Charge Transfer Studies Of Some Oxadiazole Derivatives with Different Acceptors

M-Alias * N-Al- Najjar **

Date of acceptance 12/4/2005

Abstract

The physical parameters of oxadiazole derivatives as donor molecules have been measured. The charge transfer(CT) complexes with various electron acceptors as DDQ and I_2 in chloroform and methanol as solvent have been estimated from the electronic spectra at wave lengths of maximum absorption of the charge transfer complexes by calculation Bensi-Hildbrand equation for (1:1) molecular charge- transfer complexes at 298K.

Introduction

Benzoquinones have been used wildly as electron acceptor in charge transfer processes with a lot of varieties of charge donor compounds[1]. Previously very limited work has been done on the charge – transfer complexes of heterocyclic oxadiazole and triazole derivatives as electron donors with some electron acceptors [2]. The 5-phenyl-2-mercampto-1,3,4-oxadiazole and 5-(3-pyridyl) 2-mercampto-oxadiazole have been employed as a potent coordination ligands containing –N–C=S moiety ,since they have hard nitrogen besides soft sulfur atoms, and because of their well established biological activity. Most of these complexes may be used as anticancer or it may be used catalyct or additive in chemical industries [3-5] . In this work the equilibrium constant , extinction coefficient (ε) of the charge – transfer complexes and the ionization potential for both oxadiazole derivatives have been calculated [1,6] , also physical parameters of the charge – transfer complexes for both electron donors with 2,3-dichlero-5,6-dicyano-1,4 Benzoquinone (DDQ) and iodine in chloroform and methanol as a solvent have been calculated from their electronic spectra using Bensi-Hildbrand equation for 1:1 molecular charge – transfer complex, when [D] >>[A] ,[7,8].In recent studies (CA) : 2,3,5,6-tetrachloro-1,4-benzoquinone was found to form 1:1 molecular CT complexes with various schiff bases and aliphatic , aromatic diamines as electron n-donors [9,10].

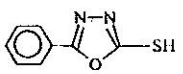
Expermintal

Oxadiazole derivatives were prepared and purified using the procedures described in the literature [11]. The two acceptors DDQ , I_2 and solvents were purchased from Fluka AG. and used without farther purification. The charge – transfer complexes of both donors have been investigated

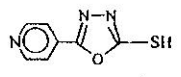
* Dr.-Asisstant Prof.- Department of Chemistry- College of Science for Women- University of Baghdad
** Asisstant teacher- Department of Chemistry- College of Science for Women- University of Baghdad

with accepters using spectrophotometer in chloroform and methanol. The concentration of any accepter was kept constant in all measurement and the concentration of donors were vary in every initial concentration of the accepter[8,12].The measurements of the optical density from the electronic spectra of charge – transfer complexes at λmax have been recorded using double beam u shimadzu-160 spectrometer.

Scheme(1)
Donors

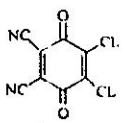


L_1= 5-Phenyl-2-mercapto-1,3,4-oxadiazole



L_2=5(3-Pyridyl) -2-mercapto-1,3,4-oxadiazole

Acceptors



2,3-dichloro-5,6-dicyano-1,4-benzoquinone,

I_2

Iodine

Result and Discussion

From figure (1), the solution of all complexes are obeyed Bensi-Hiladbrand equation [7] .Equation (1) for the CT complexes of ratios 1:1 donor-acceptor.

$$([A_o]\ell / OD_{CT}) = \left(\frac{1}{\varepsilon_{AD}}\right) + \left(\frac{1}{K_{CT}\varepsilon_{AD}}\right)\cdot\left(\frac{1}{[D_o]}\right) \quad \ldots(1)$$

Linear equation (1) was used to calculate the molar extinction coefficients (ε_{AD}) and equilibrium constants (K_{CT}) of the charge – transfer complexes . $[A_o]$ and $[D_o]$ are the initial concentration of the acceptor and electron donors respectively, ℓ is the cell path length, $O.D_{CT}$ the optical density of the charge transfer (CT) complex at λmax., from above linear equation (1) plot of $([A_o].\ell/O.D_{CT})$ Vs $(1/[D_o])$ gives us a straight line of the slope=$(1/K_{CT}.\varepsilon_{AD})$ and intercept=$(1/\varepsilon_{AD})$.

Equation (2) was used to calculate the charge – transfer equilibrium constant K.

K=(intercept /slope)

$= (1/\varepsilon_{AD}) / (1/K_{CT}.\varepsilon_{AD})$.....(2)

From Table (1) , the values of K_{CT} show that the stability of the charge-transfer complexes increase in presence of the electron donating group., where K_{CT} of L_2 (5(3-Pyridyl) -2-mercapto-1,3,4-oxadiazole) greater rather than L_1(5-Phenyl-2-mercapto-1,3,4-oxadiazole) electron donor, which is clear that the value of K_{CT} is twice time in the case of L_2 , that due to presence of nitrogen atom more donating in this ligand. It is clear from above values of equilibrium constant for these complexes of L_1 and L_2 , that the charge transfer complexes of donors compounds with iodine acceptor in present both solvent are strong complexes compare with complexes of DDQ , because of the type of electron transfer in iodine acceptor is $n \rightarrow \sigma^*$ while $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ for DDQ . As compounds L_1 and L_2 contain n-donor atoms which it will go to σ^* orbital of iodine molecule , in addition to the electron form π to π^* of carbonyl group in DDQ molecule .

The absorption band in the electronic spectra of CT complexes showed that the λmax appeared in the range (336-363nm) depending on the solvent, Table(1) and figure (2).

The ionization potentials values (Ip) of oxadiazole derivatives and **hv** change transfer complex have been calculated using equation (3).

$$h\nu_{CT} = a Ip + b \quad \ldots(3)$$

The parameter a,b are perfect constant depending on type of acceptors (a=-0.79 b=-3.8) ,(a=-0.87 b=-3.6) eV for DDQ and I_2 respectively [8,12]

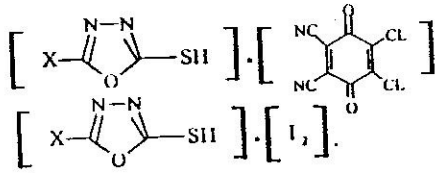
Table (2) shows the values of ionization potential (Ip) in both solvents, due

to the simple differences in molecules structure of oxadiazole derivatives , therefore the ionization potential are slightly different in each solvents. Therefore the value of ionization potential for both compounds which calculate from their charge transfer complexes for DDQ are compatible with that calculate for iodine charge-transfer complexes , then we can calculate the donors from charge transfer complexes of iodine and DDQ in different solvent as shown in Table (2) these results gives values which are nearly equal to the values obtained from charge-transfer complexes of traizale derivates in the same acceptors [13,14].

This indicate that the chemical structure of the excited state of charge transfer complexes between the donors and acceptors are very similar to each other [8].

From all these results in Table(1) and (2) and the electronic spectra of the charge transfer complexes, we suggest that the charge-transfer complexes would be formulated as follows:

Scheme (2)



Where X=phenyl,pyridl

Table (1) : The Molar Extinction Coefficient (ε_{CT}) , λ_{max} and Equilibrium Constant (K_{CT}) of the Charge Transfer Complexes With Different Acceptors and Solvents

Ligand	Acceptor DDQ Solvent $CHCl_3$/MeOH			Acceptor I_2 Solvent $CHCl_3$/MeOH		
	λ	ε	K_{CT}	λ	ε	K_{CT}
L_1	350	869.5	575.5	360	848.88	877.68
	336	909.09	611.8	363.5	1081.01	1170.8
L_2	352	1001.0	1698.97	360.3	1086.92	1472
	348	1000	1818	364.2	1043.8	1701.11

λ=nm, ε_{CT}= m^3 mol^{-1} , K_{CT} = dm^3 mol^{-1}

Table (2) : Shows the Values of Ionization Potentials in Different Solvents.

	DDQ $CHCl_3$/MeOH		I_2 $CHCl_3$/MeOH			
L_1	11.9	12.11	10.4	10.37	11.15	11.24
L_2	11.86	11.89	10.4	10.38	11.13	11.135

Ip= eV

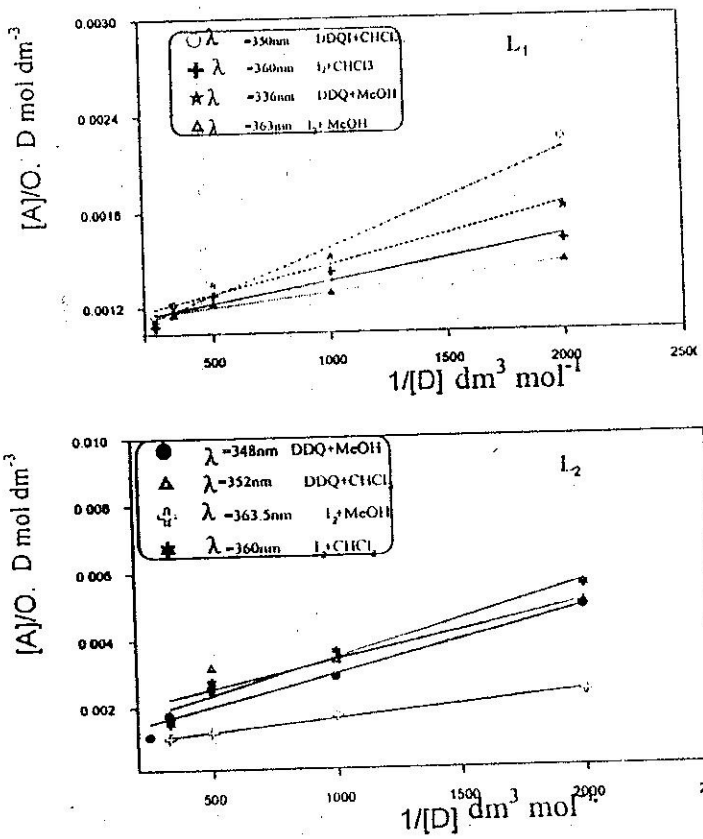


Figure (1): Application of Benesihild Equation for Charge Transfer Complexes

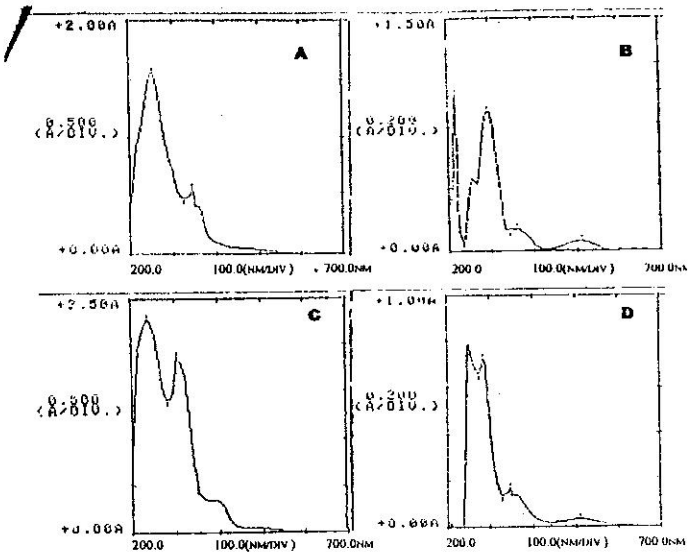


Figure (2) : Shows the Electronic Spectrum of the Charge Transfer Complexes in Different Solvents. A,B(5-Phenyl-2-mercapto-1,3,4-oxadiazole) with DDQ, I_2 in methanol and chloroform respectively C,D (5(3-Pyridyl) -2-mercapto-1,3,4-oxadiazole) with DDQ, I_2 in methanol and chloroform respectively

References

1. AL-Hussain,A.A. 1998.Spectral Studies of Charge Transfer Complexes of Some New B-Keto Schiff Bases and Schiff Bases Derived From1,3-Diamino-2 Prpanal Ph.D desertation, Univesity of Baghdad.
2. Ahmed, M.F. 1996. Synthesis and Study of Metal Complexes in Solid State and in Solution of Some Mercapto Triazole Derivatives , and Spectratl Study of The Prepared Derivatives With Some Electron Acceptors. M.Sc. desertation, University of Baghdad.
3. Singh,H. Yadav. L.Ds. and Mishra.S.B.S. 1971.Studies on some Antifungal transition Metal Chelates of N-(-5-phenyl-1,3,4-thiadiazol-2-yL)Dithiocarbamic acid. J. Inorg Nucl.Chem.43:1701-1704
4. Mir, I., Siddiqui, M.T. and Comrie. A.M.2003. Antituberculosis Agents.Part 11.1 ∝-[5-(2-Furyl)-1,3,4-oxadiazol-2-yL-thio] acetohydrazide and Related Compounds. J.Chem.,Soc.(C) :2798-2799.
5. Naman,S.A.,Alias,M.2003.Formation Dsegradation of some organometillic Compounds used as octane dditives n asoline. efereed scientific Journal Issued by the Fereration of Arab Scientific Research Councils .3: 43-63
6. Saeed,A.A.H.1988.Determination of the Equilibrium Constants of the Charge-Transfer (CT) Complexes of Benzyildene-Aniline and p-N, N-dimethylaminobenzylidene-Aniline ith Iodine.J .Iraqi .Chem . Soc.13: 173.
7. Bensard, H.A. Hildbrond. 1949. J.H. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. J.Am.,Chem.,Soc.,71:2703.
8. Fostor, R.1969.Charge Transfer Complexes. Academic press, New York.
9. Saeed,Ali-A.H. & AL-Safi,Saria A.J.2002.Preparation and Identification of Some Molecular Charge Transfer Complexes of Chloranil with Some Diamines. National Journal of Chemistry,7: 391-396.
10. AL-Razaq, K.A.A.1997. Spectral Studies of Some Schiff Bases and Some of Their Complexes.Ph.D.desertation, University of Baghdad.
11. Young, R.W. and Wood, K . H . 1955.The Cyclization of 3-Acyldithio Carbazate Esters. J.Am., Chem.,Soc.77:400
12. Slifkin, M.1971. **Charge Transfer Interaction of Biomolecules. Academic Press, New York**
13. **Saeed, A.A., Alias, M.F., Jassim, A.H. 2001. Intermolecular Charge Transfer Complexes between I_2 and DDQ as Electron Acceptors and Some Triazales Derivatives as Electron Donors. he First Arab Chemistry at Applied Science University. 31, October-2 November- Amman -Jordon**

14. .Saeed, A. A. H. and AL-Safi,Saria A.J.2002. Spectrophotometric Studies of The Stable and Unstable Charge Transfer Complexes of 3,5 –Ditertbutyl-1,2-Cbenzoquinone With Some Aliphatic and Aromatic Diamines in Chloroform nd ethanol ational Journal of Chemistry,7: 412-421.

دراسة معقدات انتقال الشحنة لبعض مشتقات الاوكسادايازول مع بعض المستقبلات الالكترونية

*محاسن فيصل الياس
**ندى علي النجار

*استاذ مساعد-كلية العلوم للبنات-جامعة بغداد
**مدرس مساعد-كلية العلوم للبنات-جامعة بغداد

الخلاصة

تم في هذا البحث دراسة طيفية لمعقدات انتقال الشحنة ،لمشتقي الاوكساديازول كواهبات للشحنة مع بعض المستقبلات للشحنة DDQ ، I_2 في مذيبي الميثانول والكلوروفورم . تم حساب جهد التاين للواهبات كما حسب ايضا بعض المعاملات الفيزيائية للمعقدات المتكونة عند اعلى طول موجي للامتصاص باستخدام معادلة بنسي- هلدابراند للمعقدات المتكونة بنسبة(١:١) مستقبل – مانح في درجة ٢٩٨ كلفن .