

Electron Transfer between Ruthenium (II)-(trisbipyridine) $Ru(phen)_3^{2+}$ and Cobalt(III)-(polypyridyl) $Co(phen)_3^{3+}$ at CH_3CN , CH_3OH , and Acetone Solvents.

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Abstract

A theoretical calculations of electron transfer at metals interfaces are performed to study the electron transfer for $Ru(phen)_3^{2+}$ - $Co(phen)_3^{3+}$ system at CH_3CN , CH_3OH , and acetone solvents. This study is based on the assumption that metals have a continuum of donor's and acceptor's states. The rate of electron transfer, the reorganization energy, the enthalpy, the effective free energy, and coupling coefficient of matrix elements, V , were calculated for the donor $Ru(phen)_3^{2+}$ and acceptor in variety of solvents. The results show that the electron transfer in $Ru(phen)_3^{2+}$ system at solvents is fast and efficient. Our calculations show good agreement with the experimentally observed results for metals complex.

الانتقال الالكتروني بين روثنوم(II) – (ترزبايردين) والكوبالت (III) – (بولي بايرديل) في مذيبات الاستونتريل، الميثانول، والاسيتون.

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الخلاصة

الحسابات النظرية للانتقال الالكتروني عند سطوح المعادن استخدمت لدراسة الانتقال الالكتروني لمنظومة روثنوم(ترزبايردين) – كوبالت(بولي بايرديل) باستخدام مذيبات الاستونتريل، الميثانول، والاسيتون.

هذه الدراسة بنيت على أساس افتراض أن المعادن تمتلك حالات واهبة ومستقبلة مستمرة. ثابت معدل الانتقال الإلكتروني ، طاقة إعادة الترتيب ، طاقة الانتالبي، الطاقة الحرة الفعالة، ومعامل الاقتران لعناصر المصفوفة، V ، قد حسبت للواهب روثونيوم(ترزبايردين) والمستقبل باستخدام مذبيبات مختلفة. النتائج أوضحت بان الانتقال الإلكتروني في منظومة روثونيوم(ترزبايردين) مع المذبيبات هو فعال وسريع. حساباتنا أظهرت تطابقا جيدا مع النتائج العملية الملاحظة لمعقدات المعادن.

Introduction

Photo induced electron transfer from a donor (D) molecules to an acceptor molecules (A) is responsible for an important class of chemical reactions [1]. Consider an organic light emitting device or field effect transistor (FET) ,a molecular switch is contacted by two metal electrodes substrate mediated surface photochemistry, and solar energy conversion on dye sensitized semiconductors[2]. All these processes involve electron transfer between a molecule and metal or semiconductor surface [2]. Electron transfer are the only reactions that proceed at a significant rates when the reactants are separated by long distance ($>10 \text{ \AA}$) [3].One of transferring type is the electron transfer at metals surfaces. Metals have a continuum of donor /acceptor states [4]. Whether electron transfer at metal solution interface is adiabatic or non adiabatic depends on the distance between the electrode and the redox agent in solution [4].Electron transfer reactions in supramolecular complexes are intended to mimic the basic steps in the photosynthetic process. All complexes are based on ruthenium (II)(trisbipyridine) as photo sensitizer, that covalently linked to electron donors or electron acceptors[5]. Ruthenium (II)(trisbipyridine) has been used in numerous investigations as a photosensitizer during the last 30 years due to the very favorable photochemical properties. The absorbance in both the visible and UV regions is high .In the excited state, $\text{Ru}(\text{phen})_3^{2+}$ is a good reduction as well as oxidant, and the lifetime is long enough to be used in bimolecular electron or energy transfer reactions[5]. In this paper we studied the electron transfer between excited states of ruthenium (II)(trisbipyridine) $\text{Ru}(\text{phen})_3^{2+}$ complex(electron donor) upon acceptor such as Cobalt(III)-(polypyridyl) $\text{Co}(\text{phen})_3^{3+}$ complex.

Theory

In quantum mechanical models the Fermi golden rule, is often used to treat non adiabatic electron transfer [5]. When a continuum of a donor or acceptor levels is involved in the electron transfer, as is the case in a metal, the rate constant for electron transfer can then be written as[4].

$$k_{ET} = \frac{2\pi}{\hbar} (4\pi\lambda K_B T)^{-1/2} e^{-\lambda/4K_B T} |V|^2 \dots\dots\dots [1]$$

Where \hbar , is the Planck's constant, λ is the reorganization energies, V is the electronic matrix elements of the coupling coefficient, K_B is the Boltzmann constant, and T , temperature.

The reorganization energy λ is the energy required to move the reactant to the equilibrium positions of the product without transferring the electron [6]. λ is expressed as the sum of the solvent independent term, λ_i , and the solvent reorganization energy λ_s [7].

λ_i is the energy required to modify the molecular structure of the reactant molecules to form the products and λ_s is the energy required to reorganize the solvent from its reactant-solvating configuration to its product-solvating configuration without actually allowing the electron transfer to occur [7].

Normally, for rigid molecules and in polar solvents, the contribution of λ_i to the total λ is minor, with typical values of 0.2eV for λ_i [6].The solvent reorganization energy λ_s , is given by [8].

$$\lambda_s = \frac{(\Delta\epsilon)^2}{4\pi\epsilon_0} \left[\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right] \left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right] \dots\dots\dots [3]$$

Where ϵ_0 , is the vacuum permittivity, ϵ_s is the static dielectric constant of the solvent, ϵ_{op} is the optical dielectric constant, r_D , and r_A , are the donor and acceptor radius respectively, and r_{DA} , is the sum r_D , and r_A .

The free reaction enthalpy ΔG^* for reduction of acceptor and donor can be estimated from the Gibbs energy parabolas with the electron transfer absorption maximum that is given by formula [9].

$$h\nu^{abs} = \Delta G^* + \lambda_i + \lambda_s \dots\dots\dots [4]$$

Where $h\nu^{abs}$ is the maximum absorption energy, ν^{abs} is absorption frequency.

The driving free energy change for any chemical reaction is the difference in the energy of the products and the reactants [10]. The free energy surfaces ΔG^\ddagger for electron transfer reaction may be determined from [9].

$$\Delta G^\ddagger = \Delta G^* - E_{\infty}(D) \dots\dots\dots [5]$$

Where $E_{\infty}(D)$ is the triplet energy of donor and, ΔG^* , can be determined by the Weller equation [9].

$$\Delta G^* = e \left[E_{\frac{1}{2}}^{ox}(D) - E_{\frac{1}{2}}^{red}(A) \right] - \frac{e^2}{4\pi\epsilon_0\epsilon_s r_{DA}} + \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r_D} + \frac{1}{r_A} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \dots\dots\dots [6]$$

Here, $E_{\frac{1}{2}}^{ox}(D)$ and $E_{\frac{1}{2}}^{red}(A)$ are the one electron electrochemical oxidation and reduction potentials of donor and acceptor, respectively and e is the electronic charge.

One of most important factor is the electronic coupling V , that describe the electronic coupling between the reactant and product state [6]. Depending on the magnitude of the electronic coupling between the donor and the acceptor, the electron transfer reaction can be classified as adiabatic or non adiabatic [6]. For a non adiabatic reaction, the probability of crossing over from the reactant state to the product state is relatively small, and the crossing is considered as a sudden event [6].

The coupling coefficient V , depends on the donor and acceptor distance, and the distance dependence of V is exponential and given by [11].

$$V = V_{(0)} e \left[-\beta/2 (r_{DA} - r_0) \right] \dots\dots\dots [7]$$

Where r_{DA} is the edge to edge distance between Ru(phen)₃²⁺ and Cobalt (polypyridyl) Co(phen)₃³⁺ acceptor, $V_{(0)}$ is the value of V at $r_{DA} = r_0$, and β is exponential distance decay constant that is sensitive to the composition of the medium separating the electron donor and acceptor.

Results

We have applied a quantum model of a weak interacting electron in an adiabatic electron transfer between metals ions in solvents. To calculate the rate of electron transfer constant k_{ET} by using equation (1), we have first obtained, the solvent λ_s and λ_i inner reorganization energies. The solvent reorganization energies λ_s for Ru(phen)₃²⁺ and Co(phen)₃³⁺ system in polar solvent was determined from equation [3], by substituting the value of static ϵ_s and optical dielectric $\epsilon_{op} \approx (\text{refractive index})^2$ for solvents from table (1), with the accurate values of radius $r_D = 6.1 \text{ \AA}$, $r_A = 6.1 \text{ \AA}$, $r_{DA} = 12.2 \text{ \AA}$ are taken from literature [12], the results are listed in table (1). So the total reorganization energy λ are calculated using equation (2), with typical value of $\lambda_i \approx 0.2 \text{ eV}$ for most organic complex molecule [6].

By using the above estimates for λ and the $h\nu^{abs}$ obtained from the fit of the absorption spectrum data[5], the enthalpy energy ΔG^* can be determined from expression[4], the result of ΔG^* for $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ system in polar solvent the results are summarized in table (2).

Next, we can estimate values of free energy ΔG^- which play important role in electron transfer for $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ system in polar solvents. ΔG^- may be calculated by inserting values of ΔG^* from table(2) and the triplet energy of donor $E_{00}(D)=2.1\text{eV}$ [10]. The resulting free energy are given in table (3).

We have used the exponential distance expression to estimate the electronic coupling between pairs of donor and acceptor states. In this approach, the electronic coupling is estimated by equation (7) for some values of $0.75\text{\AA} \geq \beta \leq 1.4\text{\AA}$ [3] with typical value of $V_{(0)}=200\text{cm}^{-1}$ [11], these results are summarized in table (4). By substituting values of reorganization energy λ and coupling matrix element from table (1) and (4) in expression (1), we have obtained the rate of electron transfer constants, the results are listed in table (5).

Discussion

Table (1) shows the reorganization energy λ (eV) which increases for $Ru(phen)_3^{2+} - (phen)_3^{3+}$ system at solvent has large dielectric constant while λ decreases for the system at solvent has small dielectric constant. Result in table (1) shows large value $\lambda(\text{eV})$ for $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ at CH_3CN solvent, because of high value of dielectric constant $\epsilon_s=37.5$, but it is small for the $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ at acetone solvent that has small dielectric constant $\epsilon_s=20.7$, this indicate that in polar solvents, the orientation of the solvent dipoles produce the main contribution to λ_s [13]. The reaction enthalpy at the reduction of the $Ru(phen)_3^{2+}$ by $Co(phen)_3^{3+}$ were calculated with the aid of equation (4). Results of these calculations show that ΔG^* for $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ system at acetone solvent is larger than for system at CH_3OH and CH_3CN solvents, this indicates that the mode of the reaction pathway of electron transfer length wave, i.e., the rate of electron transfer constant increases with increasing mode frequency because high frequency tunnel takes place more easily than do in low frequency. The most important factors controlling the rate of electron transfer constant is the electronic coupling term V , which describes the overlap of the donor and acceptor states. We can see from results in table (4) and expression (7) that it is dependent on the donor and acceptor distance.

This can be understood by the fact that the electronic wave functions in the donor and acceptor molecule extends over distance and hence the overlap should be distance dependent. The value of β varies depending on the nature of the intervening medium between the donor and acceptor. At large distance from the nucleus, the electronic wave functions decay exponentially on the distance, this has been found experimentally[6]. Table(5) shows the rate of electron transfer constant decreases with decreasing of the coupling value V , that's mean where the donor acceptor separation increases the coupling coefficient decreases and vice versa. Large value of β indicates large tunneling energy between donor and acceptor and small coupling coefficient. Table (5) shows that the rate of electron transfer constant results of $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ system at CH_3CN , CH_3OH , and acetone solvents. From result we can see that the value of K_{ET} for $Ru(phen)_3^{2+} - Co(phen)_3^{3+}$ system at acetone is larger than that of K_{ET} at both CH_3CN , CH_3OH solvents, this indicate the K_{ET} value depending on V and λ , the K_{ET} increasing with increasing the coupling coefficient V , that the distance between donor acceptor is small and the electron transfer crossing the overlap between the wave functions of donor and acceptor is most probable.

Conclusions

This paper presents the application of an electron transfer theory to calculate the rate of electron transfer constant and other parameters for $\text{Ru}(\text{phen})_3^{2+}$ - $\text{Co}(\text{phen})_3^{3+}$ complex at CH_3CN , CH_3OH and acetone solvents. Under this theory, we assume that metals have a continuum of donor/acceptor states. The solvent and total reorganization energies are calculated for $\text{Ru}(\text{phen})_3^{2+}$ - $\text{Co}(\text{phen})_3^{3+}$ system at solvents. The solvent reorganization energy increases for the system at solvent has large dielectric constant ϵ_s and decreases for the system at solvent has small ϵ_s , this indicate in polar solvent the orientation of the solvent dipoles produce the main contribution to λ . The enthalpy energies are obtained as function of the reorganization energies λ and absorption energy $h\nu^{abs}$. Result of ΔG^* shows large value at acetone than for system at other solvents, this indicate that the mode of the reaction pathway of electron transfer change depending on solvents. The energy surface results show that ΔG_s decreases with increases ϵ_s and length wave, i.e., K_{ET} increases with increasing mode frequency indicate high frequency tunnel more easily than do low frequency. The electronic coupling coefficients, are calculated for system at variety solvents, this calculation shows increasing V, where the donor acceptor separation β increasing and vice versa. The rate of electron transfer constants are obtained as functions of the reorganization energy λ , and the coupling coefficient V. The rate of electron transfer constant increases with increasing the coupling coefficient, V, where the distance between donor acceptor is small and the transferring of electron transfer crossing the overlap of the wave function of donor- acceptor is most probable.

Table (1): The solvent properties and solvent $\lambda_s(\text{eV})$, and total λ reorganization energies for $\text{Ru}(\text{phen})_3^{2+}$ donor $(\text{phen})_3^{3+}$ acceptor.

solvent	Refractive index(n)	Dielectric constant (ϵ_s) (static)	Solvent reorganization energy λ_s (eV)	Total reorganization energy(eV)
CH_3CN	1.134	37.5	0.886	1.086
CH_3OH	1,329	33	0.633	0.833
Acetone	1.3563	20.7	0.585	0.785

Table (2): The free reaction enthalpy energy ΔG^* (eV) for Ru(*phen*)₃²⁺ donor (*phen*)₃³⁺ acceptor at *CH₃CN*, *CH₃OH*, and acetone solvents.

Wave length(nm)	Energy (eV)	ΔG^* (eV) At acetone	ΔG^* (eV) <i>CH₃CN</i>	ΔG^* (eV) <i>CH₃OH</i>
400	3.094	2.309	2.008	2.261
450	2.75	1.965	1.664	1.917
500	2.475	1.690	1.381	1.642
550	2.250	1.465	1.164	1.417
600	2.0625	1.276	0.977	1.230
650	1.904	1.119	0.818	1.071
700	1-768	0.983	0.682	0.935
750	1.650	0.865	0.564	0.617
800	1.547	0.762	0.461	0.714

Table (3): The free energy ΔG_{r} (eV) for Ru(*phen*)₃²⁺ donor (*phen*)₃³⁺ acceptor at *CH₃CN*, *CH₃OH*, and acetone solvents.

Wave length(nm)	Energy (eV)	ΔG_{r} (eV) at acetone	ΔG_{r} (eV) at <i>CH₃CN</i>	ΔG_{r} (eV) at <i>CH₃OH</i>
400	3.094	0.209	-0.092	0.161
450	2.75	-0.135	-0.436	-0.183
500	2.475	-0.410	-0.711	-0.458
550	2.250	-0.635	-0.936	-0.683
600	2.0625	-0.822	-1.123	-0.870
650	1.904	-0.981	-1.282	-1.029
700	1-768	-1.117	-1.418	-1.165
750	1.650	-1.235	-1.536	-1.283
800	1.547	-1.338	-1.639	-1.386

Table(4): The coupling matrix element factor V(eV) for Ru(*phen*)₃²⁺ donor (*phen*)₃³⁺ acceptor at *CH₃CN*, *CH₃OH* and, acetone solvents.

B (A) ⁻¹	V_{AD} (eV)	V_{AD} (cm) ⁻¹
0.75	0.02380	192.01173
1	0.02348	189,42052
1.25	0.02316	186.86462
1.4	0.02297	185.34712

Table(5):Rate of electron transfer constant K_{ET} (S^{-1}) between Ru(*phen*)₃²⁺ donor (*phen*)₃³⁺ acceptor at *CH₃CN*, *CH₃OH*, and acetone solvents.

B (A) ϕ^{-1}	V_{AD} (eV)	$K_{ET}(S^{-1})$ at <i>CH₃CN</i>	$K_{ET}(S^{-1})$ at <i>CH₃OH</i>	$K_{ET}(S^{-1})$ at acetone
0.75	0.02380	1.7763 10^8	3.07222 10^9	4.23623 10^9
1	0.02348	1.71613 10^8	2.96982 10^9	4.09503 10^9
1.25	0.02316	1,67241 10^8	2.89416 10^9	3.99070 10^9
1.4	0.02297	1.64357 10^8	2.84426 10^9	3.92190 10^9

References

- 1-.Song,I.,Dorfman,R.,C.,Swallen,S.F,AND Fayer,M.D.(INFLUENCE OF DIFFUSION ON OHOTOINDUCED ELECTRON TRANSFER” J.Chem.Phes(1991),95,3454-3457
- 2-.Zhu,X,Y,Ann.REV.PHYS.CHEM(2002),53,221-247
- 3-Adrian,P.,Harry,B.,G.,AND Jay,R.W.,J Am. CHEM.SOC(2000),122 8187-8191
- 4-Shachi,S,”Electron Transfer AT METAL INTERFACES)PH.D THESIS(2002) PASDANA
- 5-Helena,B.,B.(ENERGY AND ELECTRON TRANSFER IN SUPRAMOLECULAR COMPLEXES DESIGNED “PH.D THESIS (2001)UPPSALA UNIVERSITY,Sweeden
- 6-Mikael,A.”TUNING ELECTRON TRANSFER REACTION BY SELECTIVE EXCITATION IMPORPHYRINE ACCEPTOR”PH.D THESIS(2000) ACTA UNIVERSITY, Sweeden
- 7-Malinil,A.,A.”ELECTRON TRANSFER IN RUTHENIUM MANGANESE COMPLEXS” PH.D THESIS (2001) ACTA UNIVERSITY SWEEDEN
- 8-ALAGEALY,H,”QUANTUM MECANICAL MODEL FOR ELECTRON TRANSFER AT Q SWICHING DYE USE IN SOLID STATE LASER”PH.D THESIS(2004),BAGHDAD UNIVERSITY
- 9-WIBREN.D,O”ELECTRON TRANSFER IN BLUE COPER”PH.D THESIS(2002) UTRECHT UNIVERSITY GERMANY
- 10-Cent.R.T”Electron Transfer IN Low Coper proten” PH.D Thesis(2003)
- 11-CLAUDIA,T.,JEFERY,M.Z,YANN,M,K,AND DANIEL,G.N.J.AM.CHEM.SOC(1996),118,6060-60672.
- 12.DANIELV,STEFFAN,H,CLAUDIA,T.,NICHOLAS,J.PHYS,CHEMB(1996),102.,5088-5093
- 13-.MARK,L.,AND DMITRY ,V.,M,J.CHEM.PHYS.(2003),119,3