WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.453
Volume 13, Issue 23, 1496-1502. Research Article ISSN 2277–7105

CHARAGE TRANSFER COMPLEXE OF LOSARTAN K WITH DDQ

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Article Received on
23 October 2024,

Revised on 12 Nov. 2024,
Accepted on 02 Dec. 2024

DOI: 10.20959/wjpr202423-34918

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ABSTRACT

Molecular complex of 2,3- Dichloro 5,6-dicyano –para- benzoquinone (DDQ) with some antibiotic drugs have been studied spectrophotometrically in chloroform. All the complex exhibited charge transfer bands (s) in the visible region where neither donor acceptor have any absorption. The stoichiometry of the each of the complex is found to be 1:1 and is unaffected by variation of temperature. The complex are inferred to be π-π* type. The ioniza-tion potential of the donors has been evaluated from the energies of CT bands. The stabilities and thermodynamics parameters of the complex have been determined from the absorption studies on the CT bands. The variation of position of CT bands and the stabilities of the complex have been correlated with the structures of the drugs.

KEYWORDS: DDQ, CT complex, Losartan K,, Chloroform, Stability constant.

INTRODUCTION

2,3 dichloro 5,6- dicyano –p- benzoqunione (DDQ) has been shown to form complex with a variety of organic donors ,viz. aromatics , methoxy benzenes, heterocyclics, metal complex, imidazoles, polymers etc.[1] The electron affinity of DDQ reported is 1.99 eV.[2] In continuation of our work[3] it is thought worthwhile to study charge transfer complex of DDQ with drugs like Losartan K, which are currently available in the market with a view to provide a tool for the quantitative estimation of the drugs. The results of the study are reported in this communication.

EXPERIMENTAL PROCEDURE

The commercial sample of DDQ obtained from Aldrich was recrystallized from benzene chloroform (2:3) mixture and its purity was checked by TLC (m.p 213-214^{0}C). The chloroform spectra grade sample was used without any further purification. Drugs procured from Pharmaceutical Laboratories and purified by crystallization. The UV-V is spectra of the complex were recorded on Shimadzu-240 and Elico SL 210 UV-Visible double beam spectrophotometers using a matched pair of quartz cuvettes of 10 mm path length. The concentration of DDQ was held constant. While those of drugs varied between in the range of 0.001 to 0.05M. The solution concentration was set such that it produced the complex with optical density between 0.2 to 1.8. The absorption bands due to acceptor or donor individually have fallen to the base line much more before the wavelength of CT absorption.. The complicated CT bands were analyzed by using the following relationship put forward by Briegleb and Czekella.[4]

$(\nu_h - \nu_l)/2(\nu_m - \nu_l) = 1.2$

Where ν_h and ν_l refer to the frequency at half the maximum intensity on the high and low frequency side of the peak located at ν_m.

The stability constants of the CT complex were determined by using the following Rose-Drago[5 & 11] method.

$K^{-1} = (d/\varepsilon) - ([Do] + [Ao]) + [Do]\,[Ao]\,\varepsilon/d$

Where d is the absorption; ε, the molar extinction coefficient of the complex; [Ao] and [Do] are the initial concentrations of acceptor and donor respectively.

3. RESULTS AND DISCUSSION

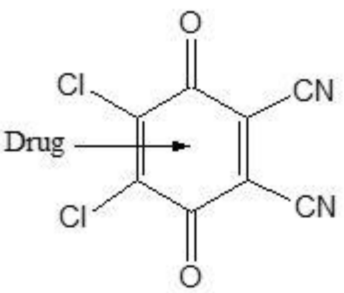
3.1 Molecular complex of drugs with DDQ

When pale yellow coloured solution of DDQ is mixed with drugs characteristic colors were observed. A solution of Losartan K exhibited Charge Transfer (CT) band in its electronic spectra with DDQ. The appearance of color and exhibition of CT bands (Fig.1) are attributed to the formation of charge transfer complex between the Losartan K and DDQ since these absorption bands are uncharacteristic of the individual components. The wavelength (λ_{max}) of CT band of the complex with other spectral characteristics are presented in Table 1.

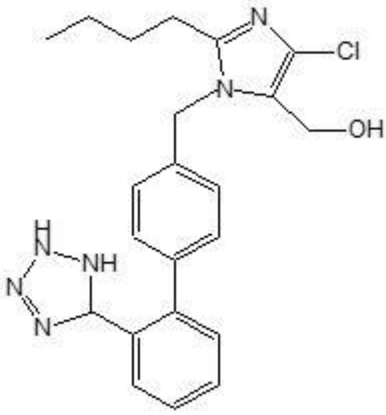
The appearance of CT band is attributed to the excitation of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital

(LUMO) of the acceptor. The appearance of double CT band is attributed to the excitation of electron from ultimate and penultimate molecular orbitals of donor to the LUMO of the acceptors. The appearance of double CT bands may occur due to (a) excitation of electrons from two different levels of donor to the same vacant level of acceptor or (b) excitation of electron from HOMO of donor to two different vacant levels of acceptor. In the former type of CT complex the energy difference between two CT bands □E = (ECT1 – ECT2) depends upon the donor whereas in the later type of complex it is independent of nature of donor i,e. ΔE is constant. In our study it is observed that ΔE differs from donor to donor hence the complex are inferred to be of former type. From the structures of the drug it is clear that Losartan K containing N,N'-dimethyl amino aniline group in its structure should have the highest donor abilities of the drugs studied.

Molecular complex of drugs
with 2,3-dichloro- 5,6 dicyano p- benzoquinone (DDQ)



DDQ



Losartan K

3.2 Energies of charge – transfer bands: The energies of the inter molecular charge transfer bands are calculated from the frequencies of absorption, using the equation

$E_{CT} = h\nu_{CT}$

the values are reported in Table 1.

3.3 Ionization potentials of the donor: The energies of CT bands of DDQ are linearly related to the ionization potentials of the donors in $CHCl_3$ by the equation.

$h\nu_{CT} = 0.70 I_d - 3.86$

where ν_{CT} is the frequency of the CT band, I_d is ionization potential of donor and h Planck's constant. The ionization potentials of the donors are calculated using this equation and are reported in Table 1.

3.4 Stoichiometry of the complex: The stoichiometry of the complex were determined by the Job's continuous variation method using equimolar solutions (2.0 x 10^{-3} M) of DDQ and drugs and stoichiometry is found to be 1:1 in each case. The Job's plot of DDQ with Losartan K is shown in Fig.1.

3.5 Extinction co-efficient (s), Oscillatory Strength (f) and Transition Dipole moments (D) of complex: The extinction coefficients of the complex are determined at different temperatures from the intersection points of Rose- Drago plots and are reported in Table 1. The extinction coefficients of a CT complex are found to be almost constant over the temperature range studied.

The oscillatory strength defined by Mullikan[6]

f = 4.319 x 10^{-9}.smax.□v1/2

have also been calculated. Transition Dipolemoment of the complex as defined by Tsubomura et al[7]

D = 0.09582 (smax.□v1/2 / v max)$^{1/2}$

have also been computed from the extinction coefficients and half–band widths and are reported in Table 4 together with the oscillatory strengths. The randomness of ε, f and D may be due to variation of .□v1/2 from drug to drug and also due to Contact Charge Transfer (CCT) which alters the ε to a greater extent.[8]

For a given complex the extinction coefficients, the oscillatory strengths and the dipole moments are also found to be almost independent of temperature. The randomness in the values of ε, f and D may be due to CCT. The observed s value is related to smax of CT and s'max of CCT by

$$\text{sobs} = \text{sCT} + \frac{\alpha s'}{K} \quad \text{...(7)}$$

Where α is number of possible contact sites for the species in excess, around and molecule of the second species, s' is the extinction coefficients for the CCT process based on the potential contact concentration and K is stability constant. Thus the sobs observed depends on the α, s' and K which cannot be evaluated a properly. The values of s'are found to be order 10^6, thus the second term of the equation determines the observed s.

3.6 Stability constants and Thermodynamic parameters: The optical density (d) at λ_{max} CT is monitored by varying the concentration of donor while concentration of acceptor is held constant. The'd' increased with increasing concentration of donor at a given temperature. The'd' also is found to decrease with increasing temperature for a set of constant donor and acceptor concentration. The stability constants have been evaluated from the intersection point of Rose- Drago plots.

The K values are also found to decrease with the increasing ionization potentials and a straight line was obtained when logarithmic functions of K are plotted against ionization potentials of donors with some exceptions because all the donors are not structurally related (there are mononuclear, binuclear aromatics and heterocyclics).

The thermodynamic parameters viz., □H and □S were evaluated from variation of stability constants with temperature using vant Hoff's method. A plot of log K Vs 1/T gave straight line, from the slope and intercept of which the □H and □S have been evaluated. The □G values at 25^0C were calculated using the equation

ΔG = □H - T□S

And are presented in Table 2. A linear relationship is obtained between □H and □S for all CT complex. It is interesting to note that the satirically unhindered complex formation indicates that the interaction is of π-π* type.

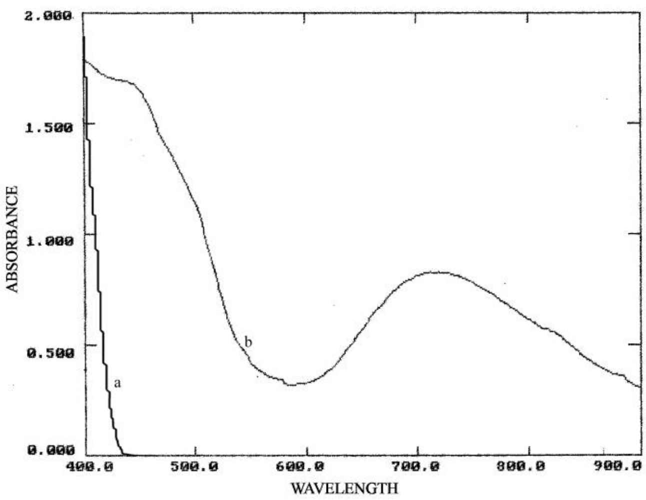


Fig. 1: Absorption spectra of Losartan K its molecular complex with DDQ.

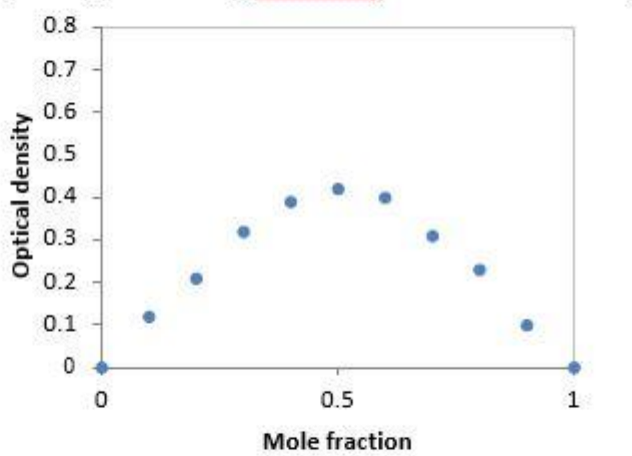


Fig.2: Job's continuous variation plot of DDQ – Ramipril [A0] = [D0]=2x10^{-3}M.

Table 1: Spectral characteristics of charge transfer complex of DDQ with Losartan K.

S. No.	Name of the drug	λ_{max} (nm)	E_{CT} (eV)	ν_{CT} x 10^{-3} (cm^{-1})	I.P (eV)	$\Delta\nu_{1/2}$ (cm^{-1})	ε_{max}	D	f
1	Losartan K	715	1.735	13.99	7.99	6232	5700	4.829	0.153

Table 2: Stability Constants and Thermodynamic parameters of Ct complex of DDQ with Losartan K.

S.No.	Name of the drug	Stability constants (K) at various temperatures					-ΔH	-ΔS	-ΔG
		K_{10}°C	K_{20}°C	K_{30}°C	K_{40}°C	K_{50}°C	K Cal mol^{-1}	Cal deg^{-1} mol^{-1}	K Cal mol^{-}
1	Losartan K	211.85	123.37	74.45	46.40	29.78	8.91	20.84	3.01

ACKNOWLEDGEMENTS

Author is thankful to Late Prof. G Venkateshwarlu, Head, Department of Chemistry, Osmania University for his helpful suggestions. Author wishes his sincere thanks to Chairman and Principal of G. Narayanamma Institute of Technology and Science. He is also thankful to Mr. Rakesh Goud Battini Asst. Prof Chemistry.

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