Photoinduced Electron Transfer Between Metalloporphyrin Complex Dihydroxy Antimony ($\ddot{V}$) Tetraphenylporphine and Halide in Acetonitrile Solution

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Abstract

Electron transfer (ET) through molecular frameworks is central to a wide range of chemical, physical , an biological processes. Atheoretical calculation investigation of (ET) between dihydroxy antimony (V) tetraphenylporphine cation [Sb^v(TPP)$(04)_2$] and halid Cl^-,Br^-,I^- ,and SCN^- is presented . These Calculations are is fiting on expermental studies Showing that the rate of Electron Transfer. The theoretical Calculation are based on a continuum theory. The transferring is treated quantum mechanically, and the solvent is represented as adielectric continuum. For electronically nonadiabatic ET , the rate expressions for (ET),K_{ET} ,depend on the electronic Coupling matrix element ,H_{AB} , the free energy change of the reaction ΔG_o , and the reorganization energy λ.

Introduction

Electron Transfer (ET) is a basic elementary process in oxidation – reduction reactions: the most fundamental are in chemical and biological reactions (1). A molecular ET reaction involves an oxidation of a donor halide molecule (D) and reduction of an acceptor molecule dilydroxy antimony (V) tetraphenylporphine (A).

Theory of Electron Transfer . The rates for ET are calculated using rate expressions derived for the electronically nonadiabatic limit due to the relatively lange distance (2), R_{DA}~6,9A^o between the two D-A Centers.

In this limit, the rate is proportional to the squares of the Coupling between the reactant and product states , H_{AB}, and is inversely proportional to the free energy barrier ΔG^* .

The most generally useful theoretical frame work for thinking about ET is Marcus theory (3) . Marcus`s essential insigtht (4), is that the equilibrium positions of the nuclei around the donor and acceptor atoms are different before and after ET , and that , according to the Franck Condon principle, nuclear rearrangements occur on much longer time scales than electronic changes . So, in order to conserve the total energy of the system , ET must proceed either by pre-equilibration to a nuclear configuration whose energy is the same for the DA and $D^+ A^-$ electronic Configuration " thermal ET reaction" or by addition of light energy to make the energy of the D^+A^- complex equal to that of a D^+A^- Complex with the DA equilibrium nuclear configuration " photoinduced ET reactions" .

The enengy that must be supplied to overcome the lack of prior rearrangement of the nuclei is the reorganization enengy , λ , defined as the change transfer enengy for a system where the ΔG_o for the reaction is zero (selfexchange reactions). The ΔG_o for an ET reaction is the difference in the reduction potentials of the donor and acceptor(4).

In the present study the ET between the anion $[Sb^V(TPP)(OH)_2]^+$ and halide x^- = cl^-,Br^-,I^-, and SCNin the tetrabutylammonium salt $N(Bu)_4X$. The tetrat butylammonium salt with X halide were commercially available "Fluka" and used without further purification . Dihydroxy antimony (V) tetraphenylporphyrin was prepared as the bromide – containing complex $[Sb^V$ TPP $(OH)_2$] Br according to published routes (5,6).

Theory and Methods , The classical Marcus theory of ET greatly simplifies this problem as it assumes that the potential surfaces for fluctuation of the nuclear positions about the equilibrium donor and acceptor states are harmonic and of the same width (7) , with this linear response assumption the activation free energy $\Delta G^{\ddagger}$ depends on two parameters:I the driving force for ET " the standard free enengy of the redox reaction ΔG_o defined as the difference between the reduction potentials of the a cceptor and donor (8). II- , the reonganization enengy , λ .(9).

By applying the Franck condon principle , Marcus has derived arelation between the $\Delta G^{\ddagger}$, ΔG_{o} , and λ (10).

$$\Delta G^{\ddagger} = \frac{1}{4}(1+\frac{\Delta G_{o}}{\lambda})^{2}\lambda ....[1]$$

So the other Variable in the Marcus eqution is the reorganization energy , λ , as defined as the energy necessary to distort the nuclear configuration from its equilibrium donor state to the acceptor state without transfer of an electron (11). The reorganization energy λ can be divided into the inner λ_{i} and outer reorganization energy λ out .

The inner reorganization enengy is the intramolecular, or inner shell, Contribution to the total reorganization energy. This is the sum of all the molecular Vibrational and rotational movements, may be expressed as :

$$\lambda = \lambda_{inner+} \quad \lambda_{out} ....[2]$$

Normally , for rigid molecules and in polar solvents . The contribution of λ_{inner} to the total λ is minor, with typicall values of 0.2 eV for λ_{i}(12,13) .

The outer reorganization energy is the solvent, or outer sphere contribution to the reorgani zation energy. If one assumes a solvent that can be described as adielectric Continuum. λ_{out} , Can be Calculated in the Simple case of spherical reactants (14).

$$\lambda_{out} = \frac{(\Delta e)^{2}}{4\pi \in_{o}}\left[\frac{1}{a_{D}}+\frac{1}{a_{A}}-\frac{1}{r_{DA}}\right]\left[\frac{1}{\in_{op}}-\frac{1}{\in_{S}}\right] ....[3]$$

Where Δe is the charge in volved (usually 1 electron), $\in_{o}$is the vacuum permittivity ,$\in_{op}$ and $\in_{s}$ is the optical and static dielectric constants, $a_{D,A}$ the donor and acceptor rodii and $r_{D,A}$ is the donor – acceptor center to center distance.

In a quantum mechanical description of nonadiabatic ET, the rate constant can be written as (7) .

$$K = \frac{2\pi}{\hbar}(H_{AB})^2(FCWD)..............................[4]$$

Where H_{AB} is the electronic matrix element describing the electronic Coupling between the reactant and product states, and FCWD is the Frank Condon weighted density of states , which can be described as a Boltzman weighted sum of overlap integrals of the solvAtional and vibrational wave functions. The expression for rate ET, $K_{D\text{-}A}$ is (15).

$$K_{DA}=\frac{2\pi}{\hbar}\frac{1}{\sqrt{4\pi\lambda KT_B}}(H_{AD})^2\exp(-\frac{\Delta G^{\mp}}{K_BT})...............[5]$$

Where $\hbar$ is the planck`s constant divided by 2π .In photo induced ET the frequency of the specteral absorption maximum is given by (11) .

$$h\upsilon_{\max}=\lambda+\Delta G_o....................................[6]$$

Results

In order to determine the rate constant of ET theoretically. Using the equation[6] , one must initially evaluate the Values of the outer reorganization energy λ_{out} from rquation[3] for a variety anions in a cetonitrile Solvent where $\in_{op}$ and $\in_s$ are the optical and static dielcctric constants of the solvent $\in_{op}$ =1.344, $\in_s$ =37.5 respectively .

The Values of radii a_D are 1.21,1.18,1.20, and 1.39A^o of the anions cl^-, Br^-,I^- and SCN^- were extracted from the literature (16). A radius of a_A =5.7 A^o for the $[Sb^v(TPP)_2]^+$ cation. (17). These results have been Summarized in table(1).

Another important factor for ET are activation energy and Free energy . The Free energy change for any chemical reaction 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 D and A together and the difference between the reduction potentials of the acceptor and donor. The overall free energy changes ΔG_o that can be calculated from eq.[6], where $h\upsilon = \frac{hc}{\lambda}$, h is plancks constant , C light Velocity , and λ wave length in nanometer. λ is taken from a bsorption spectra of $[Sb^{v}(TPP)(OH)_2]BF_4$ at 298k in CH_3CN acetonitrile (420-720) nm (18).

The values of ΔG_o that calculation by Using difference donors are summarized in table (2).

The activation free energy $\Delta G^{\ddagger}$is the height of the barrier depends on ΔG_o and λ. The activation free energy has been Calcuated using equation.[1], the results of $\Delta G^{\ddagger}$ using different donors of $[Sb^{v}(TPP)(OH)_2]^{+}$ are listed in table(3).

The Key factors controlling the rate of ET are the electronic H_{AD} coupling term . In this work the values of coupling Coefficient is (0.1) have been taken from Mulikan –Hush results for 2-state (19).

Now we can calculated the rate of photo electron Transfer Values K_{DA} between acceptor dihydroxy antimony $\ddot{V}$ tetraphenylporphine and halid donors by using equation[5] that is involves four important factors , λ ev ,H_{DA} ($e\ddot{v}$) $\Delta G_o(e\ddot{v})$, and $\Delta G^{\ddagger} ev$. The Values of rate electron transfer have been Summarized in table(4)

Discussion

All the rates reported here were calculate at 298K. for the present system , large outer –sphere reorganization enengy Values λ_{out} between 2.3275 and 2.7811 $e\ddot{v}$ are obtained according to the dielectric continuum model at ET reaction , these values can be regarded as an estimate for the total reonganization energy $\lambda \cong \lambda_{out}$ of the photoinduced ET step, which priov to subsequent Chemical bond changes produces the neutral quencher donors $c\bar{l}, B\bar{r}, \bar{I} and SC\overline{N}$ and delocaliedmetalloporbhyrin $\bar{\wedge}$ –radical anion $[Sb^{v}(Tpp)(0H)_2]$. Table (1) show that λ increases where the radius of donor is decrease at the same solvent "acetonitrile ", this indicate the ET ValuE of Rate ET K_{DA} increases whene the λ increased .

A ccordingly the K_{DA} values for the photo induced ET step increase with an increasing electrn donor strength . The overall free enengy Changes ΔG_o that can be calculated for this primary process table(2) fulfill the relation $\Delta G_o \rangle - \lambda$ which corresponds to normal Marcus region conditions.

From tables (4)and table (2) we can show that K_{DA} decreases as the reaction free energy increases , this because that the work required to bring the donor and acceptor molecules together increases due to the increase of ET barrier . A lso we can show the K_{ET} decreases when the height barrier is large, this is very clear from the table(4).

Finaly we can find the value of K_{ET} is fiting with experemeutal value , this clear in teble(5).

Conclusions

In this work, the ET reactions are electronically nonadiabatic. The transferring of electron is treated quantum mechaincally . The outer – saphere solvent reorganization energy are calcutated with dielectric continuum model and are found to be ~ 2.70,2.78, 2.73, and 2.32 for $c\bar{l}, B\bar{r}, \bar{I}$ and $SC\bar{N}$ donor for the same acceptor. Donor with highest λ possesses highest transfer electron activity .

The most electronically active donor leads to height rate of ET. The rate of ET for D-A system is afunction of the height potential barrier .

In summary ,it can be concluded from the present results that the bimolecular quenching of the dihydroxy antimony $\ddot{V}$ tetraphenylporphine cation by $c\bar{e}, B\bar{r}, \bar{I}$ and $SC\bar{N}$ ions is afast reaction. The proccss is obviously facilitated by electrostatic interactions and occurs via election transfer mechanism.

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Table(1): Reorganization energies for Acceptor $[Sb^{V}TPP(OH)_2]^{4}$

Donor x^-	Reorganization enengy $\lambda(e\ddot{v})$
$C\ell^-$	2.7060
Br^-	2.7811
I^-	2.7307
SCN^-	2.3275

Table(2): The free enengy ΔG_o (ev) for acceptor $[\mathrm{Sb^{v}TPP(OH)_2}]^{4+}$ and different donors

Wave length λ	$\Delta G_{oc\bar{\ell}}$	$\Delta G_{oB\bar{r}}$	$\Delta G_{o\bar{I}}$	$\Delta G_{OSC\bar{N}}$
420	0.24	0.165	0.216	0.618
450	0.044	-0.031	0.020	0.422
480	-0.128	-0.203	-0.152	0.250
510	-0.280	-0.355	-0.304	0.098
540	-0.414	-0.489	-0.438	-0.036
570	-0.535	-0.610	-0.559	-0.157
600	-0.643	-0.718	-0.667	-0.265
630	-0.742	-0.817	-0.766	-0.364
660	-0.831	-0.906	-0.855	-0.453
690	-0.913	-0.988	-0.937	-0.535
720	-0.987	-1.062	-1.011	-0.609

Table(3): The activation free enengy $\Delta G^{\ddagger}\ e\ddot{v}$ for $[\mathrm{Sb^{v}TPP(OH)_2}]^{4+}$ and different donors

Wave length λ	$\Delta G^{4+}{}_{c\bar{\ell}}$	$\Delta G^{\ddagger}{}_{\mathrm{Br}}$	$\Delta G_{I}{}^{\ddagger}$	$\Delta G^{\ddagger}{}_{\mathrm{SCN}}$
420	0.8018	0.780	0.795	0.932
450	0.699	0.679	0.693	0.812
480	0.614	0.597	0.609	0.714
510	0.5437	0.529	0.539	0.632
540	0.485	0.472	0.481	0.564
570	0.435	0.424	0.432	0.506
600	0.393	0.383	0.389	0.457
630	0.356	0.347	0.353	0.414
660	0.325	0.316	0.322	0.378
690	0.297	0.289	0.294	0. 345
720	0.273	0.266	0.270	0.317

Table(4):Rate of ET between [Sb^{v}TPP(OH)$_2$]$^{4+}$ and different donovs

Wave length λ	$K_{ETC}\ell$	K_{Br}	K_I	K_{SCN}
420	1.208	2.87362	1.591739	0.00718667
450	74.384	163.2974	94.144207	0.873256
480	2228.853	4339.755	2710.33555	44.01250
510	36652.714	65878.8838	44570.51076	1169.663
540	388187.118	644076.793	453535.0011	17755.911
570	2868336.392	4393221.059	3219793.309	180678.36
600	15390219.45	22647799.27	1798027.38	1282694.838
630	67608398.08	95589471.63	75892447.05	7163245.836
660	233628490.7	330320264.2	262254961.9	30233881.74
690	716037261.9	972687330.4	803773222.3	113178159.2
720	1870071992	2440754970	2099211690	34687557

Table(5): Conparing between our Calculatiom and experimental studies

Wave length λ	$K_{ETC}\lambda$		K_{Br}		K_I		K_{SCN}	
	a	b	a	b	a	b	a	b
420	1.208	1.12	2.8736	3.12	1.591	1.78	0.007	0.009
540	388187	421653	6.4X10^{5}	5.4X10^{5}	4.5X^{5}	4.1X10^{5}	1.7X10^{5}	1.9X10^{5}
600	1.5X10^{7}	1.8X10^{7}	2.2X10^{7}	2.3X10^{7}	1.7X10^{6}	1.9X10^{6}	1.2X10^{6}	1.3X10^{6}
660	2.3 X10^{8}	2.8X10^{8}	2.4X10^{9}	2.7X10^{9}	2.0X10^{9}	1.9X10^{9}	3.4X10^{7}	3.8X10^{7}

a/our Calculation

b/ Ref (6)

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد21 (1) 2008

الانتقال الالكتروني المحتث بوساطة الفوتونات بين مركب المعادن الحلقية $\ddot{V}$ والهاليدات في محلول الاسيتون

هادي جبار مجبل العكيلي
قسم الفيزياء ، كلية التربية – ابن الهيثم ، جامعة بغداد

الخلاصة

الانتقال الالكتروني خلال الجزيئات العملية يسيطر على الكثير من العمليات الكيميائية ، الفيزياوية و البايولوجية .

تمثل حسابات نظرية الانتقال الالكتروني مابين المركبات الكيميائية بين مركب $[Sb^{v}(TPP(OH)_2]^+$ والهاليدات $SCN^-\ \overline{II}\ Br^-,C\ell$ ان الحسابات النظرية لوحظت كونها موافقة للدراسات العملية لحساب معدل الانتقال الالكتروني. اعتمد التمثيل الحسابي لانتقال الالكتروني على نظرية الاستمرارية فالانتقال عولج كميا" و وعولج المذيب كمادة عازلة مستمرة .أما العلاقات الخاصة لمعدل الانتقال والانتقالات الالكترونية غير الكظيمة فتعتمد تماما" على عناصر منظومة المزدوج الالكتروني والتغير بالطاقة الحرة للتفاعل وطاقة اعادة الالتحام .