الانتقال الالكتروني المستحث فوتونيا" بين الروثونيوم (II) ترز2-2 باي يردين ومثيل الفايلوجين

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الخلاصة

الانتقال الالكتروني يمثل التفاعل الابتدائي للعمليات الكيميائية التي تحدث في أي تشكيلة كبيرة من الجزيئات ، تتراوح الازواج الايونية الصغيرة وصولا" الى النظام الحيوي الكبير .

الدراسة النظرية للانتقال الالكتروني المستحث فوتوئيا " بين الروتونيوم $Ru(bpy)_3^{2+}$ و مثيل الفالوجين MV^{2+} لمذيبات مختلفة وعند درجة الحرارة معينة حققت هنا.

هذه الدراسة معتمدة على اساس التنشيط البصري من خلال امتصاص الضوء المذيب وصف من خلال أ نموذج الاستمرارية للعوازل ، والانتقال كميا" من خلال دالة الموجة.

في هذا التطبيق ، طاقة اعادة الالتحام λ ،والطاقة الحرة ΔG^o ، وطاقة التنشيط $\Delta G^{\ddagger}$ حسبت بطريقة شبه كلاسيكية عناصر مصفوفة الازدواج الالكتروني للانتقال الالكتروني V_{DA} التي اخذت من طريقة مليكان –هش ومعدل الانتقال الالكتروني K_{ET} لنظام $Ru(bpy)_3^{2+}-MV^{2+}$ والتي حسبت على وفق أ نموذج كمي .

نتائج حساباتنا للانتقال الالكتروني لنظام $Ru(bpy)_3^{2+}-MV^{2+}$ اظهرت تطابقا" مع النتائج التجريبية الملاحظة .

Photo -induced Electron Transfer Between Ruthenium (II) tris –($2,2'$ - bipyrdine) and Methyl Viologen

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Abstract

Electron transfer (ET) reactions represent an elementary chemical process which occurs in a large variety of molecules, ranging from small ion pairs up to large biological system.

A theoretical study of photo – induced electron transfer between Ruthenium (II) tirs -($2,2'$ - bipyrdine) $Ru(bpy)^{2+}_3$ and Methyl Viologen MV^{2+} in a variety of Solvents at room temperature is presented . This study is based on an optical activation by the absorption of light .The Solvent is described by a dielectric continuum model, and the transferring is represented by a quantum mechanical wave function . In this application, the reorganization energy λ , the driving free energy ΔG^o , and the activation free energy $\Delta G^{\ddagger}$ are calculated with semi classical model . The electronic coupling for the electron transfer V_{DA} reaction is taken from Mulliken –Hush method, and the rate of electron transfer K_{ET} in $Ru(bpy)^{2+}_3 - MV^{2+}$ system are calculated with a quantum mechanical model.

Our calculation results for the electron transfer in $Ru(bpy)^{2+}_3 - MV^{2+}$ system show a good agreement with the experimentally observed results .

Introduction

Electctron transfer (ET) on a molecular level is a very important class of chemical reactions ranging from simple bimolecular reduction oxidation reactions to complex electron transport chains in protein (1).

The (ET) process is like any other chemical reaction , a transition from a metastable initial to a stable final state (2). ET can be optically or/and thermally activated and triggers photosynthesis , metabolism, polymerization reactions, electrochemical reactions(3).

A molecular (ET) reaction involves an oxidation of a Donor (D) molecule and reduction of an Acceptor molecule (A). If the donor and acceptor are freely diffusing in a solvent , then prior to ET a bimolecular diffusion creats an encounter complex . In the encounter complex , electron transfer reaction occurs at a certain distance and arrangement. The encounter complex can either be in close contact, or in a solvent separated configuration , and ET may occur at a distribution of different donor- acceptor con- figureations . If the donor and acceptor are attached to each other, no diffusion processes are needed prior to ET , and unimolecular ET reaction kinetic is observed . The theory describing ET processes was developed from the transition state theory by Marcus. For this development Marcus was awarded the 1992 Nobel Prize in Chemistry (4,5,6) .

The rate of photo induced ET are evaluated depending on the quantum mechanical theory and non adiabatic limit $R_{DA} = 10A^o$. The value of ET rate constants K are controlled by :

reorganization energy λ, driving free energy ΔG^{o} ; activation free energy $\Delta G^{\ddagger}$, and electronic coupling matrix element V_{DA}.

In this research we will study the photo induced ET from $Ru(bpy)_3^{2+}$ acting as an electron donor to $N-N'$ dimethyl- $4-4'$ bipyridine (Methyl Viologen) acting as an electron acceptor . The structures of the $Ru(bpy)_3^{2+}$ and MV^{2+} that are used in this work are shown in figure (1)

The System

Ruthenium (II) – trisbipyridine $Ru(bpy)_3^{2+}$ was used in numerous investigations as a photosensitizer during the last 30 years due to the very favorable photochemical properties (7). The absorbance in both the visible and UV regions is high (1,11) .

In the excited state , $Ru(bpy)_3^{2+}$ is both a good reductant and oxidant , and the life time is long enough to be used in bimolecular electron or energy transfer reactions . In addition both the reduced and oxidized forms are relatively stable towards degrading reactions (7,8).

One way of inducing ET is to expose aphotosensitizer $Ru(bpy)_3^{2+}$ to light of a wave length that is absorbed by $Ru(bpy)_3^{2+}$, thus transferring it to an excited state $Ru^{*}(bpy)_3^{2+}$ eq.[1] (9)

$$Ru(bpy)_3^{2+} + h\upsilon \rightarrow Ru^{*}(bpy)_3^{2+} \ldots\ldots\ldots\ldots\ldots\ldots[1]$$

Here, the frequency of the spectral absorption maximum υ_{max} is given by:

$$h\upsilon_{max} = \lambda + \Delta G^{\circ} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[2]$$

Where h, is planck constant, υ_{max} is frequency of light , λ reorganization energy and ΔG° is free energy .

If a quencher (MV^{2+}) is added to the system, this molecule is able to quench the excited state of $Ru^{*}(bpy)_3^{2+}$ .i.e. it is able to remove the excitation energy (10). The quenching mechanism can be ET from the system $Ru^{*}(bpy)_3^{2+}$ to Mthyle Viologen MV^{2+}, Fig.(2) gives a reduced Methyle Viologen radicl and oxidized ruthenium $Ru(bpy)_3^{3+}$ equation [3] (9,10).

$$Ru^{*}(bpy)_3^{2+} + MV^{2+} \xrightarrow{ET} Ru(bpy)_3^{3+} + MV^{2+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots[3]$$

Theory of Electron Transfer

In quantum mechanical models the golden rule expression for the transition probability between different electronic states (Donor- Acceptor), is often used to treat nonadiabatic electron transfer .

In the high temperature limit , when the energy of each vibration is considerably less than the thermal energy , $h\upsilon \langle\langle K_B T$ (12,13), the ET rate constant K_{ET} between the reactants at a fixed distance is determined by three parameters: the electronic couplong matrix element V_{DA} , the free energy change of the reaction ΔG° , and the reorganization energy λ , which includes both intra molecular λ in; and solvent λ_s out coordinates, the expression for K_{ET} (14).

$$K_{ET}=\frac{2\pi}{\hbar}\frac{1}{\sqrt{4\pi\lambda K_B T}}\left|V_{DA}\right|^2\exp\left(-\frac{\Delta G^{\ddagger}}{K_B T}\right)\ldots\ldots\ldots\ldots\ldots[4]$$

Where $\hbar$ is planck's constant divided by $2\pi, K_B$ which is the Boltzman constant, and $\Delta G^{\ddagger}$ is the Gibbs free energy of activation . The potential energy surfaces of the reactant and product states can be described as free energy surfaces, and ET occurs at the crossing of the reactant and product surfaces . The amount of free energy required to bring the reactant to the crossing point is the free energy of activation, $\Delta G^{\ddagger}$, defined as (13).

$$\Delta G^{\ddagger}=\frac{(\Delta G^{\circ}+\lambda)^2}{4\lambda}\ldots\ldots\ldots\ \ldots\ldots\ldots\ \ldots\ldots[5]$$

Where ΔG° is the free energy change for any chemical reaction which is the difference in the energy of the products and the reactants.

For ET reactions, this can be broken into the work it takes to bring the donor and acceptor together and the difference between the reduction potentials of the acceptor and donor.

The reorganization energy λ is the sum of the inner λ_{in}, and outer, λ_{out} , reorganization(15)

$$\lambda=\lambda_{in}+\lambda_{out}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[6]$$

The inner reorganization component is the energy required to alter bond distances and bond angles that would change with the change in oxidation state.

The outer reorganization energy is required for the reorientation of the solvent around the changed complexes (15) . In many complexes or big molecules that have asmall inner reorganization, such that , we can assume $\lambda \cong \lambda_{out}$.$\lambda_{out}$ can be estimated from a dielectric continuum model for the solvent, and give the largest contribution to λ in many ET reactions in polar media (16). The solvent reorganization energy in this model is given by (16)

$$\lambda\cong\frac{e^2}{4\pi\in_{\circ}}\left(\frac{1}{2r_D}+\frac{1}{2r_A}-\frac{1}{R_{DA}}\right)\left(\frac{1}{\in_{op}}-\frac{1}{\in_s}\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots[7]$$

Where e is the charge involved (usually one electron), $\in_{\circ}$ is the vacuum permittivity , $\in_{\circ p}$ and $\in_s$ is the optical and static dielectric constants , (r_D, r_A,) are the donor and acceptor radii and R_{DA} is the donor – acceptor center to center distance .

Results

The rate of ET is determined by many parameters . The effective free energy ΔG° for the reaction , the value of the reorganization energy of the electron donor (D) and acceptor (A) required upon ET , activation free energy $\Delta G^{\ddagger}$, and coupling coefficient matrix element of ET,V_{DA}

A more genral expression equation eq.[7] was applied to evaluate the reorganization energy λ ,for a donoer $Ru(bpy)_3^{2+}$ and acceptor MV^{2+} system in a variety solvent , where radii r_A=6.5 $\overset{\circ}{A}$ for acceptor and r_D=3.5 $\overset{\circ}{A}$ for donor (17), $\in_{\circ p}$ and $\in_s$ are the optical and static dielectric constants of the solvent[$\in_{\circ p} \cong 1.344$ and $\in_s$ =37.5for acetonitriale (16) , $\in_{\circ p}$ =1.77 and $\in_s$ =78.5 for water](16,18) .

The values of reorganization energies , in the present system are 0.952eV and 0.908 eV in acetonetriale and water solvent respectively.

So the other variable in the rate ET expression is the driving force ΔG° (effective free energy) that is provided by the absorption of light in $Ru(bpy)_3^{2+}$ -MV^{2+} system that is very clear from eq.[2] and figure (2) . The driving force is defined as the part of the work it takes to bring the donor and acceptor together , and the difference between the reduction potentials of the acceptor and donor. The theoretical calculation values of the free energy can be evaluated by using eq.[2] , where E=$h\upsilon$ is the absorption energy taken from absorption spectral of $Ru(bpy)_3^{2+}$.

These results of ΔG° (eV) in acetonitrial and water solution are sumarized in table (1). Now, by substituting the values of the driving force ΔG° (eV) and the solvent reorganization energy $\lambda(eV)$ for both solvents in eq.[5] we can calculate the ET activation barrier $\Delta G^{\ddagger}(eV)$ .These calculated values are summarized in table (2).

Another important factor for ET are the electronic coupling coefficients, $V_{DA,}$ which is the most difficult parameter to obtain experimentally. However, according to the theory by Hush (19), and the assumption that the reaction is activationless , the electronic coupling,V_{DA} ,can be estimated to be (0.01,0.03,0.2) eV

Finally we can calculate the rate of the photo induced ET values K between $Ru(bpy)_3^{2+}$ and Methyle Viologen MV^{2+} in a different solvent by inserting the values of the coefficients $\lambda(eV)$, ΔG° (eV), $\Delta G^{\ddagger}(eV)$, and V_{DA} (eV) in equation eq.[4] , the results of rate ET are listed in tables (3-4).

Discussion

when the $Ru(bpy)_3^{2+} - MV^{2+}$ solution systems are promoted to electronically excited states by the absorption of light, some of this absorption energy of light is used to distort the nuclear configuration from and its equilibrium donor state to the acceptor state without transfer of an electron .

The resulting values of the reorganization energies were unusually high [0.952 eV in acetonitrile and 0.908eV in water] , which could indicate that large structural rearrangements are necessary when V^{2+} is oxidized . The calculation result of reorganization energies are fitting with theoretical and experimental values in the same solution that is shown in table(5).

Table (1) shows the overall driving force free energy changes , ΔG° , that can be calculated for the $Ru(bpy)_3^{2+}$ -MV^{2+} solution system, which correspond to the inverted region . The Inverted region may be observed when the driving force for reaction is greater than the reorganization energy, $-\Delta G^{\circ}\rangle\lambda$ .Consequently inverted region effects are most easily discerned for those reactions with small reorganizatioin energies in both solution and large driving force ,which is very clear from table (1). The values of the driving free energy that are calculated theoretically fit with experimental values , that are clear for awave length 460A°, ΔG° =-1,7 eV , 1.73 eV (1,11).

Tables (4-5) and (1) indicate that -$\Delta G^{\circ}\rangle\lambda$ increasing , the rate of ET, K decrease with increasing - ΔG° . This view is for two solvents , because the barrier for ET increases as also in table(2).

The effect of decreasing K_{ET} in the inverted region can be explained physically as follows: increasing the driving force - ΔG° to values learger than the reorganization energy λ leads to the increasing of the free energy of activation $\Delta G^{\ddagger}$, i.e. barrier of the reaction .

The calculation results of K_{ET} fit well with the experimental values (1,11).

Conclusion

In our research, theoretical studies to calculate the rate of electron transfer for the $Ru(bpy)^{2+}_{3}-MV^{2+}$ solution molecules system in a variety solvent, are promoted to electronically excited states by the absorption of light . Upon light absorption , an electron is formally transferred from the Ru(II) metal center across one of the bipyridine ligands to the MV^{2+}.

The reorganization energies are calculated with dielectric continuum model and are found~ $0.952eV-0.908eV$ for a system in water and acetonitrile solution respectively . This result show large reorganization energy in more polar solvent, that means λ is proportional to $1/\in_{op}$

It turned out that the mode of reaction path way strongly depends on the solvent polarity whereas ET is favored in polar solvents. Also the rate of ET for system is a function of the height barrier$\Delta G^{\ddagger}$. When a treated quantum mechanically as vibrational wave functions of the reactant nuclear coordinates to coordinate space that overlaps with product coordinates space (also referred to as "nuclear tunnellig"). The probability to bridge the gab between the reactant and the product $\Delta G^{\ddagger}$ is the largest.

From the present results that are concluded , the photo induced ET in$Ru(bpy)^{2+}_{3}-MV^{2+}$ system is activated in the inverted region. The calculation results for the rate of ET in $Ru(bpy)^{2+}_{3}-MV^{2+}$ solvent system show a good agreement with the experimentally observed results.

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Table (1):The free energy $\Delta G^\circ(eV)$ for acceptor MV^{2+} and donor $Ru(bpy)_3^{2+}$

Wave length(nm)	$\Delta G^\circ_{water} eV$	$\Delta G^\circ_{acet.} eV$
300	-3.173	-3.216
320	-2.915	-2.958
340	-2.687	-2.737
360	-2.485	-2.528
380	-2.304	-2.347
400	-2.141	-2.185
420	-1.994	-2.537
440	-1.860	-1.903
460	-1.737	-1.781
480	-1625	-1.669
500	-1.522	-1.566
520	-1.427	-1.471
540	-1.339	-1.382
560	-1.257	-1.301
580	-1.181	-1.224
600	-1.110	-1.153

Table (2):The activation free energy $\Delta G^{\ddagger}(eV)$ for acceptor MV^{2+} and donor $Ru(bpy)_3^{2+}$

Wave length $\lambda(nm)$	$\Delta G^{\ddagger}{}_{water}\, eV$	$\Delta G^{\ddagger}{}_{acet.}\, eV$
300	1.294	1.345
320	1.010	1.056
340	0.790	0.830
360	0.616	0.652
380	0.479	0.511
400	0.371	0.398
420	0.284	0.309
440	0.216	0.237
460	0.162	0.180
480	0.119	0.135
500	0.085	0.098
520	0.059	0.070
540	0.039	0.048
560	0.024	0.031
580	0.013	0.019
600	0.006	0.010

Table(3): Rate of ET between $Ru(bpy)_3^{2+}$ and MV^{2+} in water solvent for different V_{DA}

Wave length $\lambda(nm)$	$K_{ET}s^{-1}$		
	V_{DA}=0.02 eV	V_{DA}=0.03 eV	V_{DA}=0.01 eV
300	$2.285\text{x}10^{-8}$	$5.140\ \text{x}10^{-10}$	$5.712\ \text{x}10^{-11}$
320	$1.914\ \text{x}10^{-3}$	$4.307\ \text{x}10^{-5}$	$4.785\ \text{x}10^{-6}$
340	13.009	0.292	0.032
360	13381.190	301.076	33.452
380	3222297.941	72501.703	8055.744
400	248165224.3	5583717.547	620413.060
420	7832952172	176241423.9	19582380.43
440	$1.21308\text{x}10^{11}$	2729448305	303272033.9
460	$1.068855\ \text{x}10^{12}$	$2.404914\ \text{x}10^{10}$	2672127376
480	$5.96902\ \text{x}10^{12}$	$1.343031\ \text{x}10^{11}$	$1.49225\ \text{x}10^{10}$
500	$2.2887\ \text{x}10^{13}$	$5.1496\ \text{x}10^{11}$	$5.7218\ \text{x}10^{10}$
520	$6.5012\ \text{x}10^{13}$	$1.4627\ \text{x}10^{12}$	$1.6253\ \text{x}10^{11}$
540	$1.4468\ \text{x}10^{14}$	$3.2554\ \text{x}10^{12}$	$3.6172\ \text{x}10^{11}$
560	$2.6258\ \text{x}10^{14}$	$5.9682\ \text{x}10^{12}$	$6.546\text{x}10^{11}$
580	$4.02385\ \text{x}10^{14}$	$9.0643\ \text{x}10^{12}$	$1.0071\ \text{x}10^{12}$
600	$5.3731\ \text{x}10^{14}$	$1.2089\ \text{x}10^{13}$	$1.3432\ \text{x}10^{12}$

Table (4): Rate of ET between $Ru(bpy)_3^{2+}$ and MV^{2+} in acetonitrile solution (CH_3CN)

Wave length $\lambda(nm)$	$K_{ET}(sec)^{-1}$		
	V_{DA}=0.02 eV	V_{DA}=0.03 eV	V_{DA}=0.01 eV
300	$3.0020x10^{-9}$	$6.754\ x10^{-11}$	$7.505\ x10^{-12}$
320	$3.173\ x10^{-4}$	$7.1404\ x10^{-6}$	$7.933\ x10^{-7}$
340	2.6593	0.0598	$6.64\ x10^{-3}$
360	3301.100	74.274	8.252
380	935735.115	21054.040	2339.337
400	837017.730	1883289.894	209254.432
420	3022181989	67999094.64	7555454.96
440	$5.3010\ x10^{10}$	1192743400	132527044.4
460	$5.2186\ x10^{11}$	$1.1741\ x10^{10}$	1304665511
480	$3.2207\ x10^{12}$	$7.2466\ x10^{10}$	8051873912
500	$1.3613\ x10^{13}$	$3.06300\ x10^{11}$	$3.4033\ x10^{10}$
520	$4.22487\ x10^{13}$	$9.5059\ x10^{12}$	$1.0562\ x10^{11}$
540	$1.0173\ x10^{14}$	$2.2890\ x10^{12}$	$2.5433\ x10^{11}$
560	$1.9879\ x10^{14}$	$4.4728\ x10^{12}$	$4.9697x10^{11}$
580	$3.2685\ x10^{14}$	$7.3543\ x10^{12}$	$8.1714\ x10^{11}$
600	$4.6572x10^{14}$	$1.04789\ x10^{13}$	$1.16432\ x10^{12}$

Table(5):Our result for reorganization energies compared with theoretical and experimental Values

Solvent	Our result $\lambda(ev)$	Experimental $\lambda(ev)$	Theoretical $\lambda(ev)$
Water (H_2O)	o.952	1.00(11)	1(16)
Acetonitrile	0.908	~1.0[11]	

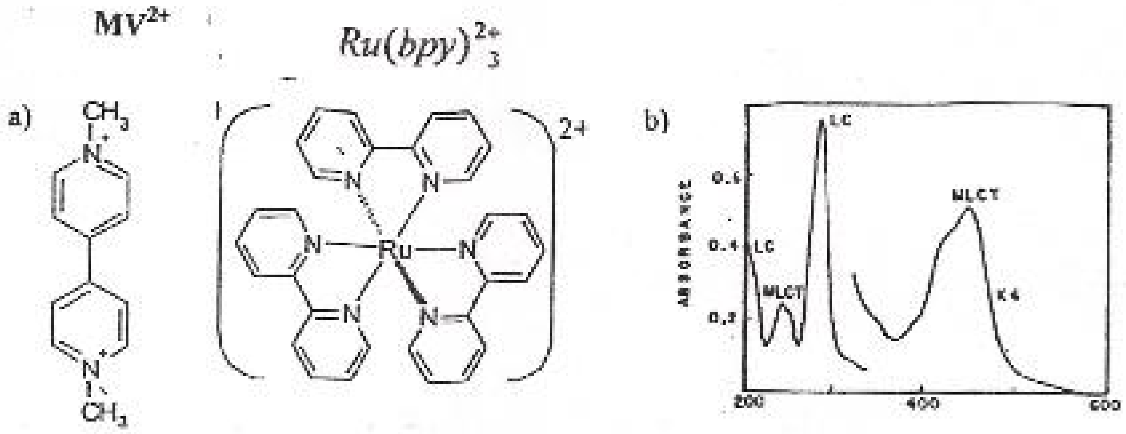

Fig.(1) a - The structure of $Ru(bpy)_3^{2+}$ and MV^{2+}
b- absorption spectrum for $Ru(bpy)_3^{2+}$

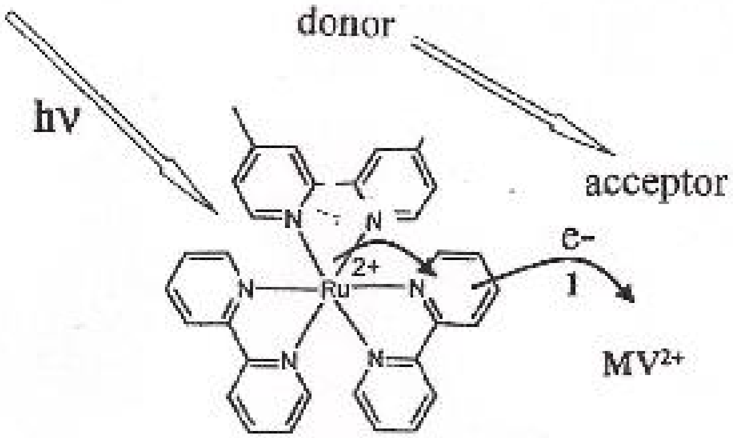

Fig.(2) Electron transfer from the excited state of Ru (II)* to MV^{2+}