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Effect Of Solvent Types On Photo Induced Electron Transfer in Methylene Blue dye MB^+ - Benzophenone Ketone (ABP) System.

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Abstract

The rates for the photo induced electron transfer reactions in the Methylene blue MB^+ dye with benzophenone (ABP) ketone in variety solvents at room temperature have been calculated . Electron transfer rates are large in strongly polar solvent and week in less polar solvent. The high values of the rates of electron transfer indicate that the dye triplet is more reactive toward ABP ketone.

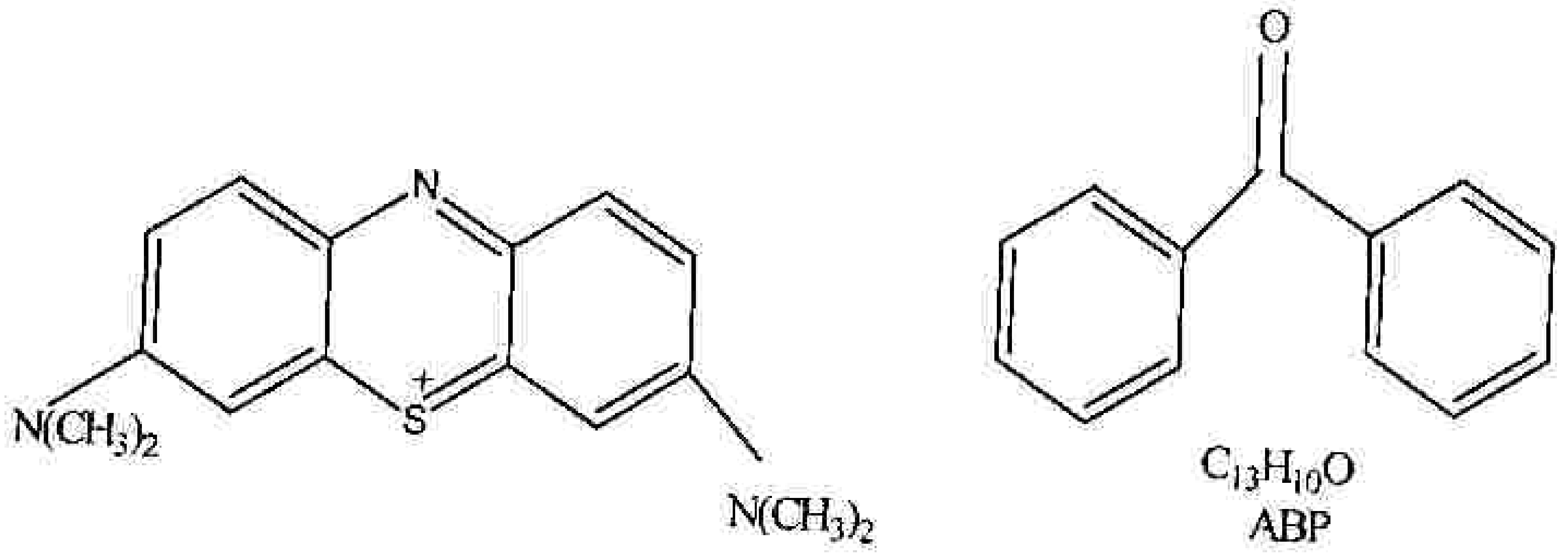
Introduction

Since the seminal work predicting solvent dynamical control of Electron transfer reactions in the early 1980 (1) a great deal of theoretical effort has gone in to clarifying the solvation dynamics E T connection (2-3).

The simplest case is expected to occur for rigidly linked donor – acceptor pairs and for electron transfer in the normal regime. In such cases, if the intra molecular contribution to the reorganization energy λ_i is small, the reaction coordinate consists primarily of solvent degrees of freedom and thus solvent motions should directly control the rate of ET. However, there are relatively few experimental systems in which such solvent control has been unambiguously demonstrated. Among the many experiments performed to data, the studies of Barbara and co- workers on bianthry (4-7) , still provide the most convincing evidence for dynamical solvent control . In addition to examining a wide variety of solvents, these workers showed how it is possible to semi quantitatively model the spectral evolution attending

ET with a photo dynamic approach (7), which corporates information about solvation dynamics derived from independent measurements on other solutes. More recent studies or reactions have often focussed upon the inverted regime (8), where solvent control is expected to be weaker or even absent (9) .In this work, we report on the time reaction of electron transfer kinetics in a donor - acceptor system (MB^+ - ketone). The predominant photo physical path way of ET depends on the physical and photo chemical properties of both MB^+ dye and ABP ketone.

The structures of the cationic organic dye (10),and ketone (11), that used in this work are shown in schem 1



Schem 1: Methylene Blue (MB^+) dye and benzophenone (ABP) ketone

Theory

We consider two electronic states | D> and | A> , which represent the electron donor and acceptor sites of the ET system , respectively, and they are coupled to each other via the electronic coupling matrix element,V. Moreover, each electronic state is coupled to bath degrees of freedom . When the electronic coupling constant is the smalest parameter of the electron transfer process (12), and on the basis Fermi's Golden rule nonadiabatic ET rate is (13).

$$K_{ET} = \frac{4\Pi^2}{h}|V|^2 F \text{.......... .....[1]}$$

Where h is Planck's constant, V is the electronic coupling between the two states and F is the Franck – Condon weighted density of states (13).

An electronically nonadiabatic ET reaction is described as a nonadiabatic transition from donor state | D> to acceptor state | A>. The simplest unimolecular rate expression for nonadiabatic ET is (14),(15).

$$K_{ET} = \frac{4\Pi^2}{h}|V|^2(4\Pi\lambda K_{BT})^{-\frac{1}{2}} exP\left\{\frac{-\Delta G^{++}}{K_B T}\right\} \ldots\ldots\ldots\ldots\ldots[2]$$

Where λ(eV) is the reorganization energy, and ΔG^{++} (eV) is the barrier height defined as (16) .

$$\Delta G^{++} = \frac{\Delta G_\circ{}^2}{4\lambda} + \frac{1}{2}\Delta G_\circ + \frac{\lambda}{4} \ldots\ldots\ldots\ldots\ldots\ldots\ldots[3]$$

The reorganization energy is the solvent contribution to the reorganization energy. If one assumes a solvent that can be described as a dielectric continuum, λ_S can be calculated in the simple case of spherical reactants (15),(17).

$$\lambda_s = \frac{e^2}{2\Pi\varepsilon_\circ}\left[\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right]\left[\frac{1}{\varepsilon_{\circ P}} - \frac{1}{\varepsilon_s}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots[4]$$

Where e is the charge of electron , ϵ_o is the vacuum permittivity ϵ_{op} and ϵ_s are the optical and static dielectric constants respectively , r_D and r_A are donor and acceptor radii and r_{DA} is the donor - acceptor center to center distance .

The r_D and r_A values can be calculated from the apparent molar volumes using spherical approach (17).

$$\frac{4}{3}\Pi r^3 = \frac{M}{N\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots[5]$$

Where M is the molecular weight, N is a Avogadro's number and ρ is the density.

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 donor and acceptor together and the difference between the reduction potentials of the acceptor and donor and determined via (18).

$$\Delta G_{\circ} = \Delta G_R - E^T \text{..........................}[6]$$

The value of ΔG_R can be determined by the Weller - equation (19).

$$\Delta G_R = e\left[E^{OX}_{(D)} - E^{red}_{(A)}\right] - \frac{e^2}{2\Pi\varepsilon_{\circ}\varepsilon_s R_{DA}} + \frac{e^2}{8\Pi\varepsilon_{\circ}}\left(\frac{1}{r_D} + \frac{1}{r_A}\right)\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_{\circ}}\right) \text{.....................}[7]$$

Where $E^{ox}{}_{(D)}$ and $E^{red}{}_{(D)}$ are the oxidation and reduction potentials of donor and acceptor respectively .

The final important factor is the electronic coupling constant V which is given by the interaction matrix element between the electron donor and acceptor wave functions It is one of the most important physical parameters and depend on its magnitude when compared with other parameters, various kinetic regimes are exhibited in the ET process (20) .

Result

According to the theory of ET, the rate constant K_{ET} between reactants at a fixed distance is determined by three parameters: the electronic coupling matrix element V the free energy change of the reaction ΔG_o and the solvent reorganization energy λ_S .

One important key factor controlling the rate of ET is the solvent reorganization energy λ_S. These values can be calculated by using equation [4] , for MV^+ – ABP system in a variety solvent where ϵ_{op} and ϵ_s are the optical and static dielectric constants are presented in table (1)(21,22) . The theoretical calculation values of the radii r_D , r_A and r_{DA} can be evaluated by using equation [5] The results are listed in table (2) .

We can calculate the solvent reorganization energy λ_S by inserting values r_D, r_A , r_{DA} , ϵ_{op} and ϵ_s from tables (1,2) in equation [4].We noticed that $e^2 / 4\prod \epsilon_o \approx 14.4$ eV , these calculated values are summarized in table (3) .

The driving force free energy ΔG_0 for MV – ABP system in solvents may be calculated as a function of two parameter ΔG_R and E_T corresponding to the free reaction enthalpy for reduction of MB^+ by ketone triplet and triplet state energy. The free reaction enthalpy ΔG_R is calculated by using equation [7], where E_{ox}(D)and E_{red} (A) are oxidation and reduction potentials for donor and acceptor respectively which are taken from table (2) .The results are listed in table (4) .

We can find the values of ΔG_0 from equation [6] by substitute the values of ΔG_R and ET from tables (4,2) in equation [6] .These results have been summarized in table (4). The activation energy barrier has been calculated by using equation [3], with the values of λ_S and ΔG_o from tables (3,4) .The results of ΔG^{++} for MV^+ – ABP system in a variety solvent are listed in table (4) .From above values of ΔG_o , λ_S , and ΔG^{++} with the electronic coupling values have been taken from the generalized mulliken hush value (23) ,we calculated of the rate of electron transfer for MV^+ – ABP system in a variety solvent by using the expression in equation [2]. The results are summarized in table (5)

Discussion

We used quantum mechanical models to treat non adiabatic electron transfer by using the Golden rule expression for the transition probability between different electronic states.

The results of calculations in ten different solvents are listed in table (3), show that the major factors controlling on λ_s are: the dielectric constant, the radii of donor and acceptor, the distance between donor and acceptor, and the refractive index of the solvent.

From the results in table (3), we can show that the reorganization energy depends on ϵ_s values. For more polar solvents, the reorganization energy is large, but it is small for the solvent which has small dielectric constant.

That indicate high strength in chloroform, one of the least polar solvent where the reorganization energy is large $\approx$0.91335734 eV, because of the small refractive index.

Formamide, one of the most polar solvents the reorganization energy is small ($\approx$0.7706948 has ϵ_s =109) compared with Acetonitrile

($\approx$1.23100137 has ϵ_s =36.6).Ther reason for this is that the large refractive index in formamide n=1.445 is compared with small refractive index in Acetonitrile n=1.134.

Table (4) shows that the reaction enthalpy energy of the dye-ketone system in of variety solvent is calculated with the aid of the weller equation is more negative. The values of ΔG_R(eV) are described by three factors caporations : the work to be done to transfer an electron from donor to an acceptor , the free energy which is released when the oppositely charged donor and acceptor are allowed to approach each other until to distance K_{DA} and the term needed to correct for the solvent dependence of the redox potentials $E^{ox}_{(D)}$ and $E^{red}_{(A)}$ respectively.

By taking the difference between ΔG_R(eV) and triplet energy E^T(eV) for ketone ,we get the results of driving force (free energy) ΔG_o (eV). This can be broken into the work which is to taken to bring the donor and acceptor togther and show the difference between the reduction potentials of the acceptor and donor .The results of ΔG_o(eV) are more negative .This indicates that cationic organic dye is efficient quencher of the triplet states of aromatic ketone.

Table(5) lists the rate of ET (K_{et}) between methylene blue MB^+ dye and p-(dimethylamino) benzophenone (ABP) ketone in ten room temperature solvents .Accordingly ,the K_{et} values for the photoinduced ET increase with an increasing electron donor strength of the quencher anions , which is also reflected by the redox potentials given in table(2).

Notably, the mechanism of the ET was observed only with ABP in the strongly polar solvent.

Result of the rate of ET show that high values where the solvents were more polar . because of the higher polarity and viscosity of these solvents which are viewed in table (1).

Values of the rate of ET are very small in benzene one of the least polar solvents which means that ET is non active .Also, in the two solvents chloroform and dichloromethane, the dielectric constant is small. This indicates that the rate of ET as low as (26-234 and 96-628)sec^{-1} respectively for coupling coefficient 0.01,0.02,and 0.03 eV.

Chloroform has a large solvent reorganization energy but low rate of ET this lead to say because of the small value of viscosity.

Also, we can show from table (4) the values of ΔG^{++}(eV) which are very high especially in benzene comparing with the other solvent.This indicates that electron suffering high barrier can transfer from donor to acceptor.

The agreement between our theoretical calculations of the rate of ET and experiment is very good .This is clear in table (6).

Conclusions

It is commonly concluded that the triplet states of p-(dimethylamino) benzophenone ketone (ABP) can be quenched by the methylene blue MB^+ dye via an electron transfer mechanism. It turns out that the mode of reaction electron transfer path way strongly depends on the solvent polarity, where as ET is favored in polar solvents like acetonitrile. This in itself is notable since it suggests that the molecular solvent properties can play an important role in the kinetics of solvents ET is beyond influencing the barrier height. Electron transfer occurs in polar solvents more than less polar solvents .The rate constant of ET is determined and the high value indicates that the MB^+ triplet dye is more reactive toward ABP ketone in polar solvents because it has large reorganization solvent energy and higher viscosity of this solvent.

The agreement between the theory and the experiment which is displayed in this study is very good.

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Table (1): Solvent properties [21,22]

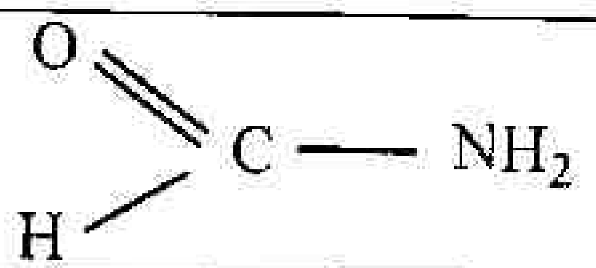
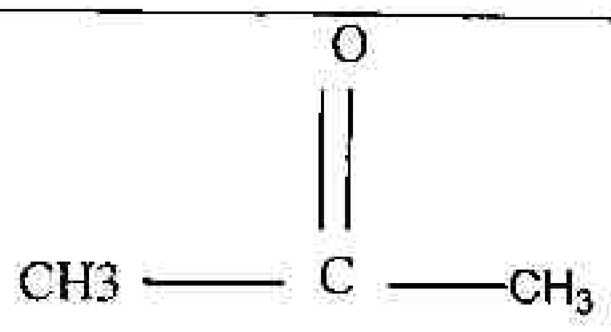
Solvent	Formula	Refractive index(y)	Viscosity (cp)	Dielectric constant (E_s)
methanol	CH_3OH	1.329	0.55	33
Ethanol	CH_3CH_2OH	1.359	1.08	24.3
1-propanol	$CH_3CH_2CH_2OH$	1.383	1.94	20.1
1-Butanol	$CH_3CH_2CH_2CH_2OH$	1.397	2.57	17.8
Formamide		1.445	3.30	109
Acetontrile	$H_3C-C\equiv N$	1.134	o.34	36.6
Acetone	 $CH3-\overset{\overset{O}{\parallel}}{C}-CH_3$	1.3563	0.30	20.7
Benzene	C_6H_6	1.5011	0.60	2.28
chloroform	$CHCL_3$	1.14	0.54	4.7
Dichloromethane	CH_2CL_2	1.4242	0.40	8.9

Table (2): properties of methylene blue (MB) dye and benzophenone (ABP) ketone

Properties	Methylene- blue(MB^+)	P-(dimethylamino) benzophenone(ABP)
formula	$C_{10}H_8ClN35.3H2O$[23]	$C_{13}H_{10}O$ [26]
Molecular weight	373.9[23]	182.22 [27]
density	1.230 gm/cm^3	1.11 gm/cm^3 [27]
E^T eV	1.50 [24]	2.7 [28]
E^{red} eV	-0.36 [25]	-
E^{oxd} eV	-	1.08
r (m)	$4.93994*10^{-10}$(present work)	$4.02280*10^{-10}$(present work)

Table (3): The reorganization energies λ_seV for(MB^+)DYE-(ABP) ketone system in variety solvent.

Solvent.	Reorganization energies eV
methanol	0.879181679
Ehanol	0.820823473
1-propanol	0.776151233
1-Butanol	0.748497991
Formamide	0.770694814
Acetonitrile	1.231001369
Aceton	0.813016474
Benzene	0.3933
Chloroform	0.91335734
Dichloromethane	0.624521815

Table (4):The free reaction enthalpy ΔG_R(eV),the driving free energy ΔG_0(eV),and the activation free energy ΔG^{++}(eV) for MB^+ Dye –ABP ketone system in variety solvents.

Solvent	ΔG_R(eV)	ΔG_0(eV)	ΔG^{++}(eV)
methanol	-0.348830315	-30.048830315	1.33856724
Ethanol	-0.2507543	-2.9507543	1.381723805
1-propanol	-0.17615121	-2.87615121	1.420970559
1-Butanol	-0.13174625	-2.831746252	1.449544077
Formamide	-0.100158166	-2.800158166	1.336041654
Acetonitrile	-1.040389931	-3.74038993	1.278843206
Aceton	-0.246800811	-2.946800811	1.400044077
Benzene	0.333498508	-2.366501492	2.474823661
Chloroform	-0.709627127	-3.409627125	1.705620179
Dichloromethane	0.02337516	-2.676624839	1.685740482

Table(5):Rate of electron transfer between MB^+ dye and ABP ketone in variety solvent for different coupling coefficient $|V|$=0.01,0.02 and 0.03eV respectively.

Solvent	V=0.01 eV	$K_{ET}(sec^{-1})$V=0.02eV	V=0.03 eV
methanol	$6.3247860*10^7$	$2.52975441*10^8$	$5.69194743*10^8$
Ethanol	$1.1647336*10^7$	$4.6589347*10^7$	$1.04826031*10^8$
1-propanol	$2.542601*10^6$	$1.0170405*10^7$	$2.2883412*10^7$
1-Butanol	$8.09277*10^5$	$3.237109*10^6$	$7.283496*10^6$
Formamide	$7.4729234*10^7$	$2.98916936*10^8$	$6.72563106*10^8$
Acetonitrile	$5.82708407*10^8$	$2.330833629*10^9$	$5.244375665*10^9$
Aceton	$5.624010*10^6$	$2.2496041*10^7$	$5.0616093*10^7$
Benzene	$1.719679658*10^{-12}$	$6.87818631*10^{-12}$	$1.54771169*10^{-11}$
Chloroform	26.084036	104.3361474	234.7563317
Dichloromethane	69.86619653	279.4647861	628.7957688

Table (6):Our Theortical calculation result for ΔG_R(eV) and K_{ET} (sec^{-1}) compared with experimental values for MB^+ -ABP system in Acetonitrile solvent.

	Experimental	Our results
ΔG_R(eV)	-0.96 [28]	-1.04
K_{ET} (sec^{-1})	$12*10^9$	$5.827*10^8$ in acetonitrile solvent $2.33*10^9$ $5.2*10^9$

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد21 (3) 2008

تأثير نوع المذيب في الانتقال الالكتروني المستحث فوتونيا" لنظام صبغة المثيلين الزرقاء (MB^+) – كيتون بينزوفينون (ABP)

هادي جبار مجبل العكيلي ،رفاه اسماعيل نوري العبيدي ،رجاء فيصل ربيع الساعدي

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الخلاصة

أحد اهم المشاهد الظاهرة في حركية عملية الانتقال الالكتروني هي تأثير ديناميكية المذيب في معدل الانتقال الالكتروني . معدلات تفاعلات الانتقال الالكتروني المستحث فوتونيا" في صبغة المثيلين الزرقاء (MB^+) مع كيتون البينزوفينون (ABP) ولمذيبات مختلفة حسبت عند درجة حرارة الغرفة . معدلات الانتقال الالكترونية كانت كبيرة لمذيبات عالية القطبية بينما كانت ضعيفة للمذيبات ذي القطبية الواطئة . القيم العالية لمعدلات الانتقال الالكتروني تشير الى أن الصبغة الثلاثية تكون فعالة بشدة بأتجاه كيتون (ABP).