Experiment: Color Changes with Complexations: Observation of Charge-Transfer Absorption

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1. Introduction

Charge-transfer complexes and reactions are of great interest in chemistry. They are extensively studied experimentally and computationally because of their importance in organic semi- and superconductors, and also because they can serve as important model systems for the studies of electron transfer reactions.

Bensei and Hildebrand (JACS, 1949, 71, 927) observed the colorful complex formation when aromatic hydrocarbons and iodine are present in nonpolar solvents. They developed a spectroscopic method for measurement the equilibrium constant for such complexes (Bensei-Hildebrand equation). A few years after the BH study, Mulliken (JACS, 1959, 72, 600) depicted the electronic structure of these systems (assuming 1:1 complex) in terms of a so-called "no-bond" wave function $\psi(A,D)$ and a dative (charge-transfer) wave function $\psi(A^- - D^+)$, where A is the electron acceptor and D is the electron donor. Using perturbation theory, Mulliken described the ground state as a resonance hybrid composed mostly of the no-bond wave function with a small quantity of the dative wave function; $\psi_G = a^* \psi(A,D) + b^* \psi(A^- - D^+)$. The excited state was mostly made up of the dative wave function with a little of the no-bond wave function; $\psi^* \sim \psi(A^- - D^+)$. Later, McGlynn (Chem Rev, 1958, 1113) presented a similar treatment of these systems in terms of the variation method. The color of these complexes is interpreted as being caused by a charge-transfer absorption band associated with an electronic transition from the ground state to the charge-transfer state. According to the Mulliken's theory, the energy of this charge-transfer band is given by

$$h\nu_{CT} = IE_D - EA_A - w \tag{1}$$

where h is Planck's constant, ν_{CT} is the frequency of the charge-transfer transition, IE_D is the ionization energy of the donor, EA_A is the electron affinity of the acceptor, and W is the Coulombic attraction energy of the complex. It has been shown by Mulliken that this equation works well in predicting the trends in many CT complex systems as well. Approximately (very crude), **you can say a photon absorption transfers an electron from the donor to the acceptor!** This phenomenon is something you don't usually see in typical single molecules.

2. Purpose

A major objective of the experiment described herein is to give you an understanding of the nature of charge-transfer complexes. Another objective is to illustrate how the spectra recorded by UV–vis spectroscopic methods are correlated with the color of the solutions. In this experiment, the CT absorption spectra of a series of electron donor (Lewis base) mixed with a same common electron acceptor (Lewis acid) will be recorded.

3. Safety

The samples prepared in this experiment consist of either organic solvent (substituted benzenes) or solutions of organic material in chloroform. Gloves and goggles should be worn when handling these chemicals. Please keep the sample containers covered during the experiment.

4. Experiments

You will make three types of CT complexes using tetrachlorobenzoquinone (TCBQ or Chloranil) as an electron acceptor and mesitylene (Mes), dithiophene (T2), and terthiophene (T3) as an electron donor. The structures are shown below.
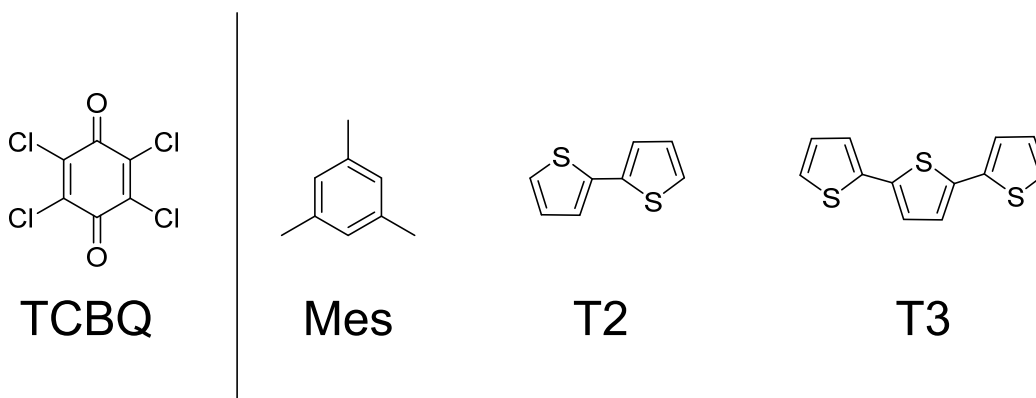
Chemicals:

TCBQ (MW = 245.86), ~62 mg

Mesitylene (MW = 120.19, d = 0.864 g/ml), ~1 mL

T3 (MW = 166.26), ~320 mg

T3 (MW = 248.39), ~480 mg

Chloroform, 100 mL

Glassware:

Syringe

Graduated cylinder

Vials

Flasks

Quartz cuvette

PASCO spectrophotometer

iPad mini

Procedures:

1. Make the stock solutions of 50mL of 5 mM TCBQ in chloroform.

2. Make the following solutions using the stock solutions of TCBQ

[Mes] = 0 mM, 125 mM, 250 mM, 500 mM, and 1M

[T2] = 0 mM, 40 mM, 80 mM, 160 mM, 320 mM

[T3] = 0 mM, 15 mM, 30 mM, 60 mM, and 120 mM

*Please first make the solutions of the highest concentrations (6 mL) and do serial dilution to make the rest. You will eventually have 3 mL of each solution.

**Make sure to dissolve all T2 and T3 initially. You may need to warm up a bit.

3. Turn on the spectrophotometer and open the PASCO software in iPad mini. Make sure the iPad is connected to the spectrophotometer.

4. Add a ~3 mL of chloroform (solvent blank) in a cuvette

5. Insert a blank and perform a Dark Calibration and a Light Calibration.

6. Once you are done, start Data recording.

7. Now, put the solution you made in a cuvette and record the spectrum (like the one below). You may need to optimize the spectrum by adjusting the parameters.

8. Record the colors of each solution (light blue, yellow, etc…) and record the absorption maximum of CT absorption bands (Table is provided below).

9. Convert the absorption maximum (λ_{max}) to the energy scale (eV) using the conversion equation: $E = \dfrac{hc}{\lambda} = \dfrac{1240\ eV*nm}{\lambda(nm)}$

10. (Optional) Save all the spectra and send to your email address so that you can perform the further analysis later (Section 6).
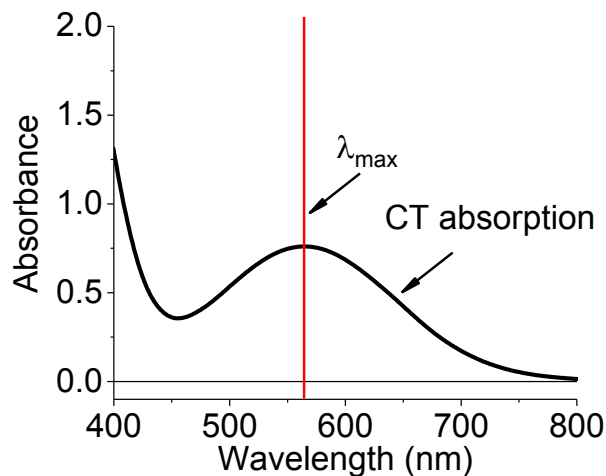
Example Absorption Spectrum

5. Remarks and Things to Consider
1. What are the colors of the solutions?

	Color	Absorption maximum (λ_{max}, nm)	Energy (eV)	IE_D (eV)
TCBQ				NA
Mes/TCBQ				8.4
T2/TCBQ				7.83
T3/TCBQ				7.38

2. Do you observe any trends in absorbance when you increase the concentration of electron donors? If so, why?
3. Why do you see different colors when TCBQ is mixed with different electron donors?
4. Do the absorption maxima correlate with ionization of energy of donor (IE_D)? Check back the equation 1. IE of Mes, T2, and T3 are 8.4, 7.83, and 7.38 eV, respectively.

6. Quantitative Analysis
6.1.   BH Analysis

The complexation equilibrium reaction involving an acceptor A, here TCBQ, and a donor D such as mesitylene is

$$D + A \rightleftharpoons DA \tag{2}$$

and the equilibrium constant expression is given by

$$K = \frac{[DA]}{[D][A]} \tag{3}$$

The initial concentrations of the donor and acceptor in the solution before the equilibrium are set as $[D]_0$ and $[A]_0$, respectively and the concentration of the complex after the equilibrium is $[DA]$. The concentrations of the donor and the acceptor at the equilibrium are $[D] = [D]_0 - [DA]$ and $[A] = [A]_0 - [DA]$. Therefore,

$$K = \frac{[DA]}{([D]_0 - [DA])([A]_0 - [DA])} \tag{4}$$

If $[D]_0 \gg [A]_0$, the concentration of the donor at equilibrium will be essentially the same before equilibrium ($[D]=[D]_0$), then we can write eq 4 as

$$K = \frac{[DA]}{[D]_0([A]_0 - [DA])} \tag{5}$$

Substituting eq 8 into eq 5 and rearranging terms will lead to the original Benesi-Hildebrand equation:

$$\frac{[A]_0}{abs} = \frac{1}{\varepsilon_{DA} l} + \frac{1}{K \varepsilon_{DA} l}\left(\frac{1}{[D]_0}\right) \tag{6}$$

You can use this equation to fit the data to find the values of ε_{DA} and K.

	BH (equation 6)
$[D]_0$ (M)	
l (cm)	
ε_{DA} (M^{-1}cm^{-1})	
K (M^{-1})	

6.2. Data Processing

We use Excel. Make the columns for 1/[D]0 and [A]0/abs. Get the absorbance at appropriate wavelength (can be absorption maxima) for each concentration. Construct the graph and perform the linear regression analysis by "Add trendline". We can also get the slope and the intercept by typing the following in Cells (here N4 and O4)

N4 = SLOPE(y-data,x-data) (in the example below, it is =SLOPE(M4:M9,L4:L9))

O4 = INTERCEPT (y-data,x-data)
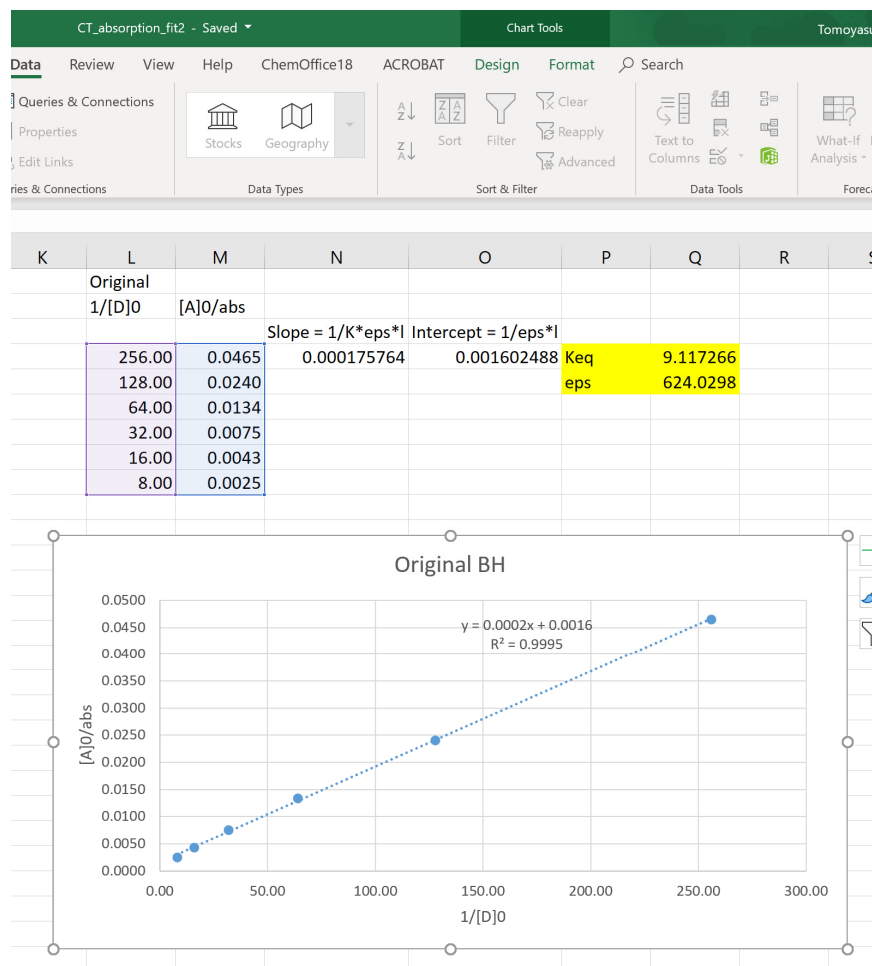
You can now calculate K and ε_{DA} (see eq 6).

With K values in hand from both the analyses, you can calculate the Gibbs energy change (ΔG^0) through the equation

$$\Delta G^0 = -RT\ln(K) \tag{7}$$

where RT at 298K is ~0.025 eV.