

Some Spectroscopic and Thermodynamic Studies of Charge Transfer Complexes of DDQ and Some Phenol Derivatives

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Abstract

The $\pi \rightarrow \pi^*$ charge transfer (CT) complexes of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) with some phenol derivatives have been investigated spectrophotometrically in chloroform solution. The equilibrium constant (K) and extinction coefficient (ϵ) and the dissociation energies of the complexes excited state (w) of charge transfer have been calculated and discussed. The ionization potential of phenol derivatives have estimated.

Key words:- Charge transfer complexes, DDQ, , Acceptor, Donor.

Introduction

Molecular complexes resulting from the physical interaction between molecule are an idespread chemical phenomenon. Their information can influence reaction pathway and may be detected spectroscopically. Many compounds[1,2]. Thiophene, Furan and Pyrrole as well as their derivatives[3-9] form CT complexes with many acceptors. The DDQ also form CT complexes with aliphatic and aromatic amines[10,11]. Some Schiff-bases form stable $n \rightarrow \sigma^*$ CT complexes with iodine in chloroform[12,13]. The charge transfer reaction of certain π -acceptor has been successfully utilized in pharmaceutical analysis, p-chloranilic acid is an π -acceptor used for the assay of certain alkoaloid[14], astemizol[15], norfloxacin[16] and pyrimethamine [17]. In this work we investigated the $\pi \rightarrow \pi^*$ CT complexes of some phenol derivatives as electron donors and DDQ as electron acceptor. The study involves the estimation of ionization potential (I.P) of phenol derivatives and calculation of CT complexes parameters, equilibrium constant K_{CT} , extinction coefficient ϵ_{CT} and the dissociation energy of the CT complex excited state, W, properties which have not fully investigated.

Experimental

All phenol derivatives through this work were purified using the procedures described in the literature[18]. Chloroform of spectroscopic grade and DDQ (99.0%) were of Wako Company, They were used directly without further purification. The visible spectra of phenol derivatives and their CT complexes with DDQ were measured on spectronic 21D spectrophotometer using quartz cell 1.0cm path length (ℓ). The reference solution used was chloroform containing the same concentratipn of phenol derivatives in every case. The CT complex was followed by measuring the absorbance of a new absorption band of the complexes in the region of 385-455nm, at 298k. The concentration of DDQ being kept constant 1×10^{-4} mol./dm³ and that of phenol derivatives was variable in every set of solution $(1-20) \times 10^{-3}$ mol./dm³. The initial concentrations of phenol derivatives were much greater than

those of DDQ. This was done because Bensi-Hildbrand equation must be held for 1:1 molecular complex under these conditions[1].

The plot of initial concentration of DDQ divided by the absorbance of complexes at λ_{\max} against the reciprocal of the initial concentration of phenol derivatives gave according to Bensi-Hildbrand equation (equation 1) a very good straight line of which the intercepts equal to $(1/\epsilon_{CT})$ and the slope equal to $(1/K_{CT} \cdot \epsilon_{CT})$ in every case. From these values ϵ_{CT} and K_{CT} can be evaluated.

$$\frac{[DDQ] \cdot \ell}{A_{CT}} = \frac{1}{K_{CT} \cdot \epsilon_{CT}} \times \frac{1}{[D]} + \frac{1}{\epsilon_{CT}} \dots \dots \dots (1).$$

Where, ℓ =path length, $[DDQ]$ =Concentration of DDQ, $[D]$ = initial concentration of phenol derivatives, ϵ_{CT} =extinction coefficient, A_{CT} =absorbance of complexes

Results and discussion

A new band in the visible spectrum (405-525) nm was observed on mixing solution of phenol derivatives and π -acceptor DDQ in chloroform at 298K, this absorption is ascribed to charge transfer complex, since neither the phenol derivatives nor the π -acceptor DDQ alone are absorbed in this region (Table 1). The stoichiometric ratio of different complexes studied was 1:1 as indicated by linear plots of Bensi-Hildbrand equation[12,13]. From equation 1 and plot between $[DDQ]/A_{CT}$ at their λ_{\max} against $1/[phenol\ derivatives]$ (Fig.1) will get a straight line, then K_{CT} will be calculated. Table 1 represents the λ_{\max} , $h\nu_{CT}$ and ΔG° (Gibbs free energy) for CT complexes of DDQ with phenol derivatives. Gibbs free energy has been calculated from equation (2).

$$\Delta G^\circ = -RT \ln K_{CT} \dots \dots \dots (2)$$

The value of ionization potential of phenol derivatives (I.P)[14], and the dissociation energies of CT complex excited states (W) listed in table 2 were estimated from energies of charge transfer band by applying the empirical equations (3) and (4)[13].

$$h\nu_{CT} = a \cdot I.P + b \dots \dots \dots (3)$$

$$W = I.P - E_a - h\nu_{CT} \dots \dots \dots (4)$$

The constants of (a) and (b) of DDQ equal to 0.7 and -3.86 eV respectively. E_a is electron affinity of DDQ which is equal to 1.24 eV[13]. Table 2 shows the close value of I.P of phenol derivatives and W of their CT complexes with DDQ which reflect the similarity of chemical nature, the higher values of K_{CT} of α -derivatives for the donor group than other derivatives. The value of ΔG (Table-1) show that the Oxine complex more stable thermodynamically than other complexes and (2-tert.butyl-4-methoxyphenol) less stable due to steric factor which effect on the ability of molecule to donor properties and this result agree with (I.P) value of complexes.

Table 1- Absorption maxima of (DDQ, phenol derivatives and CT), molar extinction coefficients, equilibrium constant and free energies of the CT complex of phenol derivatives with DDQ in chloroform at 298K

Compounds	λ_{\max} acceptor (nm)	λ_{\max} donor(nm)	λ_{\max} CT (nm)	$h\nu_{CT}$ (eV)	ϵ_{CT}	K_{CT} (mol/l)	$-\Delta G^\circ$ (KJ/mol)
Oxine	550	440	525	2.366	333.3	1979.9	18.804
α -Naphthol	550	490	405	3.958	500.0	1340.4	17.838
β -Naphthol	550	340	420	2.958	370.3	202.5	13.158
2-tert.butyl-4-methoxyphenol	550	455	470	2.608	190.5	24.54	7.928

Table 2- The ionization potential values of phenol derivatives and the Dissociation energies of CT complex excited state W

Compounds	IP(ev)	W(ev)
Oxine	8.89	5.108
α - Naphthol	9.89	5.408
β - Naphthol	9.74	5.362
2-tert.butyl-4-methoxyphenol	9.29	7.874

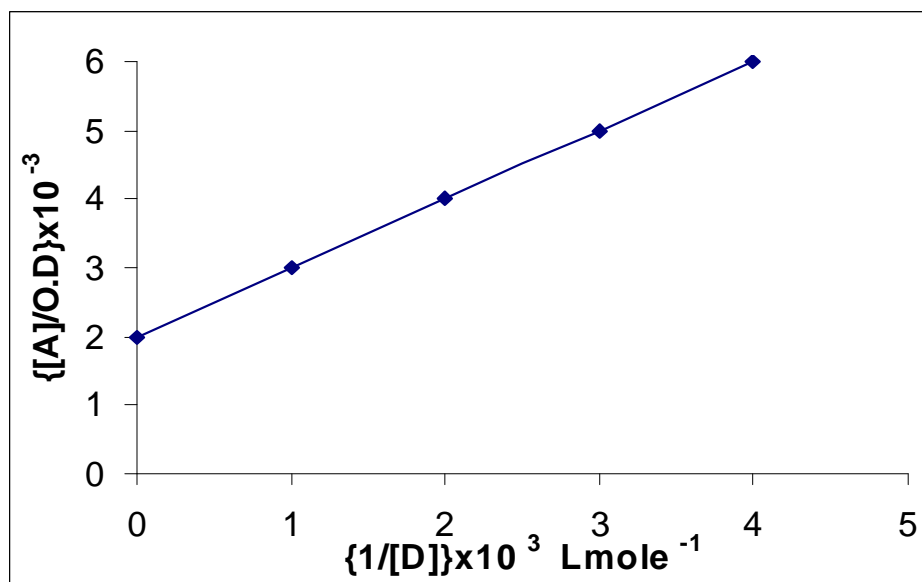


Fig. 1- Bensi-Hildbrand plots for CT complex of oxine with DDQ at 298K

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المستخلص

تضمن البحث دراسة معقدات انتقال الشحنة بين بعض مشتقات الفينول كموايد مانحه للألكتروليتات و DDQ كماده مستقبله للألكتروليتات وقد حسبت لها ثوابت الأتزان ومعامل الأمتصاصيه والمولاريه وتم حساب ثوابت تأين الفينولات المستخدمه من خلال ثوابت اتزان معقداتها مع DDQ وقد تبين من الدراسه تكوين معقدات انتقال شحنة ضعيفه بنسبة (1:1) بين هذه الفينولات وال DDQ وتم حساب طاقة تأين هذه المعقدات في حالة الأثاره وكذلك حساب الطاقه الحره(طاقة جيس) لكل معقد. وبينت الدراسه ان ثوابت الأتزان تعتمد على الفينولات كمانحه للألكتروليتات وبالتالي على ضعف حامضية ذلك الفينول.