Theoretical Study of Charge Transfer in Styryl Thiazilo Quinoxaline Dyes STQ-1, STQ-2,and STQ-3 in Organic Media System

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Abstract:

Charge transfer in styryl dyes STQ-1, STQ-2,and STQ-3 with organic media system has been studied theoretically depending on the Franck- Condon rule and continuum dielectric model . The reorientation energies λ(eV) were evaluated theoretically depending on dipole momentum, dielectric constant ϵ, and refrective index n. The rate constant of charge transfer has been calculated depending on the reorientation energy λ(eV) ,effective free energy ΔG^*, potential height barrier $\Delta G^{\#}$, and coupling coefficient V_{el}. A matlap program has been written to calculated the rate constant of charge transfer and other parameter. The results of calculations show that STQ-2 dye is more reaction for charge transfer compare with STQ-1 and STQ-3 dyes

Key words: Theoretical study,Charge transfer, STQ-1, STQ-2,and STQ-3 dye.

Introduction:

Charge transfer (CT)reactions are a boundant in chemistry and biology [1]. Studies on charge transfer in organic molecular systems have witnessed rapid growth in recently years[2]. Understanding electron transfer at the molecular level will aid in developing molecular assemblies with unique properties and novel application, such as molecular electronics devices[3]. The complete theory of charge transfer basing on early work of Rudolf Marcus . A great amount of effort has been made in the studies of the electron transfer reaction with a variety of tools such as time resolved spectroscopy, computer simulation methods, and analytical theory [4]. Theoretical treatments of charge transfer within a solution have focused on charge transfer between weakly coupled charge transfer sites [5]. For electron transfer in solution, we most commonly consider electron transfer to progress along a solvent rearrangement coordinate in which solvent reorganizes its configuration so that dipoles overcharges help to stabilize the extra negative charge the accepter site[6].The study charge transfer in organic media system become very active area in research in recent years ago. In our study the styryl dyes with charge donor – acceptor transfer on either side of the stryly bond is particular attractive for optical and electronic properties . Figure (1) shows the structure of three dyes STQ-1, STQ-2,and STQ-3 used in this study [7].

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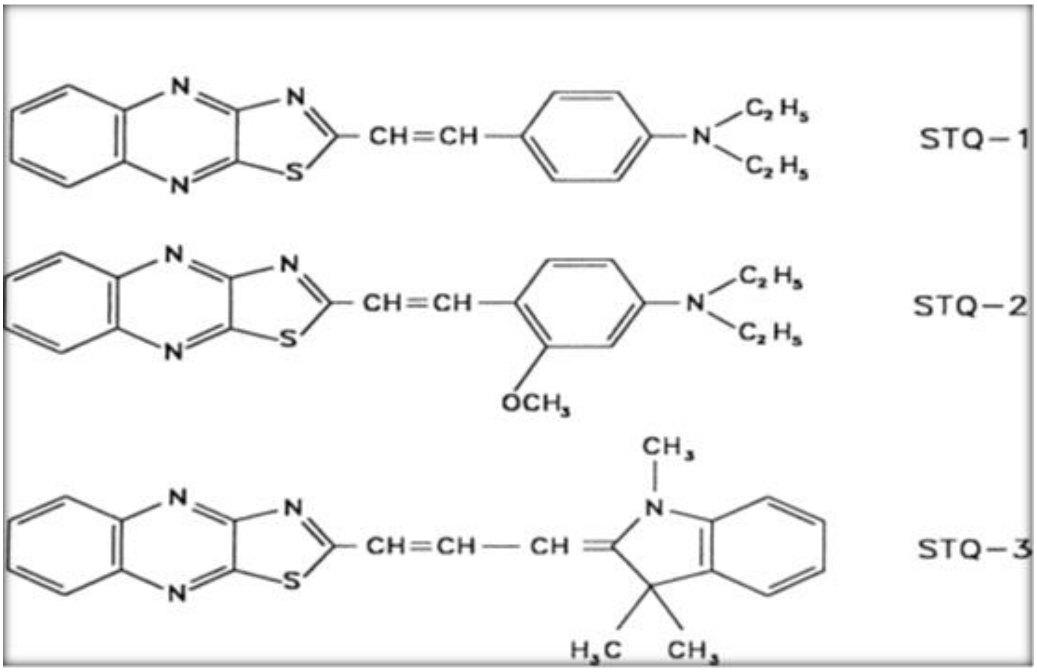

Fig. (1). Molecular structures of STQ-1, STQ-2 and STQ-3 dyes[7]

Theory

For a simple linear reactions , the reaction rate constant k_{LRC}, can be written with Franck-Condon rule[8].

$$k_{LRC} = \frac{\rho w_{\circ}}{2\pi}\, exp\left(-\frac{\Delta G^{\#}}{k_B T}\right) \quad \dots \text{(1)}$$

Where $w_{\circ}$ is the frequency of motion in the reactant potential well , ρ is the electronic transition probability at the transition region, $\Delta G^{\#}$ is the activation free energy , and $k_B T$ is the thermal energy.

The probability ρ is a function of electronic matrix element V_{el} in the case of charge transfer. V_{el} is approximately proportional to an overlap integral between the wave functions of the reactant and product. When V_{el} is small, the free energy becomes non adiabatic case [8], in this case the charge transfer rate constant can be written as [8-11].

$$k_{CT} = \left(\frac{\pi}{h^2 k_B T \lambda}\right)^{\frac{1}{2}} |V_{el}|^2 exp\left(-\frac{\Delta G^{\#}}{k_B T}\right) \dots \text{(2)}$$

Where λ is the solvent reorientation energies due to solvent and anion rearrangement in the secondary coordination sphere.

The reorientation energies can be represented by expression [12].

$$\lambda = \frac{\mu_e^2}{4\pi\epsilon_{\circ} D^3}\left[f(\epsilon_s) - f(n^2)\right] \dots \text{(3)}$$

Where

$$f(\epsilon_s) = \frac{\epsilon_s - 1}{2\epsilon_s + 1} \dots \text{(4)}$$

And $f(n^2) = \frac{n^2 - 1}{2n^2 + 1}$ ...**(5)**

Here ϵ_s is a dielectric constant for varies solvent , *n* is refractive index, *D* is the Onsager cavity radius for the dye molecule and μ_e is the dipole moment of charge transfer in excited state effectively.

The effective free energy for reaction charge transfer that broken into the work it takes to bring the donor and acceptor together and the difference between the reduction potentials and determined by [13].

$$\Delta G^{*} = e[E_{ox} - E_{red}] - \lambda - \Delta E_{oo} \dots \text{(6)}$$

Where *e* is the electron charge, E_{ox}, and E_{red} are the oxidation and reduction potentials respectively, and E_{oo} is the energy of the ground state.

The driving force $\Delta G_\circ$ for the charge recombination event can be calculated as [14].

$$h\nu = \Delta G_\circ + \lambda \quad \ldots(7)$$

where h is the planks constant, and ν is the frequency of the absorption light to excited molecule.

The height barrier of charge transfer is the energy must have the electron transfer is given by [15].

$$\Delta G^{\#} = \frac{(\Delta G_\circ + \lambda)^2}{4\lambda} = \frac{(h\nu)^2}{4\lambda} \quad \ldots(8)$$

Results:

The charge transport in some styryl thiozolo quinxaline STQ-1, STQ-2,and STQ-3 dyes in organic media have been studies here. The charge transport rate constant is determined with many parameters; the reorientation energies $\lambda(eV)$, effective free energy $\Delta G^*(eV)$, activation free energy $\Delta G^{\#}(eV)$, and the coupling coefficient matrix element $V_{el}(eV)$,

The reorientation energy λ of STQ-1, STQ-2,and STQ-3 were calculated using a more general expression equation(3) in several organic solvents, Cyclohaxane, Diaxane, Butanol, Ethanol, and Methanol, respectively. Equation (3) was applied where the values of activity radius $D \cong 2A^\circ$ for STQ dyes, and the dipole moment of charge transfer μ_e taken from table (1) with ϵ and n are the static dielectric constant and refractive index for solvent from table (2).Results are summarized in the table(3).

Table (1) Molecular and photophysical properties of STQ-1, STQ-2, and STQ-3 styryl thiozolo dyes in orginc media

Dye	Molecular weight	Melting point	λ_{ab} (nm)	λ_{em} (nm)	μ_e $(Debye)$	E_{ox}	E_{red}
STQ-1	360.4	230	490	630	7.43	0.998	-0.907
STQ-2	390.5	156	485	625	10.51	0.993	-0.927
STQ-3	384.5	205	530	623	5.22	0.933	-1.027

Table(2): Organic solvent properties. [16]

solvent	Refrective index (n) [16]	Dielectric constant ϵ [16]
Cyclohaxane	1.424	2.01
Dioxane	1.420	2.21
Butanol	1.397	17.51
Ethanol	1.359	23.40
Methanol	1.326	32.63

Table (3) The result of calculation of the reorganization energy $\lambda(eV)$ for charge transfer for styryl thiozol STQ-1, STQ-2,and STQ-3 dyes in organic media

solvent	STQ-1 Dye	STQ-2 Dye	STQ-3 Dye
Cyclohaxane	0.3925	0.7853	0.1777
Dioxane	0.4911	0.9826	0.2224
Butanol	1.5254	3.0521	0.6908
Ethanol	1.6046	3.2106	0.7266
Methanol	1.6737	3.3488	0.7579

So the other parameters in the charge transport is the effective free energy that is provided by is the absorption of light and defined as the part of the work it takes to bring part of system together, and the difference between the reduction potential of the system .The theoretical calculation values of the effective free energy $\Delta G^*(eV)$ can be estimated relative E_{oo} using equation (6),where $E_{ox}, and\, E_{red}$ are the oxidation and reduction potentials respectively are taken from table (1), and λ from table (3). These values of estimation are shown in table (4).

Table (4) The result of charge transfer effective free energy$\Delta G_\circ$ for styryl thiozol STQ-1, STQ-2,and STQ-3 dyes in organic media.

solvent	$\Delta G_\circ$(eV)STQ-1 Dye	$\Delta G_\circ$(eV)STQ-2 Dye	$\Delta G_\circ$(eV) STQ-3 Dye
Cyclohaxane	1.5125	1.1346	1.7823
Dioxane	1.4139	0.9373	1.7376
Butanol	0.3796	-1.1321	1.2692
Ethanol	0.3004	-1.2906	1.2333
Methanol	0.2313	-1.4288	1.2021

The activation free energy$\Delta G^{\#}$ is the scale of the height of the barrier depends on absorption of spectrum energy and reorientation energy. The activation free energy has been calculated using equation (8), results of $\Delta G^{\#}$ using various solvent with STQ dyes are listed in table (5).

Table (5):the activation free energy $\Delta G^{\#}$ for STQ-1, STQ-2, and STQ-3 in orginc media

Wave length(nm)	$\Delta G^{\#}$ for STQ-1					$\Delta G^{\#}$ for$_{\text{STQ-2}}$					$\Delta G^{\#}$ for$_{\text{STQ-3}}$				
	500	550	600	650	700	500	550	600	650	700	500	550	600	650	700
Cyclohaxane	3.901	3.224	2.709	2.308	1.990	1.950	1.611	1.354	1.153	0.994	8.07	7.122	5.984	5.099	4.396
Dioxane	3.118	2.577	2.165	1.845	1.590	1.558	1.288	1.082	0.922	0.795	6.885	5.690	4.781	4.074	3.512
Butanol	1.003	0.829	0.697	0.594	0.512	0.501	0.414	0.348	0.296	0.255	2.216	1.832	1.539	1.311	1.130
Ethanol	0.954	0.788	0.662	0.564	0.486	0.476	0.394	0.331	0.282	0.243	2.107	1.714	1.463	1.247	1.075
Methanol	0.914	0.756	0.635	0.541	0.466	0.457	0.377	0.317	0.270	0.233	2.02	1.669	1.403	1.195	1.030

After estimate the values of the reorientation energy λ ,free energy (driving energy) $\Delta G_\circ$, effective free energy ΔG^{*} , activation free energy $\Delta G^{\#}$,and assume the electronic coupling coefficient V_{el} ~$0.5\ eV$ that a key factors controlling of the charge transfer then parameters and expression equation (2), we can calculated the rate constant of charge transfer, the results are listed in tables (6),(7), and (8) respectively for STQ-1, STQ-2,and STQ-3 with same solvents.

Table(6)The rate of charge transfer constantSTQ-1 in organic media

Wave length	Rate of charge transfer(s^{-1})						
	500 nm	550nm	600nm	650nm	700nm	λ_{ab} 450nm	λ_{em} 630nm
Cyclohaxane	404643×10^{-13}	1.3783×10^{-10}	1.6368×10^{-7}	9.33×10^{-7}	2.9840×10^{-5}	1.233×10^{-13}	2.002×10-7
Dioxane	1.2570×10^{-7}	1.2277×10^{-5}	15.587×10-4	1.414×10-2	2.256×10^{-8}	4.4956×10^{-8}	4.135×10^{-3}
Butanol	4.9419×10^{7}	2.1601×10^{8}	7.3844×10^{8}	2.0900×10^{9}	5.0975×10^{9}	3.549×10^{7}	1.4066×10^{9}
Ethanol	1.0737×10^{8}	4.3620×10^{8}	1.4033×10^{8}	3.7730×10^{9}	8.8062×10^{9}	7.8348×10^{7}	2.5895×10^{9}
Methanol	1.9866×10^{8}	7.6199×10^{8}	2.3360×10^{9}	6.0294×10^{9}	1.3588×10^{10}	1.4691×10^{8}	4.2029×10^{9}

Table(7)The rate of charge transfer constantSTQ-2 in organic media

Wave length	Rate of charge transfer(s^{-1})						
	500 nm	550nm	600nm	650nm	700nm	λ_{ab} 485nm	λ_{em} 625nm
Cyclohaxane	15.7689	2.7673×10^{2}	3.0125×10^{3}	2.2727×10^{5}	1.2842×10^{5}	5.9532	8.613×10^{4}
Dioxane	7.8950×10^{3}	7.7942×10^{4}	5.2535×10^{5}	2.6414×10^{6}	1.0541×10^{7}	3.6245×10^{3}	1.2163×10^{6}
Butanol	1.1696×10^{11}	2.4446×10^{11}	4.5187×10^{11}	7.6005×10^{11}	1.1887×10^{12}	9.1034×10^{10}	5.9212×10^{11}
Ethanol	1.7021×10^{11}	3.4304×10^{11}	6.1514×10^{11}	1.0084×10^{12}	1.5403×10^{12}	1.3413×10^{11}	7.9537×10^{11}
Methanol	2.2905×10^{11}	4.4847×10^{11}	7.8505×10^{11}	1.2609×10^{12}	1.8927×10^{12}	1.8227×10^{11}	1.0043×10^{12}

Table(8)The rate of charge transfer constantSTQ-3 in organic media

Wave length	Rate of charge transfer(s^{-1})						
	500 nm	550nm	600nm	650nm	700nm	λ_{ab} 530nm	λ_{em} 623nm
Cyclohaxane	4.500×10^{-46}	1.698×10^{-40}	6.4800×10^{-36}	4.8898×10^{-32}	1.028×10^{-28}	7.7248×10^{-56}	4.7148×10^{-34}
Dioxane	6.724×10^{-34}	1.664×10^{-29}	7.6352×10^{-26}	9.5909×10^{-22}	4.341×10^{-20}	2.1568×10^{-35}	3.1178×10^{-24}
Butanol	0.22548	5.8489	88.278	8.7816×10^{2}	6.2890×10^{3}	6.6004×10^{-4}	2.6601×10^{2}
Ethanol	1.2871	2.8466	3.7577×10^{2}	3.3373×10^{3}	2.1687×10^{4}	5.0313×10^{-3}	1.0723×10^{3}
Methanol	5.1394	1.0003×10^{2}	1.1870×10^{3}	9.6340×10^{3}	5.7951×10^{4}	0.0252	3.2441×10^{3}

Discussion:

The charge transfer in dye-organic media complex were investigated by theoretical calculations. The Golden rule expression and the continuum model for reorientation energy applied in our theoretical studies of charge transfer reactions in dye –organic media provide a constant value for the reaction. One of the start point of these studies were calculated of reorientation energy of the STQ-1, STQ-2, and STQ-3 in several organic solvents, Cyclohaxane, Diaxane, Butanol, Ethanol, and Methanol, respectively. The results shift increasing with the high polarity solvent and large dipole moment of dye in excited state . Table (3) shows the results of reorientation energies for STQ dyes. Large dielectric constant of solvent results large values of λ for STQ dyes compare with less polarity of solvent , that's are shown in table (3). On the other hand the large values of dipole moment μ_e results to large reorientation energy, that's very view, for STQ-2 have $\mu_e = 10.5\ Debye$ compare with STQ-1 have $\mu_e = 7.43\ Debye$ and $\mu_e = 5.22\ Debye$ for STQ-3.

Table (4)give the results of the effective free energy. It is clear that the dye have small effective free energy where have large reorientation energy and vice versa. The negative results in table (5) for STQ-2 indicate the free energy $\Delta G_{\circ}$ is a part of energy that broken to rearrangement of the system to start transfer of charge .

Table (5) show the effect of the barrier height $\Delta G^{\#}$ on the rate constant of charge transfer, we note that the barrier in STQ-2 dye is small compare with the other dyes , STQ-1 more large height barrier, and STQ-3 high large barrier that give large values rate constant in STQ-2 compare with the other dyes, that’s means k_{ET} increasly, where height barrier $\Delta G^{\#}$ decreasing. Generally from the results of rate constant of charge transfer in STQ dyes in organic media ,we found the major change in rate constant occurs in large reorientation energy system and small barrier height and negatively effective free energy. On the other hand large rate constant indicate a distribution of charge in the state of dye (ground and excited state) give rise to dipole and higher order moment.

Conclusions:

In this work, the charge transfer reactions of a styryl STQ dyes has been studies theoretically in organic media . The reorientation energy are calculated according to continuum model and energy are calculated according to continuum model and dipole moment.

It should be noted that the rate constant at charge transfer for STQ-2 is always large than the rate constant for STQ-1 and STQ-2 in the same organic media, this indicate because large μ_e , and we observe that solvent much polar guide much charge transfer. The most electronically active dye leads to height rate charge transfer.

The rate of charge transfer in STQ dyes in organic media system is a function of height barrier that's mean, when the potential barrier large results small rate constant of charge transfer and vice versa.

In summary, we can concluded from present results that STQ-2 dye is more reaction for charge transfer compare with STQ-1 and STQ-2 dye, means that STQ-2 have large a distribution of charge in the ground and excited state that give dipole moment results, lead to high charge transfer rate constant.

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دراسة نظرية للشحنة المنتقلة في صبغة الكواينوكسلاين STQ-1, STQ-2, STQ-3 في انظمة الاوساط العضوية

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الخلاصة :

دُرس انتقال الشحنة في صبغات STQ-1, STQ-2, STQ-3 في انظمة الاوساط العضوية وحسبت نظريا اعتمادا على قاعدة فلرانك كوندن وانموذج ثنائي القطب المستمر .وحسبت طاقات اعادة الالتحام λ(eV) نظريا اعتمادا على زخم ثنائي للقطب μ وثابت العزل ϵ ومعامل الانكسار n.كما تم حساب ثابت معامل الانتقال للشحنة اعتمادا على طاقة اعادة الترتيب λ(eV) والطاقة الحرة الفعالة ΔG^{*} وارتفاع حاجز الجهد $\Delta G^{\#}$ ومعامل الازدواج .كتب برنمج بلغة ماتلاب لحساب ثابت معدل الانتقال للشحنة وبقية المعاملات اظهرت نتائج الحساب ان صبغة STQ-2 اكثر فعالية للانتقال الالكتروني قارن ب STQ-1 وSTQ-3 .