# An Alternative Approach to the Heterogeneous Electron Transfer Rate Constant Expression

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**Summary**: In the theoretical treatment of heterogeneous electron transfer rate constant, $k^o$, the expression for the rate constant is considered as a composite of two parts: a dynamical pre-exponential one, the other the activation barrier (exponential) part. The pre-exponential part has been treated through several models: the collision frequency, the precursor- equilibrium and the Khan models. In this work, a simple alternative approach based on random walk model is proposed. The advantage of this random walk model is that all the parameters in it are either experimentally measurable or can be easily calculated. The result of calculation shows it to be far superior to collision frequency model, even better than precursor-equilibrium model and comparable to Khan model.

Key words: Heterogeneous electron transfer, collision frequency, precursor-equilibrium model, Khan-model, Random Walk-model.

## Introduction

Marcus equation for heterogeneous electron transfer process is well known [1]. The heterogeneous electron transfer rate constant $k^o$ is expressed in terms of "dynamical effect" i.e. pre-exponential term $A$ and an activation barrier term $B$ containing exponential term ($-\Delta G^*/RT$), eq. (1).

$$k^o = A \exp [-\Delta G^*/R\,T] = A.B \qquad (1)$$

In this report we make the pre-exponential term $A$ as the subject of discourse. We investigate the efficacy / rationale of the various proposed models in use and in the process propose an alternative model – a random walk model. The suitability of the proposed model *vis a vis* other models is then tested by bringing in the barrier crossing part $B$ of eq. (1) and calculating $k^o$ for a system for which all the required parameters (for the calculation of $k^o$) are available. Such a system is the electrochemical reduction of some pyridinium compound in DMSO with tetranbutylammonium perchlorate as supporting electrolyte.

For many pyridinium compounds various parameters needed for the calculation of $k^o$ are available in literature. Of course these pyridinium compounds belong to a class of compound which is important in its own right [2-15], for example as biological active compound [2-7], potential electrochromic and nonlinear electro-chromic compounds [8-9] etc. Toxicity of some viologens towards cancer cells have also been reported [13]. Methyl viologen dichloride, also known as herbicide paraquat, is well known and well studied moiety [2-16]. However, to check the reliability of the results of present investigation methyl viologen was to be used as a reference compound.

The various models proposed [16-26], and expressions for $A$ of eq. (1) are as follows:

(a) Collision frequency Z (model) [23] along with the electronic transmission coefficient $\kappa_{el}$.. $\kappa_{el}$, manifests the adiabaticity of an electron transfer process. For adiabatic reaction $\kappa_{el} = 1$.

Thus in this "Collision frequency" model

$$A_{coll.freq.} = \kappa_{el}\, Z_{het} \qquad (2)$$

where $Z_{hel}$ is given as eq. $\qquad$ (3)

$$Z_{het} = (k_b T/2\pi m)^{1/2}, \qquad (3)$$

where m is the molar mass of the substrate; the other terms have the usual meaning.

(b) The precursor equilibrium constant model [19-22]. In this model $A$ is expressed in term of $\kappa_{el}$, precursor equilibrium constant $K_p$ and the nuclear frequency factor $\nu_n$. Thus [1, 19-25]

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$$A_{prec.\ eq.} = \kappa_{el}\ K_p\ \nu_n \qquad (4)$$

where $\nu_n$ is related to longitudinal solvent relaxation time, $\tau_L$, as [19-25].

$$\nu_n = \tau_L^{-1}\ (\lambda_o\ /\ 16\pi\ RT)^{1/2} \qquad (5)$$

$\tau_L$ is related to Debye relaxation time $\tau_D$ by [22].

$$\tau_L = (\in /\in_s)\ \tau_D$$

$$\tau_D = 3\ V_m\ \eta\ /\ RT;\ V_m = M/\rho \qquad (6)$$

$\in_s$, $V_m$ and $\eta$ are static dielectric constant, molar volume and viscosity of the solvent respectively $\in$ is the dielectric constant at high frequency. $\nu_n$ has also been taken as $kT/h$ (k = Boltzmann constant, h = Planck constant) but Khan [26] has recommended.

$$\nu_n = 1\ /\ \tau_D \qquad (7)$$

(c) Khan model [26].In this model the value of $\kappa_{el}$ may not necessarily be equal to 1. Khan proposed.

$$A_{Khan} = \kappa_{el}\ \delta\ \nu_n \qquad (8)$$

where $\delta$, a new term, is the distance between the electrode and the reaction plane, OHP (Outer Helmholtz Plane). Khan gives a simple expression for the evaluation of $\kappa_{el}$.

$$\kappa_{el} = \exp\ [-0.804\ \delta\ U_m^{1/2}] \qquad (9)$$

where $U_m = \Phi_m - 36.0\ /\ (\varepsilon_{op}\ \delta)$; $\Phi_m$ is the work function, for example 4.53 eV for the mercury electrode; generally $\delta \geq r$, where r is the radius of the substrate. $U_m$ is the barrier maximum.

(d) The random walk or hopping substrate model (the present model, proposed in the present work). In this model it is assumed that the substrate moves in the solution in "hopping" mode in a random (walk) fashion, covering an average hopping distance $\Delta x$ in time $t$ given by [27]

$$\Delta x = \sqrt{2D_o t} \qquad (10)$$

Where $D_o$ is the diffusion coefficient of the substrate. Assuming.

$$A_{R.W.} = \Delta x/t\ \text{(assuming adiabatic process).} \qquad (11)$$

Using eq (10), eliminating t from eq (11), A is expressed as eq (12)

$$A_{R.W.} = \frac{2D_o}{\Delta x} \qquad (12)$$

Eq. (12) physically means that when the substrate is at a distance $\Delta x$ (a hop distance) from the electrode, electron transfer occurs with the probability of occurrence of electron transfer (P) as unity (see later, however). For simplicity sake $\kappa_{el} = 1$ is assumed.

The advantage of this expression, eq. (12) for $A_{R.W.}$, is, that, $D_o$ unlike $K_p$, $\nu$, $\delta$, of the substrate, if not already known, can experimentally be determined from a cyclic voltammogram. $\Delta x$ may be, as a first approximation, taken equal to the thickness of double layer – when the substrate is near the electrode.

$\Delta x$ defined this way can easily be evaluated if (rigid (Helmholtz)) double layer model is assumed to exist near the electrode (eq. 12$a$); for z-z electrolyte $\Delta x$ is given by [28]

$$\Delta x = \left(\frac{\varepsilon_o DkT}{2n^0 z^2 e^2}\right)^{1/2} \qquad (12a)$$

where $\varepsilon_o$ is permittivity of the vacuum, D is dielectric constant of the solvent, $n^0$ is the (number) concentration of z-z electrolyte per m³, z is the charge on the ions of z-z electrolyte, and e is the electronic charge. For example for a 0.1M, 1:1elctrolyte (at 25°C), $\Delta x$ = 9.63x10⁻⁸cm in water (the dielectric constant = 80.0) and 6.0x10⁻⁸cm in acetone (dielectric constant 31.0) [28]. This makes $A_{R.W}$ solvent (dielectric constant) as well as charge (of electrolyte components) dependent. Since in many cases and particularly in organic solvents, a 0.1 M tetra-n,alkylamonium salts is used as electrolyte, hence $\Delta x$ is a constant in a particular solvent. The point is that $\Delta x$ is a quantity which can be easily calculated.

Thus, along with $A_{coll.freq} = Z\ (= A_Z)$; $A_{prec.\ eq}$ = $K_p\nu_n\ (= A_{PC})$ and $A_{Khan} = \delta\nu_n(=A_K)$, another term $A_{R.W.}$ = 2Do/$\Delta x$ (=$A_{RW}$) may also be considered for the calculation of $k°$.

The efficacy of $A_{RW}$ *vis a vis* other *A*'s will now be investigated. The substrates are some pyridinium compounds (see Data and Experimental Sections).

## Results and Discussion

*Data*

Data on these substrates (I–VI) are collected in Table-1. These data, besides the name of the substrate and Greek numerals (I–VI), are: radius (r), collision frequency (Z), diffusion coefficient ($D_o$) and the experimental heterogeneous electron transfer rate constants ($k^{o, exp}$) [18].

*Calculation*

Values of $A$ ($A_Z$, $A_{PC}$, $A_K$, $A_{RW}$) calculated using data in Table-1 and eqs. (2, 4, 7, 8, 12, 12a) are collected in Table-2.

Table-1: Data on compounds I-VI collected from literature [18, 34, 36, 37].

| Compounds (radius nm) | $Z^a$ cms$^{-1}$ | $D_o^b$ (± 0.2)10$^{-5}$ cm$^2$s$^{-1}$ | $k^{o, exp, c}$ cms$^{-1}$ |
|---|---|---|---|
| $MV^{2+}$I(0.55) | 4601 | 1.90 | 0.05 |
| $MPC^+$II(0.38) | 6038 | 2.80 | 0.005 |
| $DNPP^+$III(0.61) | 3493 | 1.30 | 0.004 |
| $NPP^+$IV(0.57) | 4112 | 1.50 | 0.006 |
| $NPCP^+$V(0.59) | 3907 | 1.75 | 0.006 |
| $DNP^+$VI(0.57) | 4002 | 1.80 | 0.002 |

(a) Calculated using eq.(3), (b) experimental $D_o$ as determined from peak current with $MV^{2+}$ as reference compounds, (c) as determined by Nicholson method [35, see also reference 18, 34, 36].

Table-2: Values of Pre-experimental factor A for various models A in cm/s.

| Compound | $A^a_Z$ | $A^b_{RW}$ | $A^c_K$ | $A^d_{PC}$ | $A^e_{exp}$ |
|---|---|---|---|---|---|
| I | 4601 | 513 | 2750 (275) | 3×10$^5$; (30) | 31 |
| II | 6038 | 757 | 1900 (190) | 3×10$^5$; (30) | 35 |
| III | 3493 | 176 | 3050 (305) | 3×10$^5$; (30) | 384 |
| IV | 4112 | 405 | 2850 (285) | 3×10$^5$; (30) | 2.6 |
| V | 3907 | 473 | 2950 (295) | 3×10$^5$; (30) | 9.0 |
| VI | 4002 | 486 | 2850 (285) | 3×10$^5$;(30) | 173 |

(a) $A_z = \kappa_{el}Z$, $\kappa_{el} = 1$, (b) R.W = Random Walk $\Delta\chi = 7.4 \times 10^{-8}$cm (0.74 nm), $D_o$ as per in Table I. (c) from eq (8) where $\delta = r_{reactant}$ and $v_n = 5.0 \times 10^{10}$s$^{-1}$, values in parenthesis are for $v_n = 5.0 \times 10^9$s$^{-1}$ (see text, Discussion C,) (d) Kp = 6.0×10$^{-9}$ cm (0.06 nm), $v_n = 5.0 \times 10^{13}$s$^{-1}$, values in parenthesis is for $v_n = 5.0 \times 10^9$s$^{-1}$ (see text Discussion **B**), (e) $A_{exp} = k^{o, exp} / B$, B from Table-5.

To compare the efficacy of each model, it is necessary to evaluate theoretical $k^o$ ($k^{o, calc}$) for each substrate according to each model and compare them with their experimental $k^o$. This also means the evaluation of term $B$ – the exponential (barrier crossing) part of eq. (1).

For the calculation of $B$, one needs $\Delta G^*$, which is described as follows

In the exponential term (eq.(1)), $\Delta G^*$ is the sum of outer- $\lambda_o$ and inner- $\lambda_i$ organization energies It is thus given by [1, 16, 23].

$$\Delta G^* = \frac{\lambda_o + \lambda_i}{4} \qquad (13)$$

where $\lambda_o$ is the outer sphere re-organization energy and $\lambda_i$ the inner sphere re-organizational energy "barriers". It is noted that this exponential term, $B$. has profound effect on (the numerical values of) $k^o$.

Thus, it is necessary to outline the various expressions for $\lambda_o$ and $\lambda_i$ (which are to be calculated) [1, 16, 23],

$$\lambda_o = \{Ne^2/(\in_o 32\pi)\}(1/a - 1/R_e) [(1/\in_{op}) - (1/\in_s)] \quad (14)$$

where $a$ is the radius of the substrate, $R_e$ the distance from the image, and the expression in the bracket [ ] is Pekar parameter.

$\lambda_i$ is a function of force constants $f_j$ [16,23, 29-30]

$$\lambda_i = \sum_j [(f_j \times f_j^*) / (f_j + f^*)] (\Delta q_i)^2 \quad (15)$$

The force constants of the reactant and the product can be computed from the following relation [29-30].

$$f_j = B' (1+P_j) + c \qquad (16)$$

$$f_j^* = B' (1+P_j^*) + c \qquad (17)$$

$P_j$ is given by

$$P_j = \Sigma n_m C_{rm} C_{sm} \qquad (18)$$

$P_j$ is the bond order of $j^{th}$ bond. $C_{rm}$'s are the coefficient of molecular orbitals. Under $\pi$-approximation M.O. prescription, the change in bond length $\Delta q$ may be estimated via the bond-order-bond-length relationship [29, 30].

$$\Delta q_j = D (P_j - P_j^*) \qquad (19)$$

The value of coefficients D, B' and c, in SCFMO prescription are D = 0.18 Angstrom (= 0.018 nm) B' = 9.85 mdyne / Angstrom (= 9.85×10$^2$ N/nm) and c = -9.445 mdyne / Angstrom (= -9.44×10$^2$ N/nm) [14, 16, 18]

From Tables [1-4], it is clear none of the models give satisfactory $k^{o, calc}$ values – nowhere close to $k^{o, exp}$. Hence, to get a better agreement between $k^{o, calc}$ and $k^{o, exp}$., it is necessary to make a "correction" in the pre-exponential factor $A$., while keeping $B$ as it was before (for each substrate, Table-5).

Table-3: Values of P and modified $A_{RW}$ (= $A_{mRW1}$, $A_{mRW2}$).

| Compounds | $P^b$ (for $\chi = \delta$) | $A^c_{mRW1}$ (cm s$^{-1}$) | $P^d$ | $A^e_{mRW2}$ (cm s$^{-1}$) |
|---|---|---|---|---|
| I | 0.11 | 56.43 | 0.049 | 25.1 |
| II | 0.15 | 113.6 | 0.082 | 62.1 |
| III | 0.098 | 17.2 | 0.040 | 7.04 |
| IV | 0.107 | 43.3 | 0.046 | 18.6 |
| V | 0.103 | 48.7 | 0.043 | 20.3 |
| VI | 0.107 | 52.0 | 0.046 | 22.4 |

(a) $p = \sqrt{2/\pi}\ exp\ [-\chi^2/2\Delta\chi^2]$ (eq. (20)), (b) $\chi = \delta$ = reaction site / closest approach = $r_{reactant} + r_{solvent} = r_{reactant} + 0.6$ (nm) [ref.18-20, 26, 33], (c) $mRW_1$ = modified RW for probability as in (b); (d) $\chi$ = reaction site = $r_{reactant} + 1.2$ (nm); (e) ) $mRW_2$ = modified RW for probability as in (d).

Table-4: Values of $k^{\circ,\ calc}$ ( cm s$^{-1}$ ) for models ($A$ =) Z, RW, mRW$_1$, mRW$_2$, PC and K.

| Compound | Z | RW | mRW$_1$/mRW$_2$ | PC$^b$ | PC$^c$ | K$^d$ |
|---|---|---|---|---|---|---|
| I | 6.6 | 0.72 | 0.080 *0.035* | 23 | 0.048$^c$ | 0.44 |
| II | 0.97 | 0.12 | 0.018 *0.01* | 43 | 0.004 | 0.027 |
| III | 0.035 | 0.002 | 0.0002 *0.00007* | 3.5 | 0.0003 | 0.003 |
| IV | 8.20 | 0.61 | 0.087 *0.037* | 690 | 0.069 | 0.65 |
| V | 2.60 | 0.31 | 0.032 *0.013* | 198 | 0.02 | 0.19 |
| VI | 0.05 | 0.005 | 0.0006 *0.0003* | 3.45 | 0.0003 | 0.003 |

(a) Z = collision frequency model, RW = random Walk model, mRW$_1$ = modified RW using probability factor for $x = r_{I - VI} + r_{solvent}$, mRW$_2$ = modified RW with probability factor for $x = r_{I - VI} + 2r_{solvent}$, in italics; (b) Precursor model for $v_n = 5.0 \times 10^{13} s^{-1}$ ; see text Discussion for **2**, (c)Precursor model for $v_n$ $5.0 \times 10^9 s^{-1}$ ; see text Discussion for **2**, (d) Khan model, $v_n$ $5.0 \times 10^9 s^{-1}$

Table-5: Values of B.

| Compound | $\lambda_o$(eV) | $\lambda_i$ (eV) | $B \times 10^3$ = |
|---|---|---|---|
| I | 0.575 | 0.0975 | 1.4 |
| II | 0.832 | 0.0694 | 0.16 |
| III | 0.516 | 0.668 | 0.010 |
| IV | 0.548 | 0.092 | 2.0 |
| V | 0.530 | 0.223 | 0.66 |
| VI | 0.0558 | 0.615 | 0.0115 |

(a) $\lambda_o$ for Re = $\infty$ ; (b) $B = exp[ -(\lambda_i + \lambda_o) / 4RT]$, T =298K

An *adhoc* correction factor $\alpha$ may be introduced in $A$ in order to bring $k^{\circ,\ calc}$ as close to $k^{\circ,\ exp}$ as possible.

Thus $k^\circ$ can be expressed as ( ref eq.(1))

$k^\circ = \alpha\ A.B$

$\alpha$ can take the following form

1. $\alpha = \kappa_{el}$; $\kappa_{el}$ as calculated by Khan model by taking $\delta = r$ and $r_m = \delta/2$. [26]
2. $\alpha\ A = \kappa_{el}\ K_p\ v_n$ for precursor-equilibrium model; $\kappa_{el} = 1$, $v_n$ variable.
3. $\alpha\ A = \kappa_{el}\ \delta\ v_n$ for Khan model; $\kappa_{el} = 1$. $v_n$ may be variable.
4. $\alpha = \sqrt{\dfrac{2}{\pi}}\ exp[-\chi^2/2\Delta\chi^2]$ for R.W model     (20)

From Smuluchowski's treatment of Brownian movement, [31, 32], we have

$P$ = Probability that a particle being at a position

$$\chi = \frac{\lambda}{\Delta\chi\sqrt{\pi/2}}\ exp[-\chi^2/2\Delta\chi^2] \qquad (21)$$

Here for eq.(20) $\lambda$, the length of a step, is taken the same as $\Delta\chi$. This model is notated as modified random walk (mRW) model.

It is to be noted that for our (electron transfer) purpose, $\Delta\chi$, has been taken as thickness of double layer; $\chi$ can be either the position of closest approach of the reaction site to the surface of electrode = $r_{reactant} + r_{solvent}$ [ 33 ] or the distance of the reaction site from the electrode where the reaction occurs = $r_{reactant} + 2r_{solvent}$ [19-20, 25,33].

Since we have assumed $\kappa_{el} = 1$, that is the process is adiabatic, hence option (**1**), is not to be considered any further. For (**2**), the precursor equilibrium model, the value of $K_p$ is kept fixed as $6.0 \times 10^{-9}$cm, the value of $v_n$ are varied as $5.0 \times 10^{13} s^{-1}$ or $5 \times 10^9 s^{-1}$ [18-22], as the case be. For (**3**), again, we take $\kappa_{el} = 1$, $\delta = r_{reactant}$ as fixed and $v_n = 5.0 \times 10^{10} s^{-1}$ or $5 \times 10^9 s^{-1}$[18, 26, 33, 36]. The option (**4**) is discussed in detail below. We see (Table-4) for option (**2**) the precursor model, $v_n = 5 \times 10^9$ gives good results for compounds I, II, and V, while $v_n = 5.0 \times 10^{13} s^{-1}$ does not give satisfactory results at all. Option (**3**), the Khan model gives reasonable results .for $v_n = 5 \times 10^9 s^{-1}$.

We deal option (**4**) in detail now.

Results of calculations using the modified random walk model are presented in Table-4 for $\Delta\chi = 7.4 \times 10^{-8}$cm (0.74 nm) for 0.1 M 1:1 electrolyte, $\in_s = 47$ and for **(i)** $x$ = (closest approach =) $r_{reactant} + r_{solvent}$, = $r_{reactant} + 0.6$ nm and **(ii)** $x$ = (distance from electrode where the reaction occurs =) $r_{reactant} + 2 r_{solvent} = r_{reactant} + 1.2$ nm.. It is seen there is much improvement in the $k^{\circ,\ calc}$ values.

It can thus be safely said that the Random Walk model for the pre-exponential term (eq.1), as regards to reproducing experimental results, is as good as any other model. Besides, Random Walk model is a well established model – mathematically, physically as well as philosophically (for example thought process) [7]. Hence it can not be said that this model has been used here as a "trial matter". The movement of a molecule in a fluid environment can be described by random walk model as soundly as

collision (kinetic theory) model. Besides, the heterogeneous electron transfer measurement techniques are based on the "diffusion process", that is, movement of electro-active species under the diffusion "force" (diffusion equation). Thus using Random Walk model in the theory of electron transfer, particularly in pre-exponential term, seems relevant. Besides, it did not give any worse result than other models. One great advantage in using this model is that the substrate's diffusion coefficient is to be used. This diffusion coefficient is an experimentally measurable quantity.

**Conclusion**

A new model – the random walk model – for the pre-exponential factor *A* (eq. (1)) was proposed, tested and shown as good as, if not better, than any other being used by others. The beauty of this new model is that the terms used in this model are either experimentally determinable ($D_o$), or known or easily calculable (double layer thickness and radii of the substrate and solvent). There is no *ad hoc* or variable parameter to vary.

**Experimental**

Substrate: The following compounds (ions) were studied

I = Methyl Viologen (1-1'– dimethyl, 4, 4' bipyridinium dichloride) ($MV^{2+}$,I) (as reference compound).

II = N – methyl-α-picolinium ($MP^+$, II),

III = (N-(2,4-dinitrophenyl)-4-(4'-pyridyl) pyridinium ($DNPP^+$, III),

IV = N-(phenyl)-4-(4'-pyridyl) pyridinium ($NPP^+$, IV),

V = N-(cyano-phenyl)-4-(4'-pyridyl) pyridinium ($NCPP^+$, V), and

VI = N-(2, 4-dinitrophenyl)-pyridinium ($DNP^+$, **VI**).

All these compounds were gift from ICI Runcorn, Cheshire, U. K. and were used as received. Other experimental details and procedure have been described before [ 18, 34, 36]

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