the complexes of MTA with a series of condensed benzenes in chloroform solution and evaluated the electron affinity of MTA which is about \(0.31 \pm 0.04\) eV higher than that of PMDA. It was concluded that consecutive addition of cyclic anhydride substituent to phthalic anhydride does not yield a uniform increase in electron affinity, the first addition being considerably more effective than the second addition. Their results are described in Table 1.5.
**Table 1.5.** CT transition energies of PMDA and MTA with aromatic hydrocarbon donors

<table>
<thead>
<tr>
<th>Donor</th>
<th>hv\textsubscript{CT} (PMDA) (eV)</th>
<th>hv\textsubscript{CT} (MTA) (eV)</th>
<th>Δhv\textsubscript{CT} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>3.01</td>
<td>2.74</td>
<td>0.27</td>
</tr>
<tr>
<td>Anthracene</td>
<td>2.40</td>
<td>2.10</td>
<td>0.30</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3.07</td>
<td>2.74</td>
<td>0.33</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>2.66</td>
<td>2.35</td>
<td>0.31</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.46</td>
<td>2.10</td>
<td>0.36</td>
</tr>
<tr>
<td>Fluorene</td>
<td>2.91</td>
<td>2.56</td>
<td>0.35</td>
</tr>
<tr>
<td>2-Me naphthalene</td>
<td>2.91</td>
<td>2.63</td>
<td>0.28</td>
</tr>
<tr>
<td>1, 8-dimethyl naphthalene</td>
<td>2.70</td>
<td>2.46</td>
<td>0.24</td>
</tr>
<tr>
<td>1-Chloronaphthalene</td>
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<td>2.71</td>
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<tr>
<td>1-Bromonaphthalene</td>
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<tr>
<td>2-Me anthracene</td>
<td>2.33</td>
<td>2.08</td>
<td>0.25</td>
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</table>

Av. 0.31 ± 0.04
Section II

Kinetics of reactions involving CT complexes having anhydride acceptors: A brief survey
With progress in research on electron donor-acceptor complexes it has become clear that formation of such species during the course of a chemical reaction (particularly organic reactions) may have a direct or incidental effect on the reaction. Many of the reported effects of changes in medium on reactivity can be ascribed to differences in the capacities of the various solvents to form complexes with one or more reactants along the reaction coordinates. Many, however, believe that molecular adducts which may be formed by interaction between two or more reactants may or may not be true reaction intermediates. But the possibility of donor-acceptor adducts acting as reaction intermediates is very much attractive and hence cannot be ignored. Again, there are ample evidences in which donor-acceptor complexes themselves undergo chemical changes. Many excellent articles are available on the subject.

In this section attention is focused on the kinetics of charge transfer complexes of organic Lewis bases with unsaturated cyclic anhydrides. Only dark reactions are discussed.

As early as 1918 Pratt and Perkins observed that when aniline was added to a benzene solution of tetrachlorophtallic anhydride (TCPA) a transitory yellow colour develops, immediately followed by a white precipitate of aniline tetrachlorophtalanilate which when warmed gives off aniline and water forming the anil. The scheme is shown in fig. 1.4. According to Pratt and Perkins the first step is the formation of the molecular addition product (I). The authors, however, did not study the kinetics of this step.

Nagy et al. studied the kinetics of reactions between tertiary amines and TCPA and emphasised the role of CT complex formation in such reactions. They studied the rate of reaction of Et₃N with TCPA at 20°C in twelve different solvents in the presence of approximately constant concentration of Et₃N and found the reaction to be of pseudo first order. The effect of addition of an aromatic donor species, e.g., acenaphthene or β-methoxy naphthalene to the system caused a hundred-fold decrease in the rate constant due to formation of complex between TCPA and the aromatic donor.
Fig. 1.4 Scheme for reaction between TCPA and aniline.
The kinetics of the solid state reaction of MA with pyrocatechol to give the yellow tetragonally symmetric 1:1 CT complex was studied by Singh and Singh.\textsuperscript{64}

Ferstandig \textit{et al.}\textsuperscript{7} noted that when PMDA is mixed with aniline or N-methyl-aniline, a red colour develops which disappears by reacting with PMDA. The authors, however, did not study the kinetic aspects of these reactions.

The role of charge transfer complexes in polymerisation reactions has been adequately emphasized.\textsuperscript{65,66} For example, the polymerisation of N-vinylcarbazole by the addition of a variety of electron acceptors has been described. These acceptors include among others PMDA and MA. It has been suggested\textsuperscript{65} that a charge transfer complex is formed, which undergoes electron transfer to produce a pair of radical ions; the carbazole cation radical then reacts successively with molecules of free N-vinylcarbazole to form the polymer.

\[
M + A \rightleftharpoons (MA)_{\text{CT}} \rightleftharpoons M^+ + A^- \\
M^+ + nM \rightarrow M_{n+1}^+ \rightleftharpoons \frac{nA^-}{A^-} M_{n+1}^+ A^- 
\]

There is, as yet, no final vindication of this plausible mechanism. The participation of a charge transfer complex in the copolymerization of MA with (i) 1,4-dioxane,\textsuperscript{67} (ii) 2-chloroethyl vinyl ether\textsuperscript{68}, (iii) isomeric butyl vinyl ethers\textsuperscript{69}, (iv) β-isopropenyl naphthalene\textsuperscript{70} (v) thiophene\textsuperscript{71} (vi) 4-vinyl pyridine,\textsuperscript{72} (vii) vinyl cyclohexane and its derivatives\textsuperscript{73} and (viii) dimethyl allylidene pentaerythritol and dicrotylidene pentaerythritol,\textsuperscript{74} has been postulated. Styrene-MA CT complex has been found to initiate the copolymerization of styrene and methyl methacrylate by a free radical mechanism\textsuperscript{75}. Copolymerization of acrylonitrile with MA in the presence of complexing agents has been studied\textsuperscript{76} while the role complexes of MA with electron donor monomers in radical polymerisation reactions has been elucidated.\textsuperscript{77} The kinetics of methyl methacrylate polymerisation in bulk or in acetonitrile was studied\textsuperscript{78} for initiation with complexes formed by, N,N-dimethylaniline with phthalic and tetrachlorophthalic anhydrides. The effect of polarity of the medium on the polymerisation, initiated by charge transfer complexes has been studied.\textsuperscript{79}
References


   (c) P.C. Dwivedi, A. Bansal, A. Srivastava, ibid., 27A, 753 (1988).


