

Charge- Transfer Complexes: A Short Review

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Abstract

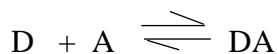
A charge- transfer complex or electron- donor- acceptor complexes is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. An electron donor may be defined as a molecule possessing a relatively high localized electron density. The charge- transfer complexes exist in two states a ground state and an excited state. The two molecules composing the charge-transfer complex undergo the normal physical forces expected between two molecules which are in close proximity to each other in the ground state. These forces include London dispersion forces and any electrostatic interactions, such as between dipole moments. Biphenyl is also an intermediate for the production of a host of other organic compounds such as emulsifiers, optical brighteners, crop protection products and plastics. Biphenyl occurs naturally in coal tar, crude oil and natural gas and can be isolated from these occurs via distillation. Biphenyl is soluble in typical organic solvents. Rotation about the single bond in biphenyl and its ortho-substituted derivatives is sterically hindered. Biphenyl prevents the growth of molds and fungus and is therefore used as a preservative, particularly in the preservation of citrus fruits during transportation.

Keywords: - Charge-transfer complex, thermodynamic, structural, biphenyl.

Introduction

Charge- transfer phenomena was introduced by Mulliken and widely discussed by Foster to define a new type of adducts. A charge- transfer complex or electron- donor- acceptor complexes is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. An electron donor may be defined as a molecule possessing a relatively high localized electron density. Conversely, an electron acceptor is relatively deficient in electrons. The nature of the attraction in a charge- transfer complex is not a stable chemical bond, and it is much weaker than covalent forces. The attraction is created by an electronic transition into an excited electronic state, and is best characterized as a resonance. The excitation energy of this resonance occurs in the visible region of the electro-magnetic spectrum, which produces the usually intense color characteristic for these complexes. These optical absorption bands are often referred to as charge-transfer(CT) bands. Optical spectroscopy is a powerful technique to characterize charge-transfer bands. The characteristic of a charge-transfer complex is the appearance of an additional electronic absorption bands, separate from the absorption bands of the both acceptor and donor molecules. The charge-transfer band occurs in the visible region of the electromagnetic spectrum, which produces the characteristic intense color for complexes. Charge- transfer complexes exist in many molecules. Organic, inorganic and in all phases of matter. A well-known example is the blue charge-transfer band exhibited by iodine when combined. In inorganic chemistry, most charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge- transfer bands in the transition metal complexes result from the movement of electrons between molecular orbitals that are predominantly metal in character and those that are predominantly ligand in character. If the electron moves from the molecular orbital with ligand like character to the metal like one, the complex is called ligand to metal charge -transfer(LMCT) complex. If the electron moves

from the molecular orbital with metal like character to the ligand like one, the complex is called a metal to ligand charge- transfer (MLCT) complex. Thus, a MLCT results in oxidation of the metal center where as a LMCT results in the reduction of the metal center. Resonance Raman spectroscopy is also a powerful technique to assign and characterize charge- transfer bands in these complexes. Charge- transfer complexes are formed by weak association of molecules or molecular subgroups, one acting as an electron donor and another as an electron acceptor. The association does not constitute a strong covalent bond and is subject to significant temperature, concentration and solvent. Weiss proposed that all molecular complexes have an essentially ionic structure D^+A^- , and charge- transfer association occurs in a chemical equilibrium with the donor (D) and acceptor (A) molecules.



Quantum mechanically, this is described as a resonance between the non-bonded state $|D, A\rangle$ and the dative state $|D^+ \dots A^-\rangle$. The formation of the dative state is an electronic transition giving rise to the colourful absorption bands. The intensity of charge- transfer bands in the absorbance spectrum depend on the equilibrium constant. The equilibrium constant for these complexes in solution by measuring the intensity of absorption bands as a function of the concentration of donor and acceptor components in the solution. The procedure is called the Benesi-Hildebrand method.

Charge-transfer transition energy

The colour of charge- transfer bands is characteristics of the specific type of donor and acceptor entities. The electron donating power of a donor molecule is measured by its ionisation potential which is the energy required to remove an electron from the highest occupied molecular orbital. The electron accepting power of the electron acceptor is determined by its electron affinity, which is the energy released when filling the lowest unoccupied molecular orbital. The overall energy balance is the energy gained in a spontaneous charge- transfer. It is determined by the difference between the acceptor's electron affinity (E_A) and donor's ionisation potential (E_I), adjusted by the resulting electrostatic attraction (J) between donor and acceptor.

$$\Delta E = E_A - E_I + J$$

The position of the characteristic charge-transfer bands in the electromagnetic spectrum is directly related to this energy difference and the balance of resonance contributions of non-bonded and dative states in the resonance equilibrium.

Identification of charge- transfer bands

Charge- transfer complexes are identified by following factors.

Colour: - The colour of charge-transfer complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from the donor to acceptor.

Solvatochromism: - In solution, the transition energy and therefore the complex colour varies with variation in solvent permittivity, indicating variations in shifts of electron density as a result of the transition. This distinguishes it from the $\pi \rightarrow \pi^*$ transition on the ligand

Intensity: - Charge -transfer absorptions bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For inorganic complexes, the typical molar absorptivities are about $50000 \text{ L mol}^{-1} \text{ cm}^{-1}$, that are three orders of magnitude higher than typical ϵ of $20 \text{ L mol}^{-1} \text{ cm}^{-1}$ or lower for d-d transitions (transition from t_{2g} to e_g). This is because the charge-transfer transitions are spin-allowed and Laporte-allowed. However, d-d transitions are only spin-allowed and Laporte-forbidden. The characteristic of a charge-transfer complex is the appearance of an additional electronic absorption bands, separate from the absorption bands of both donor and acceptor molecules. The charge-transfer absorption band occurs in the visible region of the electromagnetic spectrum. In this event the complexes are coloured.

Charge- transfer complexes

A charge-transfer transition may be regarded as an internal redox process. Charge-transfer transitions may be classified in four ways:

1. Ligand to Metal Charge Transfer (LMCT)
2. Metal to Ligand Charge Transfer (MLCT)
3. Inter Valence Charge Transfer
4. Intra Ligand Charge Transfer

If the transfer of an electron takes place from the ligand to metal, then charge-transfer is called ligand to metal charge transfer (LMCT). $L \rightarrow M$ charge transfer transition occurs when the ligands have lone pair of electrons of relatively high energy and low electron affinity while the metal ion has empty low-lying orbital. Consider a d^6 IrBr_6^{-3} octahedral complex an intense absorption band at 250 nm corresponding to a transition from ligand σ MO to the empty e_g MO. In KMnO_4 , Mn is in +7 oxidation state and have all the 3d- orbitals vacant. Mn^{+7} ion is surrounded tetrahedrally by four oxide ions. All oxide ions have filled 2p-orbitals. There is transfer of an electron from filled 2p-orbitals of oxide ion to vacant d-orbitals of Mn^{+7} ion. Since p-orbitals are ungerade and d-orbitals are gerade, therefore, electron transition from p-orbitals of o^{-2} to d-orbitals of Mn^{+7} ion is Laporte allowed. Therefore, transfer of an electron is Laporte and spin allowed. Therefore, KMnO_4 is intensely purple. Colour and orbitals involved in ligand to metal charge transfer of some compound are given in Table 1.

Table 1. Colour and orbitals involved in LMCT of compounds

| Compounds | Colour | Orbitals involved |
|--------------------------|--------|--|
| CdS | Yellow | $\text{Cd}^{+2}(4s) \leftarrow \text{S}^{-2}(\pi p)$ |
| HgS | Red | $\text{Hg}^{+2}(6s) \leftarrow \text{O}^{-2}(\pi p)$ |
| KMnO_4 | Purple | $\text{Mn}^{+7}(3d^0) \leftarrow \text{O}^{-2}(\pi p)$ |
| K_2CrO_4 | Yellow | $\text{Cr}^{+6}(3d) \leftarrow \text{O}^{-2}(\pi p)$ |
| HgI_2 | Red | $\text{Hg}^{+2}(6s) \leftarrow \text{I}^{-}(\pi p)$ |

Energy

required to transferred an electron from the ligand to metal depends upon the lowest unoccupied molecular orbital (LUMO) of the metal cation and the highest occupied molecular orbital (HOMO) of the ligand. Energy required for electron transfer from πp -orbital of oxide ion to metal ion in isoelectronic species like VO_4^{-3} , CrO_4^{-2} and MnO_4^{-} decreases in the order:



On moving from VO_4^{-3} to MnO_4^{-} size of metal cation decreases in the order $\text{V}^{+5} > \text{Cr}^{+6} > \text{Mn}^{+7}$ because in this direction effective nuclear charge increases and energy of acceptor d- orbitals decreases. Therefore, energy of charge transfer decreases. Hence energy of charge-transfer decreases in the following order:



Tetra oxo anions of 4d and 5d-series transition metals are colourless because energy difference between 2p- of oxide ion and 4d and 5d-orbitals of transition metals is very large and electron transfer from πp -orbitals of oxide to d-orbitals of metal requires a high energy which in UV-region.

2. Metal to Ligand Charge Transfer (MLCT)

In this type of charge transfer the charge(electron) is transferred from the filled metal t_{2g} orbital to the empty π^* orbitals of the ligand. π^* orbitals of the ligand should be higher in energy than the filled metal t_{2g} orbitals. This transfer is favoured if the metal is in low oxidation state and has some oxidising character and the ligand has a low lying π^* orbital. MLCT mainly occurs with the ligands having π^* orbitals such as CO, CN^- , SCN^- , pyridine, bipyridine, o-phenanthroline, pyrazine, dithiolene, NO etc. In an octahedral complex when t_{2g} and e_g^* orbitals are occupied, two MLCT bands $\pi^* \leftarrow t_{2g}$ and $\pi^* \leftarrow e_g^*$ are observed.

Fe (II) complexes containing tetraamine macrocyclic ligand have intense colour due to MLCT. The compounds and their colours arising from MLCT are given in Table 2.

Table 2. Compounds and their colours arising from MLCT

| Compounds | colour |
|-----------------|--------|
| $K_4[Fe(CN)_6]$ | Yellow |
| $K_3[Fe(CN)_6]$ | Red |
| $[Fe(phen)_3]$ | Blue |
| $[Fe(acac)_3]$ | Red |

The complexes $Cr(CO)_6$, $Mo(CO)_6$, $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$ etc show intense MLCT bands in the region 35000- 45000 cm^{-1} . MLCT bands usually lie lower in energy. $T_{2g} \rightarrow \pi^*$ charge transfer transition occurs in $[Ir(py)_6]^{+3}$ in 29000-35500 cm^{-1} region by the transfer of an electron from the filled t_{2g} orbital of the metal to the empty π^* orbital on pyridine ligand. Vogler and Kunkle considered the MLCT complex to be an isomer of the ground state which contains an oxidized metal and reduced ligand.

3. Inter Valence Charge Transfer or Metal to Metal Charge Transfer

In these transitions an electron gets excited from the valence shell of one atom to valence shell of the other atom. Electron transfer takes place from the atom of lower oxidation state to another atom of higher oxidation state. Prussian blue shows intense blue colour because of transfer of an electron from Fe^{+2} to Fe^{+3} . In Prussian blue Fe^{+2} ion is octahedrally coordinated with C atom of the CN^- ligands and Fe^{+3} is octahedrally coordinated with N atom of CN^- ligands. Thus, an electron transfer takes place through bridging cyanide ligands. Red lead (Pb_3O_4) contains Pb^{+2} and Pb^{+4} , due to electron transfer from Pb^{+2} to Pb^{+4} gives intense red colour.

4. Intra Ligand Charge Transfer

Some organic ligands behave as chromophore and the chromophore nature is responsible for colour. There are four electronic transitions $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ within a chromophore. The compounds having quadruple bonds ($Re_2Cl_8^{-2}$, $Mo_2Cl_8^{-4}$) is colour due to $\delta \rightarrow \delta^*$ transition. The metal carbonyl compounds containing single M—M bonds are often intensely coloured due to metal $\sigma \rightarrow \sigma^*$ transitions.

Colour of charge-transfer complexes

The promotion of an electron from ground state to the excited state is called electronic transition. In complexes the electronic transition take place from t_{2g} to e_g or e to t_2 orbitals in octahedral or tetrahedral complexes and such type of transitions are called d-d transitions. Many metal complexes are coloured due to d-d transitions. These colours are usually quite faint due to two selection rules:

The spin rule: $\Delta S = 0$ On promotion, the electron should not experience a change in spin. Electronic transitions which experience a change in spin are said to be spin forbidden.

Laporte's rule: $\Delta l = \pm 1$ d-d transitions for complexes which have a centre of symmetry are Laporte forbidden.

Charge- transfer complexes do not experience d-d transitions. Thus, these rules do not apply and the absorptions are generally very intense. The classical example of a charge-transfer complex is that between iodine and starch to form an intense purple colour. This has wide spread use as a rough screen for counterfeit currency. Unlike most paper, the paper used in USA currency is not sized with starch. Thus, formation of this purple colour on application of an iodine solution indicates a counterfeit. The first molecular complexes, now to be of the charge-transfer type, were aromatic hydrocarbon picric acid complexes isolated by Fritzsche. The donor-acceptor approach was reintroduced by Bryce, and it was assumed that the complex was essentially ionic. Stabilization of the complex was considered be a result of the complete donation of an electron from the donor to the acceptor. It has been known that iodine dissolves in various solvents giving of different colours. Toscano first demonstrated that iodine solutions fall into two classes brown and violet. The former are now known to be $n \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ charge-transfer

complexes. The brown solutions were considered to contain chemically iodine bound in some way to the solvent, and it was recognized that the brown solvents are electron donating species evidence for solvent binding was obtained by Mayer showed that in brown solutions iodine had a non-zero dipole moment. Benesi and Hildebrand's observations led Mulliken to suggest that the new band in the benzene iodine complex was an intermolecular absorption band and to characterize these complexes as charge-transfer in nature.

Theoretical treatment of charge- transfer complexes

The charge- transfer complexes exist in two states a ground state and an excited state. The two molecules composing the charge-transfer complex undergo the normal physical forces expected between two molecules which are in close proximity to each other in the ground state. These forces include London dispersion forces and any electrostatic interactions, such as between dipole moments. In addition to these normal forces, a small amount of charge is transferred from the donor to the acceptor. The excited state of the complex occurs when the ground state complex absorbs a photon of light having the appropriate frequency. In the excited state the electron which had only been slightly shifted toward the acceptor in the ground state is almost totally transferred. Depending on the structural features of both the donor and acceptor the wavelength of light absorbed may be in the visible range of the electromagnetic spectrum. In many cases, therefore, charge-transfer complexes are coloured. Mulliken was responsible for the development of what has been the most successful theoretical treatment of charge-transfer complexes. He described the ground state of the complex by the wave function(ψ^N), which is the hybrid of two wave functions $\psi(A, D)$ and $\psi(A^-D^+)$. The wave function $\psi(A, D)$ is referred to as the no bond function and represents the wave function of the two molecules in close proximity to each other but with no charge-transfer between them. The $\psi(A, D)$ can include, however the normal electrical interactions between molecules. Consequently, the ground state wave function for a weak complex can be described as:

$$\psi^N = a\psi(A, D) + b\psi(A^-D^+). \text{ Where } a \gg b.$$

The wave function $\psi(A^-D^+)$ is called the dative function and represents the wave function of two molecules held together by total transfer of electron from the donor(D) to acceptor(A). The excited state of the complex can be described by:

$$\psi^E = b^*\psi(A^-D^+) - a^*\psi(A, D) \text{ where } b^* \gg a^*$$

Classification of charge-transfer complexes

The charge-transfer complexes may conveniently be classified according to the types of orbitals in the donor and acceptor molecules which are undergoing the interaction. The donor and acceptor molecules may each be divided into three classes as shown in the Table 3. The ν acceptors refer to metal atoms possessing a low-lying vacant valence orbital. Hypothetically, there are nine possible types of complex. However, in practice, the n- donors do not form complexes with metal ions but form covalent bonds instead.

Table 3. Donor and acceptor types charge-transfer complexes

| Donor | Examples | Acceptor | Examples |
|----------|-----------------------------------|----------|--------------------------|
| σ | R-X, Cyclopropane | ν | Ag^+ , organometallics |
| n | R-O-R, R_3N , pyridine, dioxane | σ | I_2 , Br_2 , ICl |

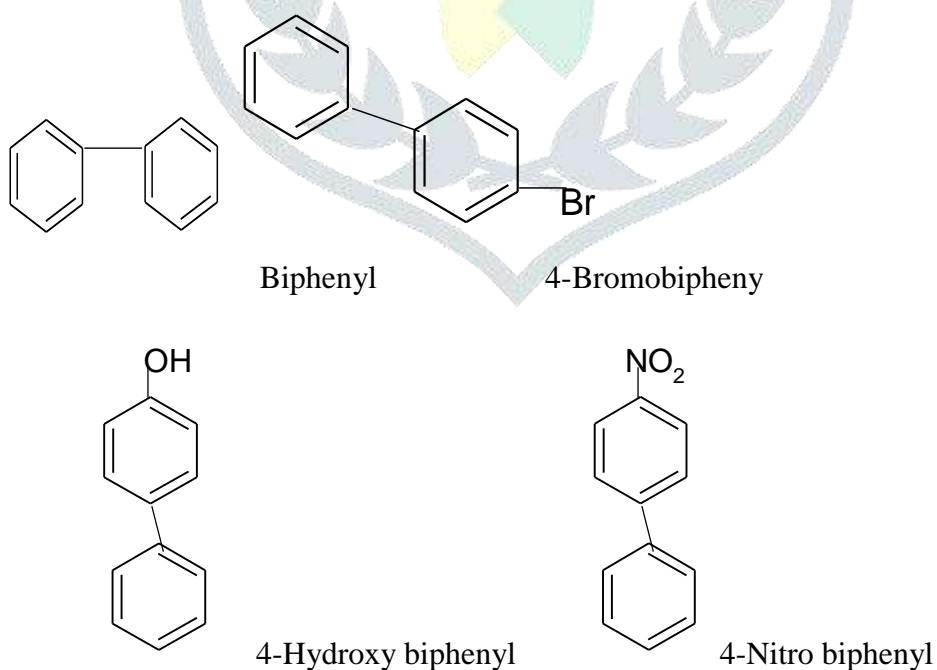
Structural considerations

The charge-transfer complexes can exist as intermolecular complexes, where the interaction takes place between two molecules or as intramolecular complexes, where both the donor and acceptor moieties are contained within one molecule. For charge-transfer interactions to occur, the donor and acceptor complexes must be close enough for their differences in electron density. The most charge-transfer

complexes exist in a 1:1 stoichiometric ratio of donor to acceptor. For some d-d types of complexes there is evidence for the existence of higher order complexes in equilibrium with the 1:1 complex. For the 2:1 complex involving two donors, D_2A , support has been found for the D-A-D form rather than D-D-A form. The crystal structure of phenol benzoquinone complexes have been found to have both 1:1 and 2:1 stoichiometries. Some aromatic crystalline charge-transfer complexes involving d donors and acceptors, are found to be composed of infinite chains of alternate donor and acceptor molecules in which the donor-acceptor distance is slightly less than the Vander Waals distances. Additionally, the aromatic d-d complexes are found to occur in staggered sandwich forms in which the plane of the donor is parallel to the plane of acceptor. Ideally, the donor and acceptor molecules are staggered one half their widths in order for their orbital overlaps to be maximized. The occurrence of a charge-transfer interaction usually requires some amount of the overlap between the molecular orbitals of the donor and acceptor. Normally, the interaction is between the HOMO of the donor with the LUMO of the acceptor. This overlap principle is certainly true for intermolecular complexes. However, for the intramolecular complexes, examples are also known of indirect, through bond interactions, besides the direct, through space interactions. The amount of orbital overlapping between the donor and acceptor plays a critical role in the magnitude of the charge-transfer interaction observed. Constraints resulting from steric hindrances are major factors in this regard. The binding energies for the charge-transfer complexes between phenol and hydroquinone with para-benzoquinone was found to be larger than those for anisole and hydroquinone, dimethyl ether with p-benzoquinone. This was attributed to the steric influence of the methyl groups. For highly substituted molecules steric hindrance may well prevent the close approach necessary in order for charge-transfer interactions to take place. The intramolecular complexes including p-m-cyclophane quinhydrones, naphthalenophane quinhydrones, cyclophane-o-quinones and substituted biphenyls have been investigated. The results from these investigations clearly show how the overlap between the donor and acceptor orbitals has a large influence on both the frequency and intensity of the charge-transfer absorptions.

Biphenyls

Biphenyl or diphenyl is an organic compound that forms colourless crystals. It has a distinctively pleasant smell. Biphenyl is an aromatic hydrocarbon with a molecular formula $C_{12}H_{10}$ or $(C_6H_5)_2$.



Biphenyl is also an intermediate for the production of a host of other organic compounds such as emulsifiers, optical brighteners, crop protection products and plastics. Biphenyl occurs naturally in coal tar, crude oil and natural gas and can be isolated from these sources via distillation. Biphenyl is soluble in

typical organic solvents. Rotation about the single bond in biphenyl and its ortho-substituted derivatives is sterically hindered. Biphenyl prevents the growth of molds and fungus and is therefore used as a preservative, particularly in the preservation of citrus fruits during transportation. Hydroxylate biphenyl and its polychlorinated biphenyls are degraded by some bacteria. It is a part of the active group in the antibiotic oritavancin. Polychlorinated biphenyls were once used as cooling and insulating fluids and polybrominated biphenyls are flame retardants.

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