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UV-visible Absorption Studies of Tetrachloro-*p*-benzoquinone and Tertiary Amines Charge Transfer Complexes in Trichloromethane

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Abstract: The spectophotometry of charge transfer (CT) complexes of tetrachloro-p-benzoquinone (TCB) with tertiary amine [triethylamine (TEA), triphylamine (TPA), N,N-dimethylphenylamine (DMPA), N-ethylcarbazole (ECZ)] have been studied in dichloromethane in UV-visible region. The CT complexes parameter, molar ratio of reactants in complex, molar extinction coefficient ε_{CT}, equilibrium constant K_{CT}, free energy ΔG and dissociation energy of the CT complex excited state E, have also been estimated and discussed.

Keywords: Spectophotometry, charge transfer , tertiary amine, tetrachloro-*p*-benzoquinone.

TCB is well known as π acceptor which can form CT complexes with many donor molecules [1,2], and also can be used in the analysis and quality control of drugs in different pharmaceutical dosage forms [3]. Although spectrophotometrical method is often used to study the character of CT complexes, very little research on CT complexes formed by TCB and simple tertiary amine have been found. Recently, we employ the spectrophotometrical method to study the CT complexes using the TCB as π acceptor and tertiary amine as donors. In this paper, we report the above results and explain some phenomena.

Experimental

Material: TCB was purchased from Acros Corp. and used as received. TEA, DMPA and TPA were purified before use. ECZ was the product of Beijing Chemical Corp. without further purification.

Methods: "The continuous variation method" [4] was used to determine the molar ratio of reactants in complexes. We used Benesi-Hildebrand method[5] to determine the molar coefficient and association constant of CT complexes. The UV-visible spectra were recorded on a Hitachi 330 UV-visible spectrophotometer.

Results and discussion

Tertiary amines can act as electron donors and participate in "n-π" charge transfer with acceptor TCB. "The continuous variation method" was applied to determine the molar ratio of tertiary amine and TCB: the method revealed a donor to acceptor of 1:1 under the described condition as shown in **Figure 1**.

The plot of the absorbance of the CT complexes at λ_{max} divided by concentration of donor against the absorbance of the CT complexes at λ_{max} is according to Bensi-Hildebrand equation (equation 1), a very good straight line of which the intercepts equals to $K_{CT}[A]\ \varepsilon_{CT}$, and slope equals to $-K_{CT}$

$$K_{CT}[A]\varepsilon_{CT}—K_{CT}\cdot OD=OD/[D] \quad (1)$$

where OD is the absorbance of the CT complexes at λ_{max}, [A], [D] are the concentration of acceptor and donor respectively. This equation is valid only for 1:1 complex. So the obtained straight lines prove further the molar ratio of reactant in complexes are 1:1. From the slope and intercept K_{CT} and ε_{CT} all can be calculated. **Table 1** shows the value of $h\nu_{CT}$, ε_{CT}, K_{CT} and ΔG for the complexes, ΔG has been calculated from the next equation:

$$\Delta G=-RT\ln K_{CT} \quad (2)$$

Using equation 3, we can also calculate dissociation energy of the CT complex excited state E (**Table 2**):

$$E=Ip-Ea-h\nu_{CT} \quad (3)$$

where Ip is ionization potential of donor and Ea is constant for a particular acceptor, Ea is 1.37ev for TCB [6].

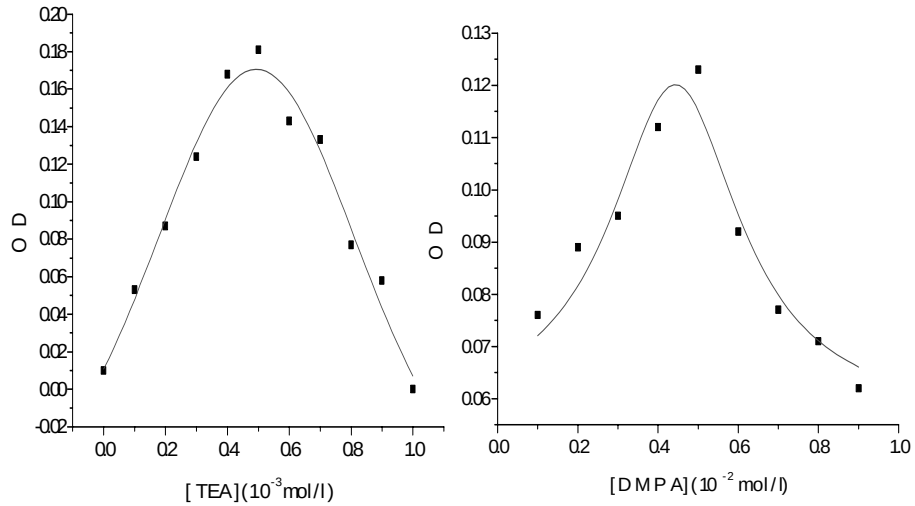
Seen from **Table 1** and **2**, the volume of substituent and Ip of donor affect strongly the character of CT complex. The λ_{max} of CT complex shows red shift with the decrease of Ip of donor. While for TPA and ECZ, they did not form CT complex with TCB under our experimental conditions even at higher concentration(10^{-2}mol/L). The major reason, we think, the volume of substituent is so large that stop the forming of CT complexes. The other reason, the Ip values of them are small. Seen from the obtained results, *e.g.*, the lower ΔG and the higher E for the complex formed by TEA and TCB, we can conclude that the forming of CT complex of TCB with TEA is much easier than other amine.

Table 1 The physical parameter of CT complexes of amine with TCB in $CHCl_3$

Mol.	$\lambda_{max,CT}$/nm	$h\nu_{CT}$/ev	ε_{CT}/mol^{-1}lcm^{-1}	K_{CT}/mol^{-1}l	ΔG/kJmol^{-1}
TEA	608	2.04	3176	231.20	-13.60
DMPA	625	1.98	1765	1.27	-0.59
TPA[a]	---	---	---	---	---
ECZ[a]	---	---	---	---	---

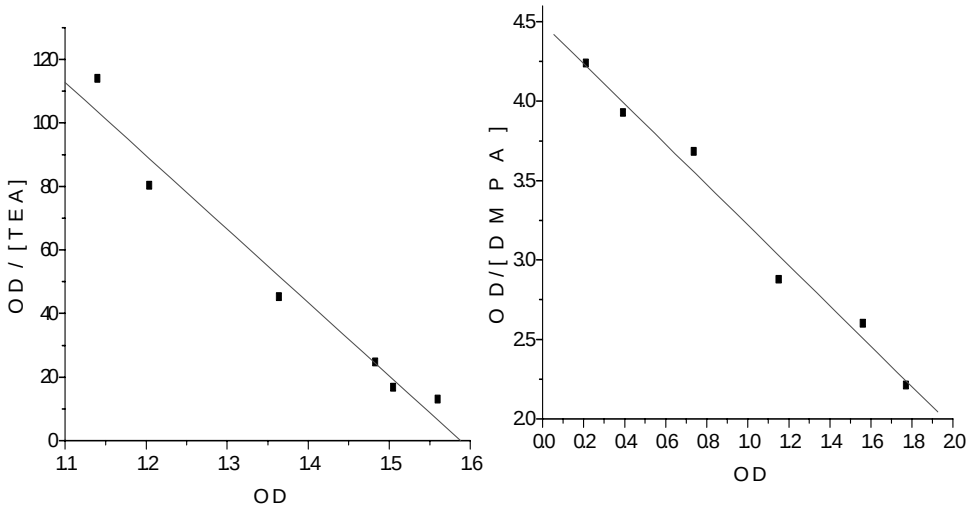
a: the compounds did not form the CT complexes with TCB under our experimental condition

Figure 1. Determination of the stoichiometry of the reaction of TCB and acceptor
(a) with TEA (b) with DMPA



a b

Figure 2. Benesi-Hilebrand graph for charge transfer complex
(a) TEA-TBC complex (b)DMPA-TCB complex



a b

Table 2 The values of Ip of amine and E of CT complexes

Mol.	Ip/ev	E/ev
TEA	7.50	4.09
DMPA	7.10	3.75
TPA	6.86	---
ECZ	----	---

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