

Spectral studies for some charge transfer complexes Derived from Oxadiazole compounds and some electronic acceptors

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Abstract :

New charge-transfer (CT) complexes are prepared derived from 1,2,4 and 1,3,4-Oxadiazoles compounds as donor molecules with three acceptors molecules dinitrobenzene, 2,4,6-trinitro benzene and 2,4,6 trinitrophenol. The formation of CT complexes were identified by FT-IR , melting points and UV-Vis spectra. The type of bonding between the donor and acceptor depends on the interaction between components were studies by UV-Vis spectra . The physical parameters of CT complexes have been estimated at the λ_{\max} of each of them. From using Benesi-Hildebrands equation at 25 °C, the equilibrium constant and thermodynamic parameters have been calculated.

Introduction :

Spectroscopic studies of electron transfer continue to be a very active area of research. Recent review articles chronicled many contemporary issues in electron transfer research^(1,2). General procedures for the preparation of oxadiazole derivative had been reported earlier⁽³⁻⁶⁾ . Literature is abundant on physico-chemical properties of various symmetrical . The delocalized π -electronic planar of the molecule is necessary to design new organic compounds. Recently much attention was paid on the use of much rigid electron-withdrawing 1,3,4-oxadiazole unit as building blocks in the synthesis of synthetic metals and organic light-emitting diodes materials⁽⁷⁻⁹⁾ and in many biological processes^(6,10) . The five – member heterocyclic ring system 1,2,4 and 1,3,4-oxadiazole already been reported and thoroughly reviewed in literature⁽¹¹⁾ The formation of molecular complexes of the charge- transfer (CT) type between donor and acceptors plays an important role in many biological processes⁽¹²⁾ The aim of this work is the preparation of new molecular complexes of the CT type derived from the reaction of oxadiazole derivative as a donor molecules with neutral molecules and acidic molecules as acceptors .The synthesized CT complexes were obeyed Benesi-Hildebrand's in dichloro ethane solution

Experimental methods

Reactive chemicals and solvents were purchased from Merck ,Aldrich Chemical Co. The compounds under study were structurally characterized by their ; Melting points (recorded with Electro thermal Melting point Appertatus), FT-IR spectra (recorded by FT-IR Spectrophotometer 8400 Schimadzu (KBr disc), C.H.N elemental analysis (performed by the micro analytical unit ministry of oil) , and UV-Visible spectra (were recorded in ethanol as a solvent by Schimadzu -1650 pc spectrophotometer (used quartz cell 1.0 cm path length). The work in this research includes three parts:-

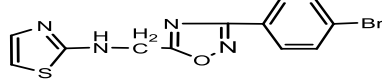
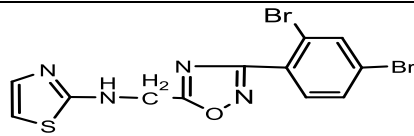
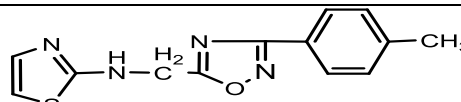
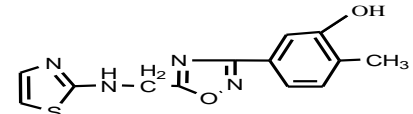
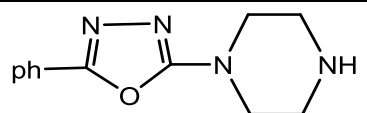
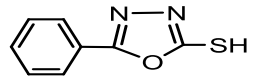
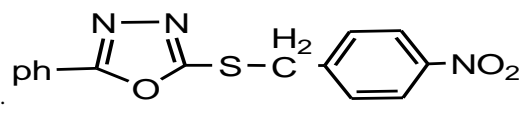
Part 1 : Organic synthesis

Compounds 1,2,4-oxadiazoles (1-4) and 1,3,4-oxadiazoles (5-7) selected for this work were prepared and purified using the procedures described in the literature⁽¹³⁾ . All these compounds were purified by recrystallization and characterized by using available spectroscopic method UV , IR ,and C.H.N analysis . The physical properties of these compounds (1-7) which used as a donor molecules in this study are listed in Table (1) .

Part 2____: Preparation of charge-transfer (CT) complexes (solid state); The (21) CT complexes under investigation were prepared by standard procedure through condensation of equimolar quantities of the compounds (1-7) as a donor molecules with three acceptors. The used acceptor are 1,3- dinitro benzene (DNB) ,1,3,5-trinitrobenzene (TNB) as non acidic and 2,4,6-trinitrophenol(TNP) with a weak acidic properties. The study is performed by following a similar procedure as in literature⁽¹⁴⁾ using Job's methods⁽¹⁵⁾.The products were purified by crystallization. Purity was checked via melting points, IR , UV-Visible spectra .

Part 3: Preparation of CT complexes solution The CT complexes (21) Solution of 1,2,4 and 1,3,4 – oxadiazole have been investigated with three acceptors DNB , TNB and TNP in $C_2H_4Cl_2$ solution spectrometrically at λ_{\max} .The measurement of the optical densities of complexes at their λ_{\max} were done after (30) minutes from the preparation of complexes⁽¹⁴⁾ . The used concentration of all acceptors (2×10^{-4} M) was kept constant ,donor molecules (1-7) were varied in every set of solutions ,and was much greater than the initial concentration of the acceptors (at least 10 times) in every solution .This was done because Benesi – Hildebrand's equation must be held for 1:1 molecular complexes under this condition and done at 25 °C

Table (1) : Melting points, λ_{\max} and C.H.N analysis for the prepared compounds (1-7) .

No.	Compounds	M.p(°C)	λ_{\max} nm (ϵ m ² mole)	Element Analysis %cal (found)		
				% C	% N	% H
1	 5-methyl amino-N(1,3-thiazole)-3-[4-bromo benzene]-1,2,4-oxadiazole	230-232	213 253 288 (393) (257) (311)	42.74 (40.20)	16.61 (14.54)	2.69 (2.00)
2	 5-methyl amino-N(1,3-thiazole)-3-[2,4-dibromo benzene]-1,2,4-oxadiazole	175-177	213 253 294 (430) (220) (360)	34.64 (33.54)	13.47 (12.21)	1.94 (1.11)
3	 5-methyl amino-N(1,3-thiazole)-3-[4-methyl benzene]-1,2,4-oxadiazole	182-184	211 237 263 (835) (426) (771)	57.34 (52.64)	20.57 (17.33)	4.20 (2.73)
4	 5-methyl amino-N(1,3-thiazole)-2-[3-hydroxy-4-methyl benzene]-1,3,4-oxadiazole	87-89	205 270 305 (692) (535) (479)	54.15 (52.22)	19.43 (18.00)	4.20 (2.73)
5	 2-phenyl-5-(piperazin-1-yl)-1,3,4-oxadiazole	168-170	201 247 301 (703) (349) (301)	62.59 (61.78)	24.33 (23.21)	6.13 (5.59)
6	 5-phenyl-1,3,4-oxadiazole-2-thione	196-198	210 255 316 (333) (279) (487)	53.92 (51.36)	15.72 (14.76)	3.39 (4.96)
7	 2-(4-nitrobenzylthio)-5-phenyl-1,3,4-oxadiazole	190-192	220 241 307 (666) (453) (619)	57.06 (53.37)	13.41 (11.70)	3.54 (5.01)

Results and discussion

Each of the compounds (1-7) under study were structurally characterized by melting points, infrared and C.H.N data and CT complexes. The absorption spectra of fresh solutions in ethanol were prepared for spectral registration in Shimadzu Rocco- 1650 UV-Vis at 25°C, in a quartz cell. Furthermore, the optimum molecular geometries of these molecules (1-7) have been obtained by means of quantum mechanical calculation applying the Semi empirical AMI approach⁽¹⁶⁾, conformation of each molecule of the bond lengths, bond angles at the lownd other parameters were calculated for energy. From Table

(1), the ultraviolet spectra of the compounds are characterized by three peaks between 307 – 237 nm, assigned to σ , π transition (of various origin) and charge transfer transition respectively⁽¹⁶⁾. However, these three spectral bands exhibit different behaviors according to the nature of the substituents on the molecular structure of the compounds (1-7). Thus, we have observed two main effects according to the electron - donor and electron – acceptor roles of the substituent.

Infrared spectra

Table (2) represent the important bands in the IR spectra of 1,2,4-oxadiazole derivative (1-4) $\nu_{C=C}$ $\nu_{C=N}$ ν_{NH} , which prepared by cyclization the N-O (substitutionamidoximyl-thiazole-2-ylaminocarboxylate-cyclo compounds by heating yielded the corresponding 1,2,4-oxadiazole. The IR spectrum of compounds showed well defined bands; the stretching vibration modes of N-H group correspond to ν (amide) and ν (C=N), respectively

,and appearance and disappearance of some bands in the IR spectra of these compounds respectively and indicating to the formation of the synthesized compounds. In the spectrum of 5-phenyl-1,3,4-oxadiazole-2-thiol the ν N-H have disappeared and a weak band appeared at 2350 cm^{-1} , this attributed to the SH group. In the spectra of the compounds (5-7) a strong band appeared at $1580\text{-}1590\text{ cm}^{-1}$ this may be attributed to the conjugated (C=N-N=C-) grouping.

Table (2) : The major IR absorption peaks(cm^{-1}) for compounds (1-7).

No.of Compound	ν_{OH}	ν_{NH}	ν_{C-H-Ar}	$\nu_{C-H-Alip}$	$\nu_{C=N}$	ν_{S-H}	$\nu_{C=C}$	ν_{NO}	ν_{NO_2}	ν_{C-O-C} asym / sym
1	3310 s	3097w 3037w	2850s	1640s	-....	1540s	-	1080s 890s
2	3345s	3100m	2850m	1646s	1511s	1090m 860m
3	3340s	2950w	2885m	1647s	1560s	1338s	1100m 890m
4	3340m	3250m	2950s	2840s	1635s	1560s	1355s	1090m 860m
5	3263m	3140m	2920s	1623s	1510m 1580s	1366s	1053m 883w
6	3100m	2850m	1650s	2350s	1520s 1590s	1360m	1460m	1090m 860m
7	3100s	2800w	1610s	1540s 1590s	1335s	1080m 870w

m:medium , s :strong , w :weak

The study has involved precipitation of that molecular charge transfer (CT) complexes by condensation molar quantities (1: 1) from each one of our compounds (1-7) as charge donor and dinitrobenzene, dinitrobenzene, trinitrophenol, as charge acceptor. The solid complexes obtained are investigated by spectral and electrical methods, these tools (complexes were identified by their, IR .Table (3-5), and studied by UV-visible spectrophotometer in ethanol solvent) and melting points, Table (6-8), proved to be very helpful in investigating the type of interactions ,the nature of the bonding in these compounds and the nature of the acceptor neutral molecules (molecular compounds through electron transfer) .The acidic molecule will be formed through proton and electron transfer .The IR spectra of the CT complexes compared to those of the free components exhibit a new group with different intense bands ,the various types of interactions are discussed in the following i - The ν_{C-H} bands of the donors part of the CT complexes are shifted to higher wave numbers where as those of the acceptors are shifted to lower values. This shift is observed with

CT complexes involving π interaction in which a π -electron is transferred from the HOMO on the donor to the LUMO of the acceptor⁽¹⁷⁾. This behavior reveals that , the electron transfer to the acceptor would originate from the donor, such CT interaction leads to obvious shifts in the NO_2 bands of the acceptors to lower wave numbers ii- The C=N bands of the donor parts of the CT complex showed different behavior depending on the n,π -electron densities beside to the proton transfer from the acceptor to the homogenous atom linkage , Tables (3-5), beside to the $\nu_{C=C}$, conjugated -C=N-N=C-, ν_{S-H} and ν_{C-O-C} bands in the CT complex shift to the lower wave number .A comparison between the IR spectra of the free components and those of the CT complexes revealed the presence of the interaction between the two molecules and formation of CT complexes .The appearance of ν_{OH} bands due to OH group indicating to the intermolecular hydrogen bonding involving the OH group (represented by the presence of broad band).

Table (3) : Important bands in the IR spectra of CT complexes (in cm^{-1}) with DNB acceptors.,

No. Complex	ν_{OH}	ν_{NH}	$\nu_{\text{C-H-Ar}}$	$\nu_{\text{C-H-Alip}}$	$\nu_{\text{C=N}}$	$\nu_{\text{S-H}}$	$\nu_{\text{C=C}}$	ν_{NO}	ν_{NO_2}	$\nu_{\text{C-O-C asym / sym}}$
1	3326m	3105w	2850s	1623s	1546s	1346s	1076s 918s
2	3093w 3033w	2923m 2856m	1649m	2370s	1537m 1521s	1361m	1449m	1074m 871m
3	3321	2925w	2850s	1621w	1533m	1359w	1157w 869m
4	3392w	3326m	3097m	2850m	1623s	1523s	1335m	1087m 860
5	3242w	3097m	2858w	1606s	1530s	1355s	1065m 867m
6	3093w 3033w	2923m 2856m	1649m	2370s	1537m 1521m	1361m	1469m	1074m 871m
7	3097m	2858w	1606m	1560s	1353s	1080s 840w

Table (4) : Important bands in the IR spectra of CT complexes (in cm^{-1}) with TNB acceptors .

No. of Complex	ν_{OH}	ν_{NH}	$\nu_{\text{C-H-Ar}}$	$\nu_{\text{C-H-Alip}}$	$\nu_{\text{C=N}}$	$\nu_{\text{S-H}}$	$\nu_{\text{C=C}}$	ν_{NO}	ν_{NO_2}	$\nu_{\text{C-O-C asym / sym}}$
1	3328s	3103w	2889s	1620s	-	1546s	1346s	-	1076m 918m
2	3100s	2850m	1630s	2370s	1540s	1350s	1450s	1080s 850s
3	3300w	2927m	2858w	1620m	1550s	1346s	1145w 860m
4	3400m	3320m	3100s	2850m	1625s	1590s	1340w	1090s 870w
5	3322s	2943s	2881s	1633s	1516m	1331m	1058m 870m
6	3100s	2850w	1630s	2370s	1540s	1350s	1080s 850s
7	3100s	2850m	1620s	1560s	1340s	1080m 870s

Table (5) : Important bands in the IR spectra of CT complexes (in cm^{-1}) with TNP acceptors .

No. of Complex	ν_{OH}	ν_{NH}	$\nu_{\text{C-H-Ar}}$	$\nu_{\text{C-H-Alip}}$	$\nu_{\text{C=N}}$	$\nu_{\text{S-H}}$	$\nu_{\text{C=C}}$	ν_{NO}	ν_{NO_2}	a
1	3375w	3321m	3101w	2862m	1627m	1531s	1342s	1080m 921m
2	3325w	2931m 2850m	1623s	2356s	1546m	1342s	1438m	1080m 925m
3	2927w	2862w	1620m	1540s	1340m	1161m 866s
4	3400w	3328s	3028s	2920w	1620s	1546s	1346s	1076s 860w
5	3400w	3250w	3101s	2854m	1620s	1540s	1342s	1070m 871m
6	3325w	2931m 2850m	1623s	2356s	1546m	1342s	1438m	1080m 925m
7	3406w	3101s	2873w	1623s	1539s	1342s	1080s 840s

UV-Visible Spectra ;

The electronic spectra of the solid compounds compared to those of the free donors and acceptors reveal the existence of the new bands within the λ_{\max} at in visible range. However, these spectra band exhibiting different behaviors according to the nature of acceptors and the substituent's on the molecular structure of the donor molecules. Thus, we have observed two main effects according to the electron donor and electron donor in the CT complexes charge-transfer complexes in solution.

UV-Visible spectra in solution :The solutions of all complexes in ethylene chloride are obeyed Benesi-Hildebrand's Equation (1) ⁽¹⁸⁾ applying for (1:1) charge-transfer complexes. (Fig-1) show a typical example of the application of this equation. The solution of our compounds (1-7) with DNB, TNB, and TNP absorb light in the visible region at wave lengths given in Tables (6-8). For there our compounds (1-7) may act as an n, π - electron donor and the other molecules as an electron acceptors. Equation of Bensi- Hildebrand's was used to calculate the equilibrium constant (K_{CT} association constant) and extinction coefficients and equilibrium constants for CT complexes at their λ_{\max} .

$$\frac{[A]}{O} = \frac{1}{K_{CT}} + \frac{1}{[D_0] \epsilon_{CT}} \quad \text{..(1)}$$

Where $[A_0]$ and $[D_0]$ are the initial concentrations of the electron acceptor and the compounds electron donor compounds respectively, L is the path length, $O.D_{CT}$ the optical density of CT complex at λ_{\max} , ϵ_{CT} is the molar extinction coefficient and K_{CT} is the

equilibrium constant (association constant) at their λ_{\max}

$$\text{The plot of } \frac{[A_0].L}{O.D_{CT}} \text{ Vs } \frac{1}{[D_0]}$$

$$\text{gave a straight line with slope} = \frac{1}{K_{CT} \cdot \epsilon_{CT}}$$

and the intercept = $1/\epsilon_{CT}$

From the value of intercept is used to calculate the ϵ_{CT} values and the values of the slope and intercept were used to calculated equilibrium constant as follow

$$\frac{\text{Intercept}}{\text{Slope}} = \frac{1/\epsilon_{CT}}{1/K_{CT} \cdot \epsilon_{CT}} = K_{CT}$$

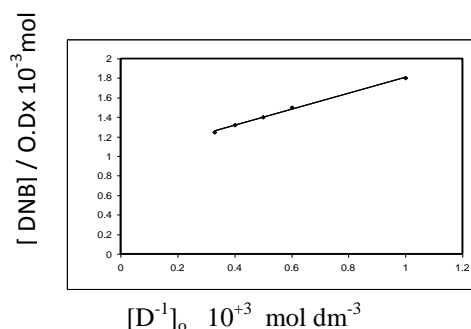


Fig (1) : A typical example of application of Benesi-Hildebrand equation for the CT complex (1)

Table (6): The Physical Parameters of compound (1-7) and their CT complexes with DNB acceptor.

No. of complex.	M.P / (°C)	λ_{\max} /nm	color	E_{CT}/ev	I_p/ev	E_A/ev	W/ev
1	215-217	430	Dark brown	2.41	10.50	2.204	5.88
2	200-202	470	Dark brown	2.63	11.00		6.35
3	99-101	462	Pale green	2.67	11.10		6.23
4	180-182	450	Pale green	2.75	11.26		6.31
5	91-92	445	Pale green	2.78	11.33		6.92
6	157-159	512	Pale green	2.87	11.50		6.43
7	137-139	410	Pale green	3.02	11.86		6.64

Table (7) : The physical parameters of compounds (1-7) and their CT complexes with TNB acceptor.

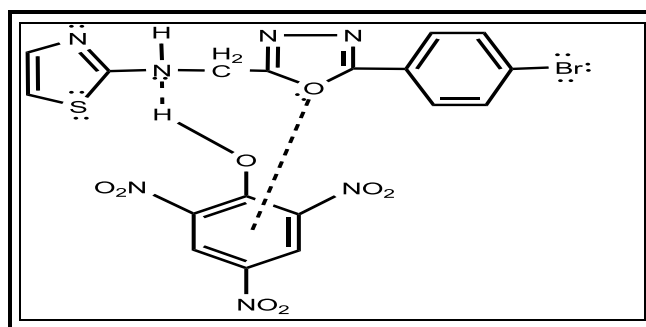
No. of complex.	M.P / (°C)	λ_{\max} /nm	Color	E_{CT}/ev	I_p/ev	E_A/ev	W/ev
1	153-155	507	Pale green	2.44	7.51	1.126	3.95
2	145-147	501	pink	2.48	7.56		3.96
3	80-81	460	Dark brown	2.69	7.79		3.98
4	187-189	457	Yellow	2.71	7.82		3.98
5	162-164	431	Orange	2.87	8.00		4.00
6	169-171	426	Yellow	2.90	8.03		4.01
7	110-112	425	Yellow	2.91	8.04		4.02

Table (8): The Physical Parameters of compound (1-7) and their CT complexes with TNP acceptor .

No. of complex.	M.P/ (°C)	λ_{\max} /nm	Color	E_{CT} / eV	I_p / eV	E_A / eV	W / eV
1	153-155	530	Pale green	2.33	6.76	0.715	3.72
2	105-107	522	Pale green	2.37	6.79		3.70
3	111-113	503	Pale green	2.46	6.85		3.67
4	191-193	483	Pale yellow	2.56	6.92		3.65
5	172-174	546	yellow	2.66	6.99		3.62
6	113-115	458	Pale yellow	2.70	7.01		3.61
7	132-134	415	Pale yellow	2.98	7.22		3.53

Table (9-11) represent the values of ϵ_{CT} and K_{CT} . The electronic spectra in ethylene chloride solution used to study the intermolecular charge-transfer complexes by considered theories compounds, as charge donor and Three charge acceptor (DNB, TNB, and TNP). The electron transfer originates from the same position of each compounds (1-7) and affected by the other group of the acceptors molecules, forming CT complexes of the same geometry for all compounds (1-7) and obey Benesi-Hildebrand's equation for 1:1

complexes⁽¹⁸⁾ (the ratio of these complexes) and the only unoccupied orbital are available in acceptors is the π^* and the compounds (1-7) molecules are very rich in n , π -electrons, therefore, the value of the physical parameters for the same compound (1-7) show similar type of CT complexes with acceptors almost are $n \rightarrow \pi^*$, beside to the proton transfer from TNP molecules to the compounds (1-7) (Scheme 1)

**(Scheme 1)**

From the electronic spectra of charge-Transfer complexes in ethanol solvent calculate some important physical parameters such as ionization potentials (I_p) of our compound (charge -donor) and dissociation energies of excited state of Charge transfer complex (W) were calculated using equation (2)⁽¹⁹⁾.

$$h\nu_{CT} = I_p - E_A - W \quad \text{.....(2)}$$

The plots of charge-transfer transition energies ($h\nu_{CT}$) of complexes at their λ_{\max} of (1-7) compounds as a function of ionization potentials were linear relations with almost identical slopes but varied intercepts. The electron affinities (E_A) of the acceptor are derived in terms of simple valance-bond descriptors. Similar linear relationships have been observed for complexes of many other acceptors, showing the correlation between these parameters. In general⁽¹⁸⁾:

$$h\nu_{CT} = a I_p + b \quad \text{.....(3)}$$

This equation (3) is very important for the estimation of the values of acceptor factors (a,b). The equilibrium constants (K_{CT}) of all CT complexes were used calculate (ΔG° , ΔH , ΔS°) quantities at 25° by using equations (4,5,6). The values of all the physical parameters (I_p , K_{CT} , ϵ_{CT} and thermodynamic functions) are affected by the nature of both donor and acceptor molecules, the nature of substituents on the donor molecules, and molar extinction coefficient (ϵ_{CT}) (less than $10^3 \text{ m}^2 \cdot \text{mol}^{-1}$ which indicate $n \rightarrow \pi^*$ transition.

$$\Delta G^\circ = -RT \ln K_{CT} \quad \text{.....(4)}$$

$$\Delta H = b^2/a (I_p - E_A - W) \quad \text{.....(5)}$$

$$\Delta S^\circ = (\Delta H - \Delta G^\circ) / T \quad \text{.....(6)}$$

Table(9) : Thermodynamic parameters of CT complexes with DNB at 25 °C in C₂H₄Cl₂.

No. of complex	ϵ_{CT} m ² .mol ⁻¹	K_{CT} Mol ⁻¹ .dm ³	$-\Delta G^\circ$ KJ.mol ⁻¹	ΔS° J.mol ⁻¹ .K ⁻¹	ΔH KJ.mol ⁻¹
1	111	2000	15.14	51.6	0.088
2	476	1800	16.23	54.3	0.082
3	877	1777	16.44	55.1	0.079
4	285	1750	18.50	62.4	0.076
5	625	1139	18.53	62.7	0.073
6	277	700	18.57	62.8	0.071
7	500	450	18.83	63.4	0.069

Table(10) : Thermodynamic parameters of CT complexes with TNB at 25 °C in C₂H₄Cl₂.

No. of complex	ϵ_{CT} m ² .mol ⁻¹	K_{CT} Mol ⁻¹ .dm ³	$-\Delta G^\circ$ KJ.mol ⁻¹	ΔS° J.mol ⁻¹ .K ⁻¹	ΔH KJ.mol ⁻¹
1	250	4500	15.39	51.8	0.059
2	526	4250	15.98	53.8	0.059
3	200	3000	16.66	56.1	0.058
4	143	875	16.78	56.5	0.055
5	666	833	19.84	66.7	0.054
6	588	634	20.69	69.6	0.050
7	555	500	20.84	70.1	0.049

Table(11) : Thermodynamic parameters of CT complexes with TNP at 25 °C in C₂H₄Cl₂.

No. of complex	ϵ_{CT} m ² .mol ⁻¹	K_{CT} Mol ⁻¹ .dm ³	$-\Delta G^\circ$ KJ.mol ⁻¹	ΔS° J.mol ⁻¹ .K ⁻¹	ΔH KJ.mol ⁻¹
1	333	5000	15.01	50.6	0.088
2	219	3666	15.14	51.1	0.082
3	335	1100	16.38	55.2	0.079
4	531	750	16.40	55.3	0.079
5	500	745	17.35	58.4	0.073
6	909	450	20.33	68.4	0.071
7	658	428	21.01	70.7	0.069

Also this study included simple kinetic measurement for the determination of dissociation constant of charge-transfer complexes and their stability (rate of hydrolysis), Table (12) and Fig(2) show good linear correlation ships obtained in all case, which indicates that the hydrolysis of CT complexes (1-5) follows strictly first –order kinetics. The slope of the linear

plot representing the observed rate constant (K_{obs}). The disappearance of these compounds(1-5) in neutral solutions at the analytical wave length was followed until 90% completion. The hydrogen ions, and the attack of water molecules on the protonated substrate represents the rate-determine step (Fig :2)^(21,22). A slower rate of the hydrolysis was observed

Table (12) ; Stability of CT complexes (1-5) with DNB, TNB and TNP in ethanol

Complex .No	DNB		TNB		TNP	
	K_{obs}/min^{-1}	$t_{1/2}/\text{min}$	K_{obs}/min^{-1}	$t_{1/2}/\text{min}$	K_{obs}/min^{-1}	$t_{1/2}/\text{min}$
1	0.012	57.75	0.015	46.20	0.01	69.30
2	0.019	36.47	0.007	99.00	0.013	53.31
3	0.011	63.00	0.015	46.20	0.01	69.30
4	0.006	115.50	0.013	53.31	0.017	40.76
5	0.012	57.57	0.009	77.00	0.015	46.20

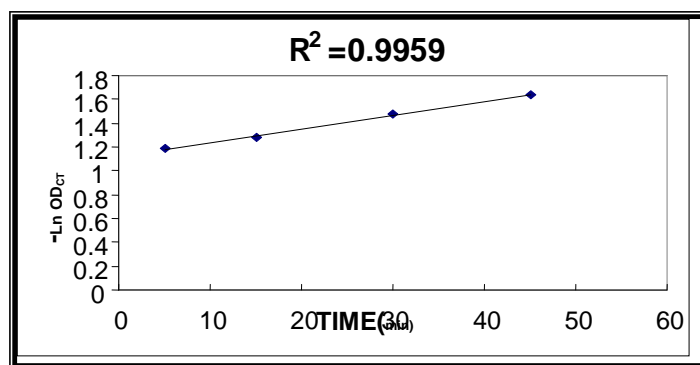


Fig (2): A typical first order kinetic plot for the hydrolysis CT complexes in ethanol.

Conclusions:

Each one of the compounds (1-7) under consideration, allowed to interact with acceptor molecules to form CT complexes under investigation takes place through $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ type transitions and proton transfer (CTC with TNP). The solutions of all complexes obeyed to Benesi-Hildbrands equation. The ratio of oxadiazole derivative : acceptor in every cases is 1:1. the values of the physical parameters for compounds (1-7) and CT complexes (I_p , E_{CT} , W , K_{CT}

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, ϵ_{CT} , ΔG° , ΔH , ΔS°) were calculated, and found to be affected with both the nature of acceptors and the substituentson compounds (1-7). The values of ionization potentials for the compounds (1-7) vary with the following order DNB > TNB > TNP. The CT complex were stable in solid state⁽²³⁾ and spontaneously formation ,but very weak in solution (positive value ΔH) and have a slower rate of the hydrolysis was observed .

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دراسة طيفية لبعض معقدات انتقال الشحنة الجديدة المشتقة من الاوكساد ايازولات مع بعض المستقبلات الالكترونية

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الملخص

يتضمن البحث دراسة طيفية لبعض معقدات انتقال الشحنة المكونة بين مشتقات مركبات (٤،٢،١) و (٤،٣،١) - اوكساد ايازول الجديدة (٧ مركبات) المحضرة والمخصصة طيفيا كجزيئات مانحة للالكترونات مع ثلاث جزيئات مستقبلية للإلكترون هي ثنائي نيترو بنزين و ٦،٤،٢ - ثلاثي نيترو بنزين و ٦،٤،٢ - ثلاثي نيترو فينول ، وتم تشخيص هذه المعقدات المحضرة طيفيا باستخدام تقنية الأشعة تحت الحمراء وأطياف الأشعة فوق البنفسجية . ودرس هذا التداخل المعتمد على نوعية الجزيئين المكونة للمعقد . بالإضافة إلى ذلك تم حساب بعض المعاملات الفيزيائية لهذه المركبات والمعقدات عند أقصى طول موجي λ_{max} للمعقد وهذه المعقدات طاوحت معادلة بنسي هلدبراند عند قيم λ_{max} لها ومنها تم حساب ثابت الاتزان في درجة حرارة ٢٥ مئوي وتم حسبت الدوال الترموديناميكية لهذه المعقدات عند هذه الدرجة.