

Charge Transfer Studies Of Some Oxadiazole Derivatives with Different Acceptors

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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 I₂ 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 widely 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-mercapto-1,3,4-oxadiazole and 5-(3-pyridyl) 2-mercapto-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-dichloro-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 $[D] \gg [A]$ [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

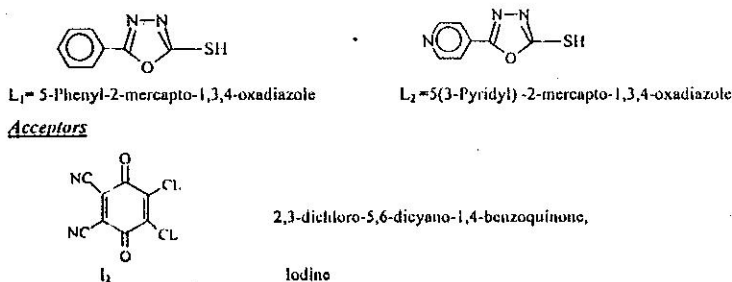
Oxadiazole derivatives were prepared and purified using the procedures described in the literature [11]. The two acceptors DDQ, I₂ and solvents were purchased from Fluka AG. and used without farther purification. The charge-transfer complexes of both donors have been investigated

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

Scheme(1)
Donors



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.

$$([A_0] \ell / OD_{CT}) \sim \left(\frac{1}{\epsilon_{AD}} \right) + \left(\frac{1}{k_{CT} \epsilon_{AD}} \right) \cdot \left(\frac{1}{[D_0]} \right) \dots (1)$$

Linear equation (1) was used to calculate the molar extinction coefficients (ϵ_{AD}) and equilibrium constants (K_{CT}) of the charge – transfer complexes. $[A_0]$ and $[D_0]$ 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 λ_{max} , from above linear equation (1) plot of $([A_0] \cdot \ell / O.D_{CT})$ Vs $(1/[D_0])$ gives us a straight line of the

slope= $(1/K_{CT} \cdot \epsilon_{AD})$ and intercept= $(1/\epsilon_{AD})$.

Equation (2) was used to calculate the charge – transfer equilibrium constant K_{CT} .

$$K_{CT} = (\text{intercept} / \text{slope}) = (1/\epsilon_{AD}) / (1/K_{CT} \cdot \epsilon_{AD}) \dots \dots \dots (2)$$

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 L₂ (5(3-Pyridyl)-2-mercapto-1,3,4-oxadiazole) greater rather than L₁ (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 L₂, 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 L₁ and L₂, 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 L₁ and L₂ 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 λ_{max} 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).

$$h\nu_{CT} = aIp + b \dots \dots \dots (3)$$

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 I₂ respectively [8,12]

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