

Pre and Post electronic changes in charge transfer complex: Mini Review

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ABSTRACT

The UV electronic absorption spectra of several organic CT (Charge Transfer) interactions have showed appearance and/or disappearance of spectral CT-bands. The stoichiometry was determined by Job's, spectrophotometric and conductometric titration methods. The conductivity values of the CT-complex are found to have the range of semiconductors indicating the dissociation of CTC to produce ionic species. The electronic change of CTC leads to the formation of protonated inner sigma complex. All spectral results confirm the formation of a thermodynamically stable mono substituted product via inner sigma complex. The DFT studies support the CTC and inner sigma complex.

Keywords: 1-Benzoylpiperazine; P-chloranil; Donor; Acceptor; DFT; Charge transfer complex

INTRODUCTION

Donor-Acceptor complexes: Brief introduction

A ground state charge transfer interaction between organic donor and acceptor was reported in 1960 by R. Foster. This results a charge transfer complex (CTC) involving van der Waal forces which in turn undergoes dissociation partially in vapour as well as in solution phase [1]. A Lewis acid-base type [2] CTCs were also reported (RS Mulliken, 1950). These CTCs are found to have various physical and biological properties [3-11].

P-chloranil (Acceptor): A brief introduction

The acceptor p-chloranil (CHL: 2, 3, 5, 6-tetrachloro p-benzoquinone) is an important quinone π -acceptor. The quinone compounds are used as agriculture fungicides, dye intermediates etc. It was suggested that the radical anion or inner σ -complex resulted by the transfer of electron from donor precursor to CHL acceptor [12].

1-Benzoylpiperazine: A brief introduction

1-Benzoylpiperazine (1-BNZZP) is used as chemical intermediate in pharmaceutical industries. The piperazine derivatives are generally found in bio-active compounds. The 1-BNZZP shows antitumor, inotropic, nootropic and cardiovascular properties

[13]. It acts as a good electron donor due to the presence of -NH group contains lone pair of electrons.

LITERATURE SURVEY

Donor-Acceptor complexation involving chloranil as a typical acceptor

CHL shows electrochemical behaviour in aluminum chloride (AlCl₃) and n-butylpyridinium chloride (BuPyCl) ionic liquid system. Generally, CHL complexes exhibit lavender or purple color in polar solvent. This can be observed from the shift of CT-band wavelength in electronic absorption spectra.

The Mechanistic way of CT-complex formation was explained through the theoretical DFT method [14]. The formation of CT-complex is based on the electronic interaction of the highest occupied molecular orbital (HOMO) of the donor with the lowest unoccupied molecular orbital (LUMO) of the acceptor. The formation of molecular CTCs accompanied with magnetic, dielectric, and structural properties.

Synthesis, characterization and DNA binding properties of CT-complex formed between a bio active donor 1-(2-Methylbenzyl) piperazine and CHL have reported. The proposed mechanistic scheme is supported by DFT method. The reduction of positive charges on the chlorine atoms of the CTC relative to p-chloranil

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indicates formation of radical ion pair. The strong intercalative mode binding of complex with CT-DNA was explored with achieving high binding constant [15].

Donor-Acceptor complexation involving piperazines

Piperazine moieties are well known e-donors which can easily form CT-complexes in vapour phase as well as in solution.

A spectrophotometric method was applied for identifying the stoichiometry of benzhydryl piperazine (BHP) and 2, 3-dichloro-5, 6-dicyano-1,4-benzoquinone (DDQ) donor-acceptor complex. It was reported as 1:2(D:A) stable CT-complex [16].

The CT-complex of 1-benzoylpiperazine and DDQ was studied spectrophotometrically in acetonitrile (ACN) at different temperatures [17]. The bonding nature of CT-complex was studied. A typical conductometric titration technique was used in addition to job's continuous variation and spectrophotometric techniques to find the composition of CTC. The reactivity of N-atoms was estimated from the DFT computational work. The spectroscopic study is facilitated in understanding the electron transfer process.

((1-BNZZP) (CHL)) COMPLEX ANALYSIS

Synthesis of mono substituted product

Mostly, the charge transfer complexes have 1:1 molecular compositions.

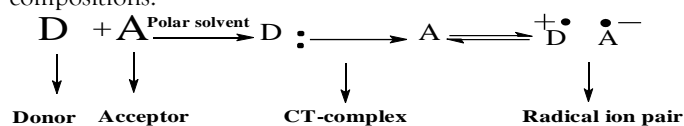


Figure 1: Synthesis of mono substituted product.

The stability parameters like formation constant, molar extinction coefficient are estimated by using famous Benesi-Hildebrand equations [18]. The higher values of KCT, ϵ are attributed to the donating power of 1-BNZZP, high electron affinity of CHL (~1.34 eV) and the high electric permittivity of ACN solvent (Figure 1).

1:1 B-H equation:

$$\frac{C_a}{A} \frac{C_d}{d} = \frac{1}{K_{ct} \epsilon} + \frac{(C_a + C_d)}{\epsilon}$$

1:2 B-H equation:

$$\frac{C_a^2 C_d}{A^2 d} = \frac{1}{K_{CT} \epsilon} + \frac{1}{\epsilon} \frac{C_a}{d} + \frac{C_d}{4A}$$

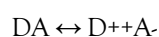
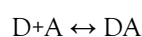
Here,

C_a -concentration of acceptor, C_d -concentration of donor, A - Absorbance, KCT - Formation constant or Stability constant, ϵ -Molar extinction coefficient.

The stoichiometry was determined by Job's, photometric and conductometric titration methods. The 1:1 equivalents of 1-Benzoylpiperazine (1-BNZZP) and p-chloranil (CHL) are mixed in saturated solution gives a purple color. It was protected from light for 3-4 days. The purple coloured solid crystalline mono substituted product of CT-complex was formed. The N-atom lone pair and ring electrons of 1-BNZZP are responsible for donation,

but the N-atom which is nearer to the carbonyl group does not easily participate in the electron transfer process. The free-NH group participates in the donation of electrons to the acceptor. The electron transfer from N-center to CHL generates the radical anion. As time passes (3-4 days), the solution transforms into solid phase of stable mono substituted product of CT-complex. This indicates the intermediate step is inner $\pi\pi$ complex formation [19]. The Mechanistic scheme was confirmed from the different spectral and DFT optimization analysis. Especially, ESI-Mass spectral presence/absence peaks confirm the product. All spectral analyses indicate the stable mono substituted product. Prior to this compound, 1:1 stoichiometry ratio CTC is resulted as an intermediate.

Generally, the conductivity values of semiconductors range is 10^{-6} to 10^4 (Ωm)⁻¹, the conductivity values in the present organic charge transfer complex range is 1.5×10^{-4} to 3.5×10^{-4} (Ωm)⁻¹. This indicates in ACN medium, the resulting ((1-BNZZP)(CHL)) complex dissociates into ions and giving rise to appreciable conductivity as per the scheme given below:



Where DA represents the Donor-Acceptor complex.

CT-band characterization study

Generally, organic CTCs shows charge transfer band in the visible region i.e., 380-750 nm. In a similar way ((1-BNZZP)(CHL)) complex shows CT-band at $\lambda = 549.5$ nm in ACN. The Job's and spectrophotometric methods were performed by considering this wavelength [20].

The energy of 1-BNZZP, CHL interaction (ECT), oscillator strength (f), transition dipole moment (μ) were calculated using the following relations

$$E_{CT} = \frac{1243.667}{\lambda_{CT}}$$

$$f = 4.32 \times 10^{-9} \left[\frac{\epsilon_{\max} \Delta \nu_{1/2}}{\nu_{\max}^2} \right]$$

$$\mu = 0.0958 \left[\frac{\epsilon_{\max} \Delta \nu_{1/2}}{\nu_{\max}^2} \right]^{1/2}$$

where λ_{CT} is the wavelength of the band, ϵ_{\max} is the maximum molar extinction coefficient, $\Delta \nu_{(1/2)}$ is the band width at half absorbance and ν_{\max} is wave number at the maximum absorption of the CT-band, respectively.

The values of ΔH° and ΔS° were calculated by using van't Hoff plot. The endothermic nature of the process with a positive entropic contribution results negative sign of ΔG° at room temperature. The ΔG° becomes high negative when the bonds between the components become stronger. The reactants are expected to have less physical strain or gain of freedom so that

forward reaction proceeds in order to achieve equilibrium. The physical parameters viz., ionization potential of donor (ID), resonance energy (RN) and dissociation energy (W) indicate the stability of CT-complex.

DFT studies

The density functional theory (DFT) of the acceptor, donor and CT complex were carried out using Gaussian 09 w program [21] in gas phase as well as in Polarizable continuum model (PCM). The protonated form, HOMO-LUMO orbital energy calculations reveal that there is a conceivable opportunity for charge transfer from donor to CHL in the CT complex. The MEP (Molecular Electrostatic Potential) maps showed that the center maximum negative value of 1-BNTP decreases to some extent upon the CT-interaction. The optimized bond parameters (bond lengths, bond angles) of reactants and CTC indicate the electron transfer. The computational results like Mulliken atomic charges and theoretical reactive descriptors (ionization potential I, electron affinity A, chemical potential μ , hardness η , electrophilicity index ω , Softness σ) support the e-transfer. The TD-DFT study also supports the CT-complex.

Spectroscopic studies

The IR data show the characteristic peaks of mono substituted product of CT-complex. The N-H-O- peak with very weak intensity confirms the product via inner sigma (σ) complex formation. The ¹H-NMR data of the complex indicate the absence of -NH proton signal which confirms the mono substituted product of the CT-complex. The Mass characteristic peak of molecular ion (M⁺ at 399 a.m.u.), confirms the mono substituted product via CT-complex. TGA study supports the thermal stability of compound. The SEM-EDX study confirms the product.

CONCLUSION

The organic CT-complexes are the association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. Since CHL acceptor is derived from any acidic centers, it is concluded that the CT-complexes are formed through π - π^* and/or n- π^* charge migration from HOMO of the donor to the LUMO of the acceptor. The Benesi-Hildebrand method is used for estimation of the molecular composition. FT-IR, ¹H-NMR, Mass, SEM-EDX, TGA-DTA spectroscopic techniques were used to characterize the CT-complex. The protonated form of CT complex was examined from DFT gas phase and PCM models. The models give good support for understand the mechanism of the CT-complex. An inner σ -complex resulted by the transfer of electron from donor precursor to CHL acceptor. A new thermodynamically stable mono substituted product is resulted via inner σ -complex by eliminating HCl.

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