The Distances of the Closest Approach and of the Reaction Site-From the Electrode-for Adiabatic Heterogeneous Electron Transfer. The Case of Pyridinium (Mono) Cations.

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Summary: In investigating the heterogeneous electron transfer process in some pyridinium compounds, those physical (distance) parameters were investigated which could be relevant to the adiabaticity of a heterogeneous electron transfer process. These distance parameters are: the closest approach, the position of the interfacial potential-energy barrier maximum and the reaction site.
The pyridinium (mono) cations were treated as charged (hard) sphere with the reaction site at the center of the sphere. With this assumption the distance of the closest approach and the distance of the reaction site - from the electrode surface - were investigated under the constraint κ_{el} (electronic transmission coefficient) = 1. Various models were considered and the Khan model was found to be quite sound, versatile as well as convenient to use. Results of these calculations are presented the reaction site as calculated through Khan model came close to the sum of radii of the solvent and the pyridinium cations under study.

Introduction

Pyridinium mono-cations are of great interest as part of NADH. Besides, Kosower's polarity parameter Z-value involves pyridinium cation [1-4]. Recently there is resurgence in interest in pyridinium cation: its electrochemistry [3, 5], optical properties [6] and solvatochromic properties [7]. Electrochemistry of dipyridinium di-cations [viologens] is well known [8-12] but electrochemistry of mono-pyridinium salts is sparce [10]. Measurement of heterogeneous electron transfer rate constants on these pyridinium mono-cations is even more rare [11].

Generally in interpreting standard heterogeneous electron transfer rate constant (k^o) through Marcus / modified Marcus equations, κ_{el}, the transmission coefficient is assumed to be unity and the process is assumed to be adiabatic process [13-19].

$$k^o = \kappa_{el} A\, e^{-\Delta G^*/RT} \qquad (1)$$

κ_{el} = 1 is generally used in precursor equilibrium model [13-19], where, mostly, workers have focused on the exponential (barrier crossing) part of the expression (eq (1)) for the investigation of the dynamical solvent effect [13-18, 19].

However, it is important to emphasize that κ_{el} may not necessarily be unity in every case [20]. In other words, not every heterogeneous electron transfer process, necessarily, be adiabatic [20]. Here we discuss the distance parameters: the distance of closest approach, the position of the interfacial potential-energy barrier maximum and the reaction site, which seem to have relevance to adiabaticity [19-21]. The pyridinium mono-cations have been used as substrate to investigate these parameters while considering these pyridinium cations as charged (hard) sphere with positive charge, the reaction site, at the center of the sphere.

Khan [20] has defined a distance δ (here δ_K) as a distance "from electrode surface at which the reaction occurs". This may be identified as reaction site [20] .Weaver and Hupp [19] introduced a parameter σ as the distance of closest approach of the reaction site to the surface of the electrode.
The distance δ_K is related to κ_{el} through Khan model [20], eq.(2)

$$\kappa_{el} = \exp[-(\pi^2 \delta_K / h)\{(2m_e U_m)\}^{1/2}] \quad (2)$$

where U_m is itself δ_K dependent, eq.(3)

$$U_m = \phi_m - [e_o{}^2 / (\pi\, \varepsilon_o \in_{op})]\ \{(1/16\, r_m) - 1/(4\,(\delta_K - r_m)\} \qquad (3)$$

where U_m = barrier maximum, h is Plank constant, m_e = mass of electron, ϕ_m is the work function of the metal electrode, r_m is the distance between the metal surface and the position of the interfacial potential-energy barrier maximum, ε_o permittivity of vacuum and $\in_{op}$ is optical dietetic constant [20].

From eq.(2), when $U_m = 0$, $\kappa_{el} = 1$ and from eq.(3)

$$\phi_m = (e_o^2/4\pi\, \varepsilon_o \in_{op}) [(1/4r_m) - 1/(\delta_K - r_m)] \quad (4)$$

Since ϕ_m of the electrode and $\in_{op}$ of the solvent used are known, one can obtain the values of δ_K provided r_m is known. r_m *may be equated to the radius of the reactant, here pyridinium cations* (see later).

Weaver and Hupp, and Gennett, Milner and Weaver, dwelt upon this subject matter in the way as "estimating the electron tunneling distance for an outer-sphere electro-chemical reaction" in. an important papers [19, 21]. They stated that for outer-sphere transition state with an inner layer of solvent molecule, the reaction center (reaction site), δ_W will be

$$\begin{aligned} \delta_W &= r_{reactant} + 2r_{solvent} \\ &= X + \alpha^{-1} + \sigma \qquad (5) \end{aligned}$$

where σ, as stated before, is identified as the distance of closest approach [19,21] while X is defined as the distance beyond the closest approach; for $\kappa_{el} = 1$, $X > 0$ whereas for $\kappa_{el} < 1$, $X = 0$. For $\kappa_{el} = 1$ the value of $\alpha^{-1} = 0.7$ nm [6].

As a first approximation, one may identify δ_W as δ_K, the distance of the reaction site, then,

$$\begin{aligned} \delta_W = \delta_K &= r_{reactant} + 2r_{solvent} \\ &= \sigma + 0.7 + X \qquad (6) \end{aligned}$$

If σ is taken as $r_{reactant}$, then this will give $X = 2r_{solvent} - 0.7$ (all parameters in nm). Since $r_{solvent}$ is always known, *X's* value can be calculated.

Yet another expression for the reaction site ,χ_p ($= \delta_K$) is given by Hale [22], for $\kappa_{el} = 1$

$$\chi_p (= \delta_K) = \sqrt{\frac{k_BT}{2\pi m}}\, \frac{h}{4\pi^2 \rho(\Delta_{cr})^2} = Z \,.\, \frac{h}{4\pi^2 \rho(\Delta_{cr})^2} \quad (7)$$

where k_B = Boltzmann constant, ρ = number of energy levels in the conduction band of the electrode per unit range of energy, Δ_{cr} = energy separation between the upper and lower states derived from the interaction of the degenerate reactant and product systems in the transition state. Hale gives the value of Δ_{cr} = [O] 10^{-13} eV, [O] means order of; Δ_{cr} is the critical value of Δ which separates the adiabatic reactions from the diabatic (non adiabatic) ones.

δ_K or χ_p [22], is supposed to be the same as ionic atmosphere or thickness of double layer [22]. This, if true, makes χ_p (δ_K) easier to calculate.

The value of Δ_{cr} is given as about 10^{-13} eV by Hale [22], however, at the same time, it is claimed to be dependent upon χ_p *i.e.* δ_K. Thus Hale [22] gave a value of $\Delta_{cr} = 1 \times 10^{-13}$ e.V at *a separation* 1.5 nm (for $\kappa_{el} = 1$).

The problem with eq. (7) is that to find δ_K, one has to know Δ_{cr} as well as ρ, the "density" of energy levels. The last parameter has to be calculated theoretically. Besides, δ_K, according to eq (7), is dependent on temperature.

From the above discourse it is seen that though Hupp-Weaver-Gennett-Milner (HWGM) expression, eq.(6) is easier to use, the more theoretically sound expression for calculating δ_K is that of Khan (eq. 4) where the only unknown parameter, besides δ itself is r_m. Besides, Khan's expressions are easy to use.

Thus in this study, the distance of closest approach, the reaction site and the position of the interfacial potential-energy barrier maximum using Khan Model, are investigated. For comparison these parameters are also calculated according to HWGM equations.

The selection of pyridinium compounds for the study is made because of their mono-cation character and biological relevance [1,23-24]. They are potential electrochromic as well as electron accepting ligands in nonlinear-optical-chromophore-compounds [5-7, 25]. Coe [5] has noted the importance of the "metal ion induced displacement of reduction potential to more positive reduction". He has not mentioned the importance / relevance, if any, of the electron transfer rate constant k^o and r_m, σ and / or δ_K in the metal ion induced displacement process.

Calculations, Results

This section is organized as: sections: (2-1), the model(s) used; (2-2), the system understudy; and (2-3), results of calculations

The Model(s) Used

Khan Model

As mentioned above, in using Khan model one encounters two parameters r_m and δ_K. One way to eliminate one of the two parameters is to take the ratio (δ_K / r_m) and deal with one parameter. This is the course adopted by Khan [20] in his investigation of k° for the redox process of ferrocene. He used $r_m = \delta_K/2$ and δ_K = radius of ferrocene. The advantage of using the ratio method and taking δ_K = radius of the reactant [19] is that one could use eq (3) to evaluate U_m and hence κ_{el}. However, since in the present case κ_{el} is taken as unity, hence equation (4) is to be used. Instead of $\delta_K = r_{reactant}$ and $r_m = \delta_K / 2$, which will not give $\kappa_{el} = 1$, one can leave r_m as floating parameter but under the constraint that $\kappa_{el} = 1$ be obeyed.

Another approach is to take $r_m = r_{reactant}$ and evaluate δ_K again under the constraint $\kappa_{el} = 1$. Both these approaches have been adopted here.

Hupp-Weaver-Gennet-Milner (HWGM) Equation

The expression obtained through the **HWGM** model for δ_W ($=\delta_K$) (eq.5) is easy to use, particularly when σ, the distance of closest approach, is taken as equal to the radius of the charged (hard) sphere – the pyridinium ions.

The system

The system is:
Electrode, Hg, φ_m = 4.53 e.V = 7.25×10^{-19} J
Solvent, Dimethyl Sulfoxide (DMSO), $\in_{op} = n^2$ = 2.1747 (n = refractive index); radius 0.6 nm
Reactants: Pyridinium cations:

I = N-methyl α-picolinium (MPC^+) radius, r = 0.38 nm
II = N- (2, 4-dinitro phenyl)- 4(4'- pyridyl pyridinium ($DNPP^+$), r = 0.61 nm
III = N – phenyl- 4 (4- pyridyl) pyridinium (NPP^+), r = 0.57 nm
IV = N – (p-cyano phenyl)- 4(4'–pyridyl) pyridinium($NPCP^+$), r = 0.59 nm
V = N – (2, 4 – dinitro phenyl pyridinium) (DNP^+), r = 0.57 nm
VI = 1- ethyl – 4 – carbomethoxy pyridinium (Py^+), r = 0.58 nm

The reaction site: Model: charged sphere, charge residing at the centre, the radius $r = r_{reactant}$
Process: adiabatic $\kappa_{el} = 1$ (however, see Discussion, later)

Results of Calculations

Results of various calculations are collected in Table-1. Details of various calculations are given below.

Khan Model calculations

δ_K –values when r_m = $r_{reactant}$: The position of interfacial potential-energy barrier maximum r_m assumed as the distance $r_{reactant}$, that is $r_m = r_{reactant}$.

Using this approximation and using the data given in section 2-2, and using eq. (4) for κ_{el} = 1, values of δ_K were obtained; these values are collected in the Table-1 (3rd column).

r_m-values: when $\delta_K = r_{reactant}$, r_m floating under the constraint $\kappa_{el} = 1$

If $\delta_k = r_{reactant}$ is used, as Khan [20] suggested, but instead of taking $\delta = 2r_m$, which would not give adiabatic process, that is $\kappa \neq 1$ the value of r_m was kept floating to follow the condition $\kappa_{el} = 1$ which allows the use of eq.(4). Results of the calculations for r_m thus calculated are also collected in Table-1 (5th column).

While Khan [20] had $\delta > r_m$,as a basis for calculations, in the present case, for adiabatic process ($\kappa_{el} = 1$), $r_m > \delta_K$.

HWGM simplified expression for δ_W (= δ_K) as $r_{reactant} + 2r_{solvent}$

δ_W ($=\delta_K$) values calculated using eq.(5) are also collected in the Table-1(6th column). Interestingly, from eq.(5) and $\sigma = r_{reactant}$, values of X can be evaluated [$X = 2r_{solvnt} - 0.7$ nm). The value

Table-1[a]: Distance parameters for some pyridinium cations as charged sphere model when $\kappa_{el} = 1$, except column 7.

Py^+ (Radius r in nm)	$r = r_m$ (nm)	$\delta_K{}^b$ (calcd) (nm)	$r_{react} + r_{solv}$ (nm)	$r_m{}^c$ (calcd) (nm)	$\delta_W{}^d = r_{react} + 2r_{solv}$ (nm)	Khan[e] $r_m = \delta/2$(nm)
MPC^+ (0.38) I	0.38	0.98	0.98	0.66 or 0.05	1.58	0.19
$DNPP^+$ (0.61) II	0.61	1.14	1.21	0.86 or 0.078	1.81	0.305
NPP^+ (0.57) III	0.57	1.10	1.17	0.82 or 0.075	1.77	0.285
$NPCP^+$ (0.59) IV	0.59	1.12	1.19	0.84 or 0.075	1.79	0.295
DNP^+ (0.57) V	0.57	1.10	1.17	0.82 or 0.075	1.77	0.285
PY^+ (0.58) VI	0.58	1.11	1.18	0.83 or 0.075	1.78	0.29

(a) (i) the distance of closest approach (r_m or σ or $r_{reactant}$ as the case be) and (ii) the distance of the reaction site δ_K, from the "surface" of electrode; electrode Hg and solvent DMSO (b) from eq. (4), when $r = r_m$ (c) for $\delta = r_{raectant}$, r_m = floating and $\kappa_{el} = 1$ (from eq. (4)) (d) Hupp & Weaver $\delta = \delta_W = r_{reactant} + 2r_{solvent}$ ref. eq. (5,6) (e) $\delta = r_{raectant} = 2r_m$ from eq (2) & (3) for $\kappa_{el} \neq 1$ (Khan Model)

of X comes out to be 0.5 nm, close to $r_{reactant}$ of pyridiniumm cations.

Discussion

It is seen that various distance parameter terms are encountered in the discussion of the heterogeneous electron transfer process – the closest approach (σ), the interfacial potential barrier-maximum distance (r_m), and the reaction site δ_k (or δ_W), depending upon which model used. We also have radius of the charged (hard) sphere – the pyridinium ion. So, which of these parameter values (collected in the Table) are realistic in general and in pyridinium ions case in particular?

In the present case cations are the reactants. It has been assumed that these cations are charged (hard) sphere with positive charge, the reaction site, residing at the center of the charged sphere. It is easy to conclude that the closest approach of the reaction site to the "surface" of electrode can not be less than the radius of the sphere. Thus it may not be an unrealistic assumption that σ, the distance of closest approach, is equal to the radius of pyridinium ions.

It may be noted that the closest approach distance σ, the interfacial potential barrier-maximum distance parameter r_m and radius of reactants $r_{reactant}$ may or may not be the same (see later).

In using the equation (4) where U_m has been taken as zero, r_m loses the physical meaning in the sense when there is no energy maximum, how can there be a r_m? So we make an assumption that we replace r_m (in eq.(4)) by the radius of the reactants – the radius of a hard sphere – a pyridinium cation.

If r_m is assumed to be equal to $r_{reactant}$, then it becomes easy to calculate the distance of the reaction site (or reaction plain) (δ_K), from the "surface" of the electrode. Here it is found $\delta_K > r_m$. It is interesting to note that the numerical values $\delta_K - r_{reactant}$ ($= \delta_K - r_m$) in pyridinium ions is between 0.5 and 0.6 nm. We see that this value is close to the X-values of Hupp and Weaver [19]. Thus the physical meaning of X-values is the same: the distance beyond the closest approach when the adiabatic reaction takes place. Since, as mentioned before, σ, the distance of closest approach, can not be (in the present case) less than the radius of the reactant, hence, as an approximation, it (σ) can be taken equal to the radius of the reactant ($r_{reactant}$), which in turn has been equated to r_m. In this way r_m has a physical meaning: it is same as distance of closest approach.

Making $\delta_K = r_{reactant}$ (Khan's approach), and making r_m as floating, keeping $\kappa_{el} = 1$, makes $r_m > \delta_K$ The physical meaning of this condition becomes intriguing. For example, if $r_m > \delta_K$ then the chances of reaction being non-adiabatic is greater: Contrary to our charged sphere model, the reaction site comes quite close to the electrode surface and no barrier to cross. At the same time in the Hupp and Weaver [19,21] expression (eq. (5)) for $\delta_W = \delta_K$), the reaction site for the electrode, tells $\delta_K > r_m$ (r_m assumed to be equal to σ), since solvent molecules are supposed to be between the reaction site and the surface of the electrode, so under the present assumption that $\kappa_{el} = 1$ precludes the situation $r_m > \delta_K$

Before we end this section of results it is worth presenting the result of Khan's approach [20] ($r_m = \delta_K/2$ and $\delta_K = r_{reactant}$, $\kappa \neq 1$) to the two parameters r_m and δ_K. Using his procedure, that is, $r_m = \delta_K/2$ and $\delta_K = r_{reactant}$, it is easy to evaluate r_m. Values of r_m thus evaluated are collected in the Table (last column). It has to be mentioned that under this condition of Khan [20] ($r_m = \delta_K/2$ and $\delta_K = r_{reactant}$), $\kappa_{el} \neq 1$, that is the process is non-adiabatic. And one can see the reason. The interfacial potential energy barrier – though not activation energy barrier, is sharp, of $(1/2)r_{reactant}$ width, offering tunneling of electron. Hence $\kappa_{el} \neq 1$

Conclusion

It is inferred that r_m = radius of charged sphere of pyridinium mono-cation, in Khan model, for calculating heterogeneous electron transfer rate constant, gives a simple way to calculate the distance of the reaction plain (site) where the reactant, here the "+" charge, resides This is when the reaction is adiabatic. It may, however, be also noted that δ_K, according to the Khan model, depends also upon the work function of the electrode and refractive index of the solvent which means δ_K is solvent and electrode material dependent. It is also to be mentioned that if $\kappa_{el} = 1$, in one solvent under one condition, its value may not necessarily be unity in another solvent or on another electrode. This means that an electron transfer process adiabatic in one solvent and on one electrode does not necessarily mean it be adiabatic in another solvent; a point not considered explicitly by other workers in this field.

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