# SOLVENT DYNAMICAL AND SYMMETRIZED POTENTIAL ASPECTS OF ELECTRON TRANSFER RATES

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ABSTRACT. Recent experiments on very fast electron transfers have provided evidence for slow solvent dynamics under such conditions. The role of the vibrational motion of the reactants is included in the present treatment. The overall decay can be single- or multi-exponential. A simple approximate expression is given for a characteristic reaction time. The "symmetrization" approximation in the cross-relation is also discussed.

## 1. INTRODUCTION

It is a great pleasure to participate in this celebration honoring our colleague Carl Ballhausen on his sixtieth birthday. For this festive occasion I should like to describe some results that Hitoshi Sumi and I obtained[1-3] on the theory of solvent dynamical effects on electron transfer reaction rates. Our studies were prompted by recent experimental results on very fast intramolecular charge transfers.[4-6] Indeed, until recently such data had been almost absent in the literature. A review of many facets of the electron transfer literature is given in Ref. 7.

Among the aspects that we focussed our attention on in Ref. 1 was the role of the vibrational reorganization in influencing the relative extent of activation versus slow solvent dynamical control of the reaction rate. The problem has interesting experimental aspects, including one of single-exponential *vs* multiexponential decay.

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A second aspect of electron transfers which I would like to examine in this article is the effect of "symmetrization" of potential energy surfaces on the "cross-relation." Can it cause sizable deviations from the latter, and explain thereby some anomalies in reaction rates?

## 2. SOLVENT DYNAMICAL EFFECTS

The advent of picosecond techniques has permitted the study of intrinsically very fast intramolecular electron transfer reactions – so fast that the slow step in some cases is not the activation process itself but rather the dynamics of dielectric reorganization of the solvent.[4-6] The evidence for slow solvent dynamics in these special cases is the agreement of the rate constant with the reciprocal of a "constant charge" dielectric relaxation time, for a dielectrically "slow" series of alcohols.[4-6] Evidence has also been offered for some reactions which are at least partly activation controlled.[8-12] In such cases, of course, the interpretation of the results is not as direct.

In treating this problem of the dynamics of solvent dielectric relaxation or of fluctuations, the role of vibrational reorganization in the reactant(s) was also considered.[1] Previous theoretical investigations in the literature have primarily treated the role of the solvent alone and typically the steady-state solution. Detailed references to the literature are given in Refs. 1 and 2.

During an electron transfer there is a change in dielectric polarization everywhere in the solvent, from a function appropriate to the initial charge distribution to one appropriate to the final distribution. This change has been has been conveniently mapped by Zusman[13a] and by Wolynes[13b] onto a scalar progress variable $X$. (Perhaps the $m$ in Ref. 14 can also serve the same purpose.) A diffusional-type differential equation for the probability $P(X,t)$ of finding the system at any $X$ at time $t$ was used,[1] containing in our case a reaction term, $k(X)$. In the absence of the vibrational effect the $k(X)$ becomes a Dirac delta function, making the differential equation easier to solve.

The equation described a time-evolution of the initial state which varied from single exponential to multi-exponential, depending on the conditions.[1] It was convenient to obtain a description of this behavior by defining a time-dependent survival probability $Q(t)$.[1] From it two kinds of average survival time were defined – the mean first passage time $\tau_a$ for passage through the transition state and a time $\tau_b$ related to the second moment of the first passage time. The former describes mainly the early time behavior in the reaction while the latter describes a later temporal behavior. When $\tau_a$ and $\tau_b$ are essentially equal the time-evolution is a single exponential. The $\tau$'s themselves were easier to calculate than $Q(t)$.

The values of $\tau_a$ and $\tau_b$ could be calculated exactly in four limiting situations, described as the slow reaction limit, the "wide reaction window" limit, the "narrow reaction window" limit and the non-diffusing limit in Refs. 1 and 3. A "decoupling" approximation was then introduced for the more general case, which simplified the solution of the equations and led to a solution for $\tau_a$ and $\tau_b$. This approximate solution reduced to the correct answer in each of the four limiting cases. In the "decoupling" approximation, the average of a particular product was replaced by a product of averages in a second-order term in an expression for $Q(t)$, or, more precisely, for its Laplace transform.[1] The process of thermalization around $t=0$ was, at the same time, treated with some care (via a function $h$ in Ref. 1).

An expression which proved to represent well [3] our many calculations of $\tau_b$ over the wide range of conditions investigated was

$$\tau_b \simeq k_e^{-1} + F\tau_L \quad (1)$$

(The agreement was typically better than a factor of two, the results themselves varying by many orders of magnitude). Here, $F$ is a known function [3] of the dimensionless free energy barrier $\Delta G^*/k_BT$ and of the ratio $\lambda_i/\lambda_o$ of the vibrational and solvational contributions to the reorganizational term $\lambda$ (described in Sec. 3). $F$ is given for completeness in the present Appendix. The $k_e$ in Eq. (1) denotes the usual rate constant, calculated for the case that the population in the transition state region has its thermally equilibrated value. $\tau_L$ is the so-called constant-charge dielectric relaxation time ($= \tau_D\varepsilon_o/\varepsilon_s$), where $\tau_D$ is the usual constant-field relaxation time and $\varepsilon_o/\varepsilon_s$ is a ratio of dielectric constants discussed more fully in Ref. 2.

Equation (1) for $\tau_b$ reduces to the correct limiting form. There are at least four such limiting situations: (1) When the solvent relaxation time $\tau_L$ is sufficiently small $\tau_b$ in Eq. (1) approaches the reciprocal $k_e^{-1}$ of the normal rate constant. (2) When $\tau_L$ is very large, $\tau_b$ becomes directly proportional to $\tau_L$ and independent of $k_e$. (3) When $\Delta G^*/k_BT$ is small, $k_e^{-1}$ usually becomes small also. When, in addition, $\lambda_i/\lambda_o$ is small, $F$ approaches unity, and so when these two conditions are fulfilled $\tau_b$ appproaches $\tau_L$, as found experimentally in Ref. 4. (This theoretical result is even more noticeable in the treatment in Ref. 1, for which Eq. (1) is only an approximation.) (4) When $\lambda_i/\lambda_o$ is large enough, $F$ (given in the Appendix) tends to zero, even when $\Delta G^*/k_BT \simeq 0$, and $\tau_b$ then becomes independent of $\tau_L$ and approaches $k_e^{-1}$.

For the solutes studied in Refs. 4 and 5, some twisting of an amino group relative to the aromatic ring is expected to accompany the intramolecular charge transfer, and some (minor) equilibrium bond length changes are also expected. Thus, $\lambda_i$ is non-zero. However, the approximate equality[4,5] of the observed lifetime and $\tau_L$ indicates that $\lambda_i/\lambda_o$ is relatively small, of the order of 0.1 or less, judging from Fig. 2 of Ref. 1. The study of a series of related compounds with increasing values of $\lambda_i/\lambda_o$ would be of interest, since it could serve to show $\tau_b$ becoming independent of $\tau_L$.

In intramolecular charge transfers there have been two types of systems which have been studied experimentally: relaxation on a single potential energy surface [5] and the transition, via an electron transfer, from one potential energy surface to a second.[4] The first of these is easier to treat theoretically (cf Ref. 2), while the second was treated in Ref. 1. In Ref. 2 an interesting paradox regarding $\varepsilon_o/\varepsilon_s$ is considered, and the reader is referred to that article for details.

## 3. SYMMETRIZATION OF SURFACES APPROXIMATION

The "cross-relation," it may be recalled, involves the prediction of the rate constant $k_{12}$ of a cross-reaction

$$A_{ox} + B_{red} \xrightarrow{k_{12}} A_{red} + B_{ox} \tag{2}$$

from those ($k_{11}$ and $k_{22}$) of the individual self-exchange reactions,

$$A_{ox} + A_{red} \xrightarrow{k_{11}} A_{red} + A_{ox} \tag{3}$$

$$B_{ox} + B_{red} \xrightarrow{k_{22}} B_{red} + B_{ox} \ , \tag{4}$$

and from the equilibrium constant $K_{12}$ of reaction (2).

For the case that work terms cancel or can be neglected the relation is

$$k_{12} \simeq (k_{11}\ \ k_{12}K_{22}f_{12})^{\frac{1}{2}} \tag{5}$$

where $f_{12}$ is a known function of $k_{11}$, $k_{22}$ and $K_{12}$. The quantities $k_{11}$ and $k_{22}$ have been measured experimentally by isotopic exchange or by nmr or esr line broadening techniques.

This simple relation has been perhaps the most widely used and tested aspect of electron transfer theory. Its derivation entailed several approximations, one of which (described below) might be termed "symmetrization" of the potential energy surfaces. One can assess this particular approximation numerically, using the original[15] equations, and we do so here for a typical case. The results are then used to evaluate a recent interesting *ad hoc* suggestion regarding use of a different λ for the two redox forms of each ion.[16]

The expression obtained for the free energy barrier to the reaction (2) can be written in terms of the normal mode force constants $f_k^r$ (reactants) and $f_k^p$ (products), as in Eqs. (6) and (7), after a "symmetrization" of the potential energy surfaces of the reactants and products:

$$\Delta G^* = w^r + (\lambda/4)(1 + \Delta G_R^{o'}/\lambda)^2 \tag{6}$$

$$\lambda_i = \sum_k \frac{f_k^r f_k^p}{f_k^r + f_k^p} (\Delta q_k^o)^2 \tag{7}$$

Here, λ is $\lambda_o + \lambda_i$, $\lambda_o$ being the solvational reorganizational term and $\lambda_i$ being the vibrational one. $\Delta G_R^{o'}$ equals $\Delta G^{o'} + w^p - w^r$, where $\Delta G^{o'}$ is the standard free energy of reaction in the prevailing medium; $w^r$ ($w^p$) is the work required to bring the reactants (products) from infinite separation, in the case of a bimolecular reaction. The $w$'s are absent for an intramolecular one. $\Delta q_k{}^o$ is the difference in equilibrium position values for the $k$'th normal mode in the products as compared with reactants. The summation is over the normal modes of the reactants. The relation between the barrier $\Delta G^*$ and the rate constant [the $k_e$ in Eq. (1)] is described elsewhere.[1,15]

In deriving Eq. (6) the force constants $f_k{}^r$ and $f_k{}^p$ were first expressed in terms of the symmetric combination given in Eq. (7) and of an antisymmetric combination $(f_k{}^p - f_k{}^r)/(f_k{}^p + f_k{}^r)$.[15] The approximation introduced there of neglecting the antisymmetric terms can be regarded as a "symmetrization" of the two potential energy surfaces. The result was to simplify the expression for $\Delta G^*$ and thereby yield the cross-relation, Eq. (5).[15]

The error introduced by this approximation for various values of $\Delta G_R{}^{o'}$ can readily be calculated numerically by using the original equations. Typical values of the force constants and various values of the other quantities contained in Eq. (6) are used, and we do so next.

The equations prior to symmetrization are Eqs. (A6) – (A9) and (64) of Ref. 15. They can be written as Eqs. (8) – (10) neglecting minor logarithmic terms:

$$\Delta G^* = w^r + \frac{m^2}{2}\left(\sum_k f_k^p \, \Delta q_k{}^2 + \lambda_o\right) \quad , \tag{8}$$

where $\Delta q_k$ is related to the $\Delta q_k{}^o$ appearing in Eq. (7) by

$$\Delta q_k = \Delta q_k^o \left(f_k^r f_k^p\right)^{\frac{1}{2}} / \left([m+1]\, f_k^r - m f_k^p\right) \quad . \tag{9}$$

The free energy $\Delta G^{*p}$ of formation of the transition state from the products rather than the reactants is obtained from Eq. (8) by interchanging the $r$ and $p$ superscripts and by replacing $m$ by $-(m + 1)$.[15] The equation to be solved for $m$ is then [15]

$$\Delta G^* - \Delta G^{*p} = \Delta G^{o'} \quad . \tag{10}$$

The simplest way of comparing Eqs. (8) – (10) with Eq. (6), for given values of the $f_k$'s, $\Delta q_k{}^o$'s and $\lambda_o$, is to select first an $m$. From it the value of $\Delta G^* - w^r$ and that of $\Delta G_R{}^{o'}$ (i.e., of $\Delta G^{o'} + w^p - w^r$) can be calculated using Eqs. (8) –(10). This $\Delta G^* - w^r$ is then compared with that calculated from Eq. (6) for this $\Delta G_R{}^{o'}$.

We consider as an example the case where the reactant B in Eq. (2) is an aquo cation, such as $Fe^{2+}$, with a relatively large $\Delta q_k{}^o$, and where reactant A is some large ion $ML_3{}^{3+}$, such as $Ru(bpy)_3{}^{3+}$, with a small $\Delta q_k{}^o$. There will then be no tendency to compensation and so one may obtain a magnified difference between Eq. (6) and Eqs. (8) – (10). In the case of reactant B there is only one normal mode which need be considered for the electron transfer, namely the symmetric stretching mode. Typical frequencies are those for $Fe(H_2O)_6^{2+/3+}$, namely about 380 and 525 $cm^{-1}$, respectively.[17] The $\Delta q_k^o$ for that subsystem is about 0.13 Å[18]. For the $ML_3^{3+}$ subsystem, we shall take $\Delta q_k^o$ to be zero. A value of $\lambda_o$ of 35 kcal $mol^{-1}$ (the estimated theoretical mean of those of the two subsystems)[19] was used.

In Table I values of $\Delta G_R^{o'}$ and of $\Delta G^* - w^r$ are given, the latter of these calculated from (8) to (10) and also from Eq. (6). The last row of Table I contains calculations for a system where the aquo reactant is $Fe^{3+}$–like instead of $Fe^{2+}$–like.

TABLE I. Comparison of Eqs. (8) – (10) with Eq. (6)

| $m$ | $\Delta G_R^{o'}$ | $\Delta G^* - w^r$ | |
|---|---|---|---|
| | | Eqs. (8) – (10) | Eq. (6) |
| –0.5 | +1.0 | 4.6 | 4.6 |
| –0.4 | –2.3 | 3.1 | 3.1 |
| –0.3 | –5.8 | 1.9 | 1.7 |
| –0.2 | –9.7 | 0.9 | 0.7 |
| –0.1 | –14.1 | 0.2 | 0.1 |
| –0.2[a] | –9.7 | 0.5 | 0.7 |

[a]For this row $f_k{}^r / f_k{}^p = (525/380)^2$ for the aquo cation. For all other rows it equals $(380/525)^2$. All free energies are in kcal $mol^{-1}$.

It is seen from the results in Table I that over this large range of values of $\Delta G_R^{o'}$ the $\Delta G^* - w^r$'s calculated with and without the symmetrization approximation (Eqs. 6 and 8-10, respectively) agree quite closely. Since $k_e$ varies as $\exp(-\Delta G^* / k_B T)$, the resulting $k_e$'s are seen to differ by a factor of about 1.4 or less at room temperature, for the given values of the parameters in Table I.

These results show that an anomalous behavior of the aquo $Co^{2+/3+}$ and $Fe^{2+/3+}$ pairs, where the measured self-exchange $k_{11}$'s are about $10^6$ and $10^3$, respectively,[20-22] faster than those inferred from series of cross-reactions and hence from Eq. (6), is not due to the symmetrization approximation. Accordingly, the suggestion made in Ref. 22 is not justified, namely that one should compensate for the difference in $f_R{}^r$ and $f_k{}^p$ by assigning different λ's ($\lambda_{red}$ and $\lambda_{ox}$) to ions such as $Fe^{2+}$ and $Fe^{3+}$ (incorrectly ascribed there to the present writer). For the cases examined in Table I the error in Eq. (6) is extremely small compared with these discrepancies. Several other possible explanations for the $Co^{2+/3+}$ behavior are discussed in Ref. 23.

In summary, we have described an example of the stimulation of new experimental techniques on the theoretical study of electron transfers, picosecond techniques here. We have also given an example of an old system, $Co^{2+/3+}$ or $Fe^{2+/3+}$ where, despite the current extensive understanding of electron transfers, there remains something to be understood.

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## APPENDIX

For completeness we give here the expression for the $F$ appearing in Eq. (1), and taken from Eq. (8.3′) of Ref. 1:

$$F = \ln[2(1+c^2)/(1+c^2)] + 2\int_c^1 dx\,\{\exp[(1-x^2)\Delta G^*/k_B T] - 1\}/(1-x^2)$$

with

$$c = [\lambda_i/(\lambda_i + 2\lambda_o)]^{\frac{1}{2}} \quad .$$

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