Spectrophotometricstudies of charge transfer complexes of 2, 3-Dichloro5, 6-Dicyano-P-Benzoquinone as Π-Acceptor

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Abstract

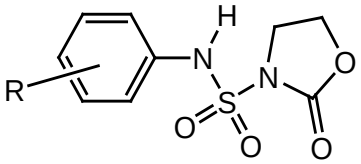
Charge transfer (CT) complexes formed between N-Sulfamoyloxazolidinones as donor, and 2, 3-Dichloro 5, 6-Dicyano-P-Benzoquinone (DDQ) as acceptor have been studied by UV-Vis Spectrophotometric method in chloroform medium. Benesi-Hildebrand and Job continuous variation methods were applied to the determination of formation constant (KTC) and molar extinction coefficient (εTC).The ionization potential of donor (IP) was calculated from the complex band energy using the CT transition energy. Oscillatorstrength and transition dipole moment of the abovementioned CT complexes indicatethat polar environmentfacilitate the extent of CT between the donor and the acceptor. The thermodynamic parameters (ΔH0,ΔS0,ΔG0) were calculated by Van't Hoff equation. Stoechiometry of the complexes formed between donors and acceptor were defined by the Job's method of the continuous variation and found in 1:1 complexation with donor and acceptor at the maximum absorption bands in all cases.

Keywords: *CT complex; UV-Visible spectrophotometry; Π-acceptors; Benesi-Hildebrand equation; Thermodynamic parameters.*

I. Introduction

The study of the charge-transfer interactions in solution between various electron donors with donor atoms like nitrogen, oxygen or sulphur and π-electron acceptors have been the subject of many investigations[**1-3]**. Those studies dealt mainly with the determination of the electron affinities of the acceptors or the ionization potential of the donor molecules[**4-5**and the investigation of the charge transfer interaction within the complex molecules.

N-sulfamoyloxazolidinones are attractive compounds, which combine an oxazolidinone pharmacophore and a sulfamoyl moiety **[6]**, they have been shown to be effective as antibacterial agent [**7]**, and have been used as precursors in the synthesis of 2-chloro-ethyl-nitroso-sulfamides CENS [**8]**.



R= H, CH_3, OCH_3, NO_2.

Figure 1. N-Sulfamoyloxazolidinones used in thisstudy.

The results reported in this paper are concerned with the preparation, characterization and structural studies of the new charge-transfer complexes formed during the reaction of Sulfamoyloxazolidinones as electron donors withthe π-acceptor2, 3-dichloro-5, 6-dicyano-p-benzoquinone(DDQ) in chloroform as the solvent.

The principal techniques used in these studies are based on ultraviolet-visible, mid infraredspectroscopy, as well as elemental analysis.

These complexes were investigated and many different quantities and many different quantities and parameters concerning their behaviour in those solvents, were calculated[**9-10].**

II. Experimental

The electron donors 1-5 were prepared according to the procedure described in ref (4-7)**.**

The electron acceptor: DDQ (Janssen Chemica) were used without further purification. Solvents used were from Merck with percentage purity ranging from 98% to 99%.

-The Spectrophotometric measurements were performed at 20 °C on a Jasco (Tokyo, Japan) double beam UV–Vis spectrophotometer (model V530) connected to PC computer fitted with spectra analysis program and equipped with a cell compartment thermostated by a Jasco EHCT temperature controller

The Infrared spectra measurements were performed on Spectrum one FT-IR model Perkin Elmer at university of Guelma. (Algeria). The preparation of the complexes and working procedure are the same as described earlier[**10]**.

II.1. Preparation of CT complexes:

The solid CT complexes ofsulfamoylwith the acceptorslistedabovewassynthesis by adding a saturated solution of DDQ (8.10^{-3} mole) in 40 ml of $CHCl_3$ mixture with a saturated solution of donor [Sulfamoyloxazolidinones (10^{-2} mole)] in 20ml of chloroform.

The mixture wasstirred at room temperature for72-96 h, where the solidprecipitatedafter the reduction of the volume of the solvent. The separated complexes werefiltered off and washedseveral times with minimum a mounts of $CHCl_3$ (2-5ml), and thendried.

III. Results and discussion

III.1 Spectral Characteristics of CT complexesin solution:

The absorption spectra of solutions containing the Sulfamoyloxazolidinones and DDQ togetherexhibit new absorptions at longer wavelengththaneither the sulfamoyloxazolidinone (λ < 350 nm) or the acceptors (λ <400 nm) alone.

When a solution of DDQ in any one of solventswas mixed with a solution of donors in chloroform, a slightcolor change wasobserved; a new band appearedwhich not the characteristic of eitherdonor or acceptorisalone. It clearlyindicates the formation of charge transfercomplex on mixing of donors and acceptors solution in the samesolvent.

The electronic absorption spectra in the wavelength range 220 -500 nm wererecorded for the CT complex solutions of the studiedsulfamoyloxazolidinoneswith DDQ in chloroform. The spectra for CT complexes are shown in**Figs.2-4.**

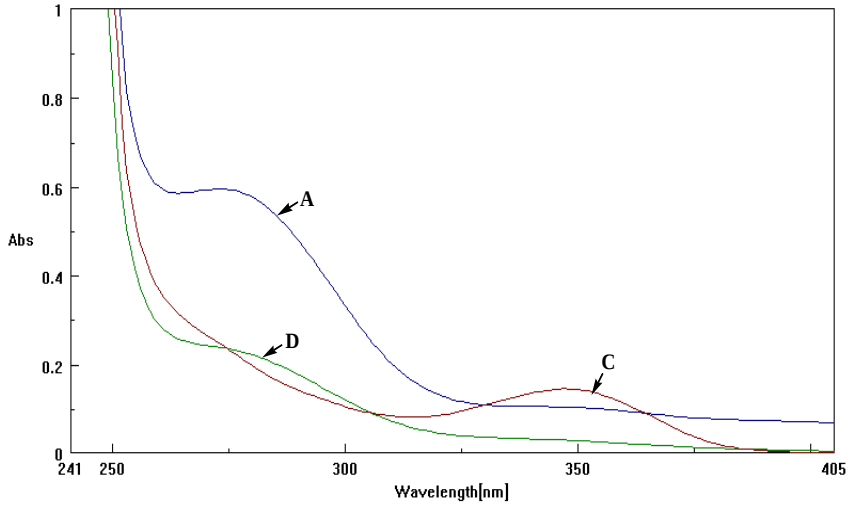


Figure.2 Absorption spectra of (**D**) sulfamoyloxazolidinone, (**A**) DDQ. (**C**) CT complexin chloroform à T=20°C

Following the progressive addition of DDQ in donor solutions, characteristicphenomena of the complexes formation werenoticed: bathochromic shifts, reduction of the Absorbance at a givenwavelength and the formation of an isobestic point.versus 1/ [D] clearlyindicates the formation of 1:1 complexes. Fromwhichmolarabsorptivity, correlation coefficient ad formation constant given in **Table1**.

III.2 Determination of stoichiometry and stability constants:

The formation constant (K_{TC}) and molar extinction coefficient (ε_{TC}) values for the formed CT complexes studies have been determinedusing the rearrangedfrom of the Benesi-Hildebrand equation[**11**]:

$$\frac{[A]}{Abs} = \frac{1}{K_{TC}.\varepsilon}.\frac{1}{[D]} + \frac{1}{\varepsilon} \quad \textbf{(1)}$$

Where: [A] and [D] are the initial molarconcentrations of the acceptor and donor, respectively, Abs: is the absorbance of the charge transfer band complexes,

K_{TC}: the formation constant of charge transfercomplex in solution for the equation:

DDQ + Sulfamoyloxazolidinones → complex

and **ε**: is the molar extinction coefficient of charge transfercomplex. The linearity of plots of [A]/Abs

The resultsshown in **Table1**revealthat the high values of K_{TC}may show the high stability of the complex in chloroform solutions, also shows the K_{TC} values of charge transfer complexes with DDQ are higherthan the corresponding values with TCNE. This is consistent with the decrease in electron affinity of TCNE relative to DDQ [**12]**.On the other hands, the results indicate the ability of DDQ to accept electrons are higher than that of other acceptor.

III.3 Ionizationpotentials of the donors:

One of the very important applications of the CT-complexes is to calculate the ionizationpotentials of the donors. The ionizationpotentials (PI) of Sulfamoyloxazolidinoneswith DDQ have been estimatedfrom the empiricalequationsreported by Aloisi and Pingnataro[**13]**and are compiled in Table 1. Theseempiricalequations are:

PI (ev) = 5.76 +1.52 .10^{-4}v' $_{DDQ}$ (cm^{-1})

Where: **v'** is the wavenumbercorresponding to the charge transfer band.

Moreover, the stability of the formed CT complexes increases as the experimentallydetermined n-ionizationpotential of the donorisincreased (Table1).

Table 1. The ionization potentials (PI) of Sulfamoyloxazolidinones with DDQ

Donors	Acceptor	λ (max)(nm)	$10^{-3}K_{TC}$(J.mol^{-1})20°C	10^{14}v' (s^{-1})	PI (ev)
1	DDQ	347,2	2.32	2.89	5,7600004
2	DDQ	345	7831.25	2.90	5,7600004
3	DDQ	344,5	107.93	2.89	5,7600004
4	DDQ	346	254.59	2.85	5,7600004
5	DDQ	350	159.44	2.85	5,7600004

III.4 Determination of Thermodynamics Parameters of CT complexes:

The thermodynamicsparameters(ΔH^0,ΔS^0, ΔG^0) associated with the CT complex formation of Sulfamoyloxazolidinones with DDQ weredetermined and are compiled in Table 2.

The enthalpy (ΔH^0) and entropy (ΔS^0) changes of the complex formation were determined from the obtained K_{TC} at different values of temperatures using Van't Hoff'sequation[**14-15]**.

$$lnK_{TC} = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \textbf{(2)}$$

with **T**is the absolute temperature.

The values of ΔH^0 and ΔS^0 generally become more negative as the stability constant for molecular complexes increases.The Gibbs free energy (ΔG^0) of the complex formation was evaluated according to the well-known equation**:**

Δ **G^0 = -- R T Ln K $_{TC}$**

(3)

The values of thermodynamic parameters listed in Table 2.3 show that complexation is thermodynamically favoured. The enthalpy change of the complexation also reveals that the CT complex formation between the used donor and the acceptors is of exothermic in nature. Thus the results of K and ΔH^0 are in good agreement with each other.

The obtained CT results (Table 1) reveal that the formed complex is better stabilized as the temperature is lowering. This indicates the exothermic nature of the CT complex formation process of the system under investigation and spontaneous. The obtained values for ΔH^0, ΔS^0, and

ΔG^0 are of the same magnitudes as those reported for middle strength CT complexes.

Comparison of the results in Table 2 reveals that the CT complexation of these DDQ is more exothermic .This could again be donors with explained to be due to the relatively high electron affinity of DDQ.

This could be supported by the determined $\mathbf{b^2/a^2}$ ratios using the proposed relation:

$$\mathbf{b^2/a^2 = - \Delta H^0 / h\nu.} \quad \mathbf{(4)}$$

with $h\nu$ the energy of the absorption band of the complex and **a** and **b** are the coefficients of the dative bond and the nonbonding wave functions ($\Psi_{D^+ A^-}$and Ψ_{D-A} respectively) of the CT complex. Referring to many studied CT complexes, one can deduce that the obtained $\mathbf{b^2/a^2}$ ratios here are close to those of many CT complexes of middle strength [**16-17]**.

Table 2.Thermodynamicsparameters of CT complexes with DDQ ($C_{1,D} - C_{5,D}$) .

Complexes	***10^{-3} - ΔG^0 (J.mol-1)***						***10^{-3}-ΔS^0 J.mol^{-1}***	***10^{-3} - ΔH^0 J.mol^{-1}***
	10°C	**15°C**	**20°C**	**25°C**	**30°C**	**35°C**		
$\mathbf{C_{1,D}}$	20.92	25.11	18.87	22.26	27.64	24.59	0.17	25.69
$\mathbf{C_{2,D}}$	31.71	26.03	38.65	36.25	30.79	30.86	0.06	-15.45
$\mathbf{C_{3,D}}$	25.59	27.25	28.22	25.61	28.96	29.79	0.13	11.16
$\mathbf{C_{4,D}}$	32.87	28.70	30.31	27.04	36.29	34.52	0.15	12.95

Table 3.Thermodynamicsparameters of CT complexes withDDQ ($C_{1,D} - C_{5,D}$) . indifferentsolvents.

solvents	**Dichloromethane**			***Ethanol***			***Acetone***		
Complexes	***10^{-3} K_{TC} (J.mol-1)***		***10^{-3} ε_{max} à 20°C***	***10^{-3} K_{TC} (J.mol-1***		***10^{-3} ε_{max} à 20°C***	***10^{-3} K_{TC} (J.mol-1***		***10^{-3} ε_{max} à 20°C***
	20°C	**25°C**		**20°C**	**25°C**		**20°C**	**25°C**	
$\mathbf{C_{1,D}}$	12.38	215.29	3.22	*52.10*	*544.43*	*8.37*	68.44	236.50	40.32
$\mathbf{C_{2,D}}$	138.43	201.60	81.53	*120.20*	*189.62*	*52.52*	87.55	537.36	14.27
$\mathbf{C_{3,D}}$	377.02	191.53	89.69	*8.55*	*13.14*	*80.33*	25.51	36.15	49.27
$\mathbf{C_{4,D}}$	138.64	201.63	81.55	*65.56*	*49.84*	*40.88*	104.08	73.66	16.77

III.5 Solvent Effects:

The solvent plays an important role in the CT complexation by affecting both Thermodynamic as well as Spectrophotometric properties. Thermodynamic and Spectrophotometric properties of Sulfamoyloxazolidinones and DDQ complexes in different solvent such as: chloroform, dichloromethane, acetone, ethanol, in a temperature range of 10-35°C.Spectral characteristics of the formed CT complexes are listed in **Table 3**.

The obtainedresultrevealsthat the formation constant of the CT complexbetweendonor and DDQ increases as the dielectric constant of the solventisincreased.

This behaviorcanbeinterpreted on the basis of the high stabilization of the group electronic state of the complex upon increase in the solvent polarity **(Fig.3)**. Further, the chlorinated solvents were chosen since they are more suitable than any others such as acetone; ethanol .Analysis of the data in **Table3** reveals that the thermodynamic and Spectrophotometric dats are affected by the variation of the solvent. For example the observed increase in K values measured in chloroform suggests that the complex is better solvated by chloroform than by other solvents. This can be ascribed to the presence of a certain competition between donor and solvent via formation of a hydrogen bond between the nitrogen-lone pair of the donor and the hydrogen atom of $CHCl_3$. Since dichloromethane, acetone and, ethanol are of comparable polarity their effect on complex formation is similar.

Compared to the other chlorinated solvents carbon tetrachloride shows a strange DDQbehaviour since it behaves as a weak acceptor, and thus competes with for the formation of CT complexes with donors; hence lower values of K were obtained.

Therefore, the formation constant is increased as the polarity of the solvent is increaseddue to the increased interaction between the dipole of the donor–acceptor bond and theSolvent[**18-19]**.

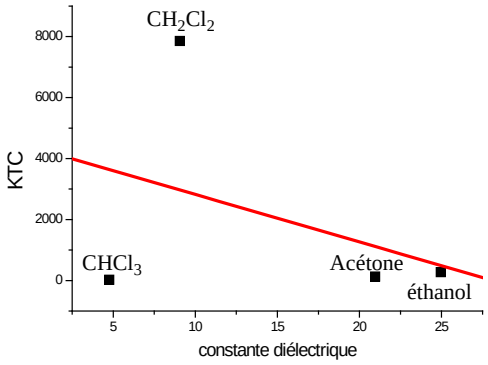


Figure.3 Effects of the dielectric constant of the solvent on the formation of the CT complex of DDQ à 20°C.

The most important infrared bands of the donor (Sulfamoyloxazolidinones),Acceptor (DDQ) andtheir CT-complexes withtheir probable assignments are given in (**Fig.4).**

The formation of CT-complexes through the interaction of sulfamoylwith DDQ, isstronglysupported by detecting the main infrared bands (function groups) of the donor and acceptors in the spectra of the solid CT-complexes.

A comparison of the relevant IR spectral bands of both the free donor and acceptor in the resulted complexes spectrawhich, clearlyindicatethat the complexes spectrarevealsmall shifts in theintensitiescomparedwiththose of the free donor and acceptors. This couldbeelucidated the expectedsymmetry and electronic structure changes upon the formation of CT-complexes. Generally, in case of the [(Sulfamoyloxazolidinones) (DDQ)] complexes, the proton (–NH) migratedfrom the donor to the acceptor(DDQ), thisfactisstronglysupported by the absence of a bands concerns (N–H) for the donor in the spectra of both complexes.

This interpretationmakes sure by the appearance of a new band of medium strongintensitycomparedwith the free acceptor (DDQ) [**21-22]**.

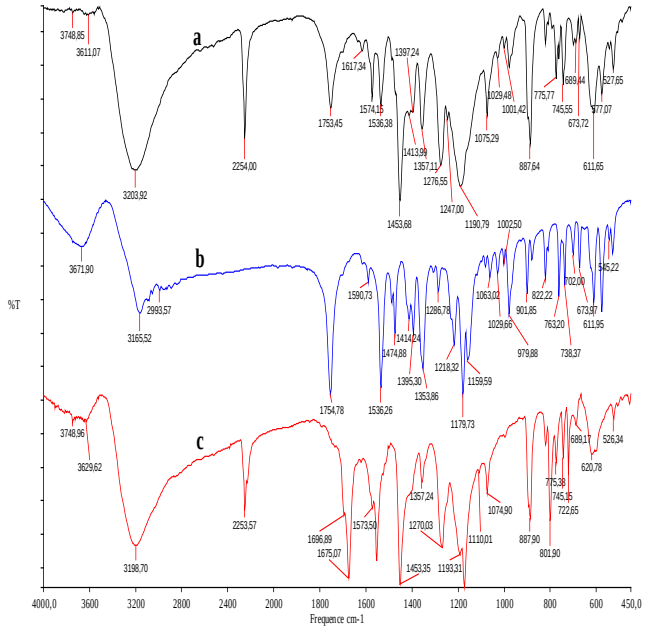


Figure 4.Infrared spectra of: **(a)** complexe $C_{4,D}$**(b)** compose 4. **(c)** DDQ.

IV. Conclusion

In Conclusion, the spectroscopic methods have advantage of being simple, sensitive. Accurate and suitable for routine analysis in laboratories.Chloroformusedhere as a solvent to avoidany interactions of solventwithdonor and acceptors.

References:

[1].R.S. Mulliken, Recl. Trav. Chim, (1957), Pays-Bas,57, pp.845.

[2]Alain.G,(1996),Liaisons intermoléculaires, Editions, EDP Sciences.

[3]R. Foster, (1996), Charge Transfer Complexes, AcademicPress, London.

[4]Bulent.B,peter.C,(2004),Appel baum, International journal of Antimicrobial Agents. 23, 2, pp.113-119.

[5] Abdaoui.M., Dewynter. G, Montero. J.L, (1996), TetrahedronLett. , Vol 37, 32, pp.5695-5698

[6]Dewynter.G,Abdaoui. M, Toupet. L, Montero. J.L,(1996),TetrahedronLett,Vol 38, 50, pp.8691-8694.

[7]KADRI.M,DJEMIL.R, Abdaoui.M , J-Y. Winum ,F. COUTROT, J –L.Montero,(2005), Bioorganic&MedicinalChemistryLetters 15 ,pp. 889-894.

[8]Dewynter.G,Abdaoui.M,Regainia.Z,Monter,J.L,(1996),Tetrahedron,52,45,pp.14217 -14224

[9]R.S.Mulliken,(1964),J.Phys.-Chim.Biol, 61,20.
[10]A.H.Al-TAIAR,S.K.SHUBBER,(2002),Turk J Chem 26,pp.351-355.
[11]BenesiHA ,Hildebrand JH J,(1949), Amer Chem Soc71,pp. 2703.
[12] H.M, A.Salman, M.M, Abu-Krisha and H.S.El-sheshtawy,(2004),Canadian Journal of Analytical Sciences and Spectroscopy ,volume 49,5.
[13]H.Dumus,M. Arslan,(2006), Spectrochimica Acta Part A 65,pp.1120-1124.
[14]R.S. Mulliken, W.B. Pearson, (1969), Molecular Complexes, WileyPublishers, New York.
[15]M.Pandeeswaran,K.P.Elango,(2006), Spectrochimica Acta Part A 65,pp.1148–1153
[16] P.R. Bangal, (2005), Chemical PhysicsLetters 401, pp.200–204.
[17]R.C.Schulz, J. Schwaab, Makromolek, (1965), Chem. 87,pp.297.
[18]Mohamed E, El-Zaria,(2008), Spectrochimica Acta Part A: Molecular and BiomolecularSpectroscopy, Volume 69,1,pp.216-221.
[19]H.Razzaq ,al,(2007), Spectrochimica Acta Part A. M. Fuentealba et al.,2007, Journal of OrganometallicChemistry 692,pp.1099–1109.
[20]S.Bhattacharya et al.,(2006),Journal of Molecular Structure 784,pp.124–137.
[21]Christine Goze,(2005),Thèse de doctorat; Université de Louis Pasteur de Strasbourg.
[22]SihamY.Alqaradawi,E.M.Nour,(2007), Spectrochim, Acta Part A: Mol, Biomol, Spectrosc.