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SOLVENT DYNAMICS AND VIBRATIONAL EFFECTS IN ELECTRON TRANSFER REACTIONS *

R.A. MARCUS

Department of Chemistry **, *California Institute of Technology, Pasadena, CA 91125 (U.S.A.)*

H. SUMI

Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki 305 (Japan)

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ABSTRACT

Intramolecular vibrational effects can modify considerably the effect of solvent dynamics on the rates of electron transfer reactions, even for a fixed free energy barrier. Results of a previous paper by the authors are applied in an approximate way to provide a simplified formula for the reaction rate. The formula includes these effects and reduces to a well-known one of Kramers under appropriate conditions and when, in addition, vibrational effects are absent.

INTRODUCTION

It was with a sense of shock that we learned about the untimely death of our colleague Rezo Dogonadze. One of us (R.A.M.) met Rezo only infrequently — and not since 1971 — but his cheerfulness and the depth of his insight so evident in his work will always be remembered.

Nowadays, in the electron transfer field to which Rezo devoted so much of his interest, there have been an increasing number of studies on the possible extent of solvent dynamics effects on some electron transfer rates. The work has been both experimental and theoretical. Although Rezo's bent was often towards the quantum side of the electron transfer, his interest in relaxation was evident, and we could well have imagined his plunging into this new area. In the present paper, dedicated to his memory, we would like to describe some of our recent work in this field [1,2]. Our study revealed to us the richness of the phenomenon involved, which includes the role of inner (vibrational) and outer (solvent) contributions, the potential occurrence of a non-exponential decay rate in the relaxation and, in general, various aspects which sometimes require the supplementing of transition state theory. A number of the salient findings are described, together with a relatively simple expression which summarizes to a reasonable approximation the extensive results we obtained for one

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* Dedicated to the memory of Professor R.R. Dogonadze.

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of the important relaxation times in ref. 1. The reader is referred to that article for the derivation of the formula.

THEORETICAL CONSIDERATIONS

We have considered earlier experimental [3–7] and theoretical [8–15] literature in solvent dynamics and electron transfers [1,16]. These theoretical studies have been concerned, for the most part, with systems in which there is little or no vibrational contribution to the Gibbs energy * barrier, and in which, typically, the lowest eigenvalue ("steady-state behavior") has been calculated for the dynamics. The influence of the vibrational contribution can be nevertheless quite dramatic, influencing the rate even by orders of magnitude for a fixed total activation Gibbs energy barrier ΔG^* [1]. When ΔG^* was small and when, in addition, the solvent contribution was dominant, the reaction time approached a solvent dielectric relaxation time τ_L, defined later in eqn. (13) [1]. At fixed ΔG^*, the vibrational term influenced the conditions under which this reaction time came closer to the reciprocal of the usual thermal equilibrium rate constant k_e given by current theories of electron transfer [1]. At fixed ΔG^* the vibrational term affected not only the pre-exponential factor in the rate constant, an effect sometimes treated, but also the other factors.

We first outline briefly the treatment given in ref. 1. Typically, an electron transfer reaction requires suitable fluctuations in the solvent dielectric polarization at each point in the solvent. The fluctuations are needed so that this polarization can change from a function appropriate to the charge distribution of the reactants to one appropriate to that of the products. In treating the solvent dynamics it is convenient to introduce a scaled progress variable (coordinate) X describing these fluctuations along the most probable path in some "polarization space". An example of X is given by Zusman [9] and by Calef and Wolynes [13]. One can well imagine that a Lagrangian multiplier m which appeared in an early paper [17] would also serve as this X.

With this generalized solvent polarization coordinate X the differential equation for the probability $P(X;t)$ of finding the system with a particular X at time t satisfies, in the "overdamped case", a diffusion equation containing a reaction term $k(X)$:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial X^2} + \frac{D\partial}{k_B T\partial X}\left(P\frac{dV}{dX}\right) - k(X)P \tag{1}$$

Here, D is related to the solvent relaxation time τ_L, being equal to $k_B T/\tau_L$; $V(X)$ is a "potential", namely the Gibbs energy of formation of the fluctuation defined by X. The $k(X)$ depends on X in the following way: For each X there is an intersection of the reactants' and products' potential energy surfaces, and electron transfer can occur there (thereby satisfying the Franck–Condon principle). The

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* More commonly known in the U.S. as the Gibbs free energy.

vibrational reorganization needed to reach the "intersection surface" depends on this X. (The connection is given by eqn. (3.4) of ref. 1 and is seen graphically in Fig. 1 there.) The vibrational Gibbs energy barrier for the reaction of a system at that X, $\Delta G^*(X)$, is given in terms of the usual [16] λ-reorganization terms and the standard Gibbs energy of reaction in the prevailing medium ΔG° by [1]

$$\Delta G^*(X) = \tfrac{1}{2}(X - X_c)^2(\lambda_o/\lambda_i) \tag{2}$$

where λ_o is the λ from the solvent outside any inner coordination shell of each reactant and λ_i is the vibrational contribution. Further,

$$X_c = (\lambda + \Delta G^\circ)/(2\lambda_o)^{1/2} \tag{3}$$

and the rate constant $k(X)$ for a system at that X is given by

$$k(X) = \nu_q \exp[-\Delta G^*(X)/k_B T] \tag{4}$$

In turn, ν_q is given in ref. 1. The standard (thermal equilibrium) expression for the rate constant k_e is obtained by multiplying $k(X)$ by the thermal equilibrium distribution of X and integrating over all X; k_e can be written as $\nu \exp(-\Delta G^*/k_B T)$, where ΔG^* has the usual value $(\lambda/4)(1 + \Delta G^\circ/\lambda)^2$ [1,16], with $\lambda = \lambda_o + \lambda_i$. Depending on whether the k_e is for an adiabatic or non-adiabatic reaction, ν is given by its usual values, as in eqn. (4.10) (and footnote 28) or eqn. (4.12), respectively, of ref. 1.

Equation (1) has been written for the case of an intramolecular electron transfer, or for the case of a bimolecular electron transfer in which, to simplify the calculation, the reactants are regarded during the polarization fluctuation process as being held in some solvent cage. In the latter case one also considers the translational diffusion of the two reactants towards and away from each other, resulting in their entering and leaving the cage. The D in eqn. (1) refers, instead, to the solvent orientational relaxation "diffusion constant".

Solution of the partial differential equation (1) is, of course, not a straightforward problem. Solutions or approximate solutions have been given earlier for special cases, such as when there is essentially no vibrational contribution to the barrier, [e.g. 9,11,18]. In the latter case $k(X)$ becomes proportional to a delta function of $X - X_c$. A steady-state approximation to the latter problem was given, for example, in a different context, in a pioneering paper by Kramers [18]. However, because the vibrational contribution plays such a major role in many electron transfers it was desirable to obtain a more general solution.

Because of the solvent orientational diffusion, the kinetic decay law associated with the solution of eqn. (1) is not necessarily a single exponential. An initial transient setting-up of a steady-state distribution of X occurs, for example. Because of this potentially highly non-exponential behavior it was convenient to introduce a survival probability $Q(t)$

$$Q(t) = \int P(X;t)\,\mathrm{d}X \tag{5}$$

and then to define [1] two kinds of average survival time, τ_a and τ_b. The first of these is the "mean first passage time" and characterizes, particularly, the behavior at short times:

$$\tau_a = \int_0^\infty t[-\mathrm{d}Q(t)/\mathrm{d}t]\,\mathrm{d}t = \int_0^\infty Q(t)\,\mathrm{d}t \tag{6}$$

This τ_a (and indeed τ_b below) can be much less than the dielectric relaxation time τ_L when there is some vibrational contribution to the activation barrier (cf. Figs. 2–4 [1]).

In intramolecular electron transfers the initial transient may be obscured by the experiment. For example, the transient can occur in some photo-induced intramolecular electron transfers within the laser pulse used to initiate the reaction. We therefore introduced in ref. 1 an average survival time τ_b of the second kind, defined by

$$\tau_b = \int_0^\infty tQ(t)\,\mathrm{d}t \Big/ \int_0^\infty Q(t)\,\mathrm{d}t \tag{7}$$

The τ_b describes information for a time regime later than that described by τ_a.

Only in the case of single-exponential decay are τ_a and τ_b equal. Indeed, they then also equal the reciprocal of the steady-state rate constant k_r. The approximate calculation of τ_a and τ_b is somewhat simpler than that of $Q(t)$ and serves to provide experimentally useful information.

To solve eqn. (1) approximately, a "decoupling" approximation was introduced into a second-order term [1] and, via a function h, added care was taken to represent the short-time behavior. It was then shown that the resulting solution led to the correct description for four limiting situations and hence there was some hope that it was a reasonable approximation for the more general case. These limiting situations consisted of:

(1) the slow reaction limit, where the orientational diffusional process is rapid relative to the intrinsic reaction rate ($\tau_L^{-1} \gg k_e$),

(2) the "wide reaction window" limit ($\lambda_i/\lambda_o \gg 1$), where the "width" of the "reaction window" in X-space is larger than the thermal width of the distribution of X,

(3) the "narrow reaction window" limit ($\lambda_i/\lambda_o \ll 1$), which in the limit corresponds to $k(X)$ being a delta function and

(4) the non-diffusing limit, where τ_L approaches a value so large that $Q(t)$ becomes independent of τ_L. In effect, reaction occurs without solvent orientational dipolar fluctuations.

Upon obtaining an approximate solution of eqn. (1) or more precisely a solution for τ_a and τ_b, plots were made of the quantity $\tau_j k_e$ ($j =$ a,b) vs. $\tau_L k_e$, for various values of $\Delta G^*/k_B T$ and of λ_i/λ_o. (It was shown in ref. 1 that $\tau_j k_e$ depended only on these dimensionless variables.) In these plots each of the four limiting regions could be seen, as could the regimes where there is single-exponential ($\tau_a \simeq \tau_b$) and non-single-exponential decay. The plots are given in ref. 1. However, it would be particularly desirable for comparison with experiments to have an easily used simple formula, particularly for τ_b.

TABLE 1

Values of the factor F for the various values of $\Delta G^*/k_BT$ and of λ_i/λ_o

λ_i/λ_o	$\Delta G^*/k_BT$						
	0	1	2	3	5	10	15
0	0.6932	3.583	9.696	23.42	133.1	13,090	1,552,000
0.2	0.2531	2.125	5.551	12.17	53.54	2686	174,100
0.5	0.1362	1.547	3.883	7.930	28.77	805	29,180
1	0.06934	1.095	2.627	4.989	14.87	216.8	3929
2	0.02901	0.7020	1.597	2.811	6.850	48.61	378.5
5	0.007025	0.3410	0.7305	1.188	2.371	8.216	24.69

A simple formula was indeed derived in ref. 1, but seemingly for the relatively stringent condition that the reaction time k_r^{-1} be substantially greater than τ_L, where k_r is the rate constant given by the formula. In this case, the decay of $Q(t)$ was single-exponential and so τ_a and τ_b became equal to each other and to the reciprocal of the "steady-state" rate constant. However, this condition is too stringent for many interesting applications. If, instead, in an equation for τ_b (eqns. (7.7) and (7.9) of ref. 1) the sum of the k_e^{-2} terms were relatively small (perhaps by partial cancellation), then one sees there that τ_b is given by the same relatively simple formula (the right hand side of eqn. (8.3) and, hence, of eqn. (8.3′)). The conditions for this possibility remain to be investigated, but for the moment we shall use it as a hypothesis and test it for the range of variables considered in ref. 1.

This expression for τ_b is then given by

$$\tau_b = k_e^{-1} + F\tau_L \tag{8}$$

where $F(\lambda_i/\lambda_o, \Delta G^*/k_BT)$ is [1]

$$F \simeq \ln\left[2(1+c^2)/(1+c)^2\right] + 2\int_c^1 \mathrm{d}x\left[\exp\{(1-x^2)\Delta G^*/k_BT\} - 1\right]/(1-x^2) \tag{9}$$

with

$$c = \left[\lambda_i/(\lambda_i + 2\lambda_o)\right]^{1/2} \tag{10}$$

Equation (8) has the right functional form: τ_b equals k_e^{-1} when τ_L is very small, and is expected to be proportional to τ_L when τ_L is large. The integral in eqn. (9) is readily calculated using a standard numerical integration technique *. Values of F for various values of $\Delta G^*/k_BT$ and λ_i/λ_o are given in Table 1. The reciprocal of the τ_b in eqn. (8) is the quantity typically to be compared with experimentally

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* A Gaussian quadrature technique was used, employing Legendre polynomials [19]. We are indebted to Mr. Steve Klippenstein for the integration.

measured rate constants. An approximation to the integral in eqn. (9) is also available *.

In ref. 1 and hence in eqn. (8) one approximation used was that a reacting system which crossed to the products' potential energy surface upon electron transfer did not diffuse back to the reactants' surface. This approximation affects the results by a factor of between one and two for a reaction for which $-\Delta G^\circ > 0$, depending on the conditions, and was made purely for simplicity of presentation of an already complicated analysis. (It will be removed in a subsequent article.) The closeness of τ_b and of the steady-state value for τ was already seen in the treatment of $Q(t)$ for the "narrow reaction-window" limit (Appendix E of ref. 1). Here, for the case of $|\Delta G^*/k_BT| \ll 1$, $Q(t)$ was found to be

$$Q(t) = (2/\pi)\sin^{-1}\exp(-t/\tau_L) \tag{11}$$

In this case, $Q(t)$ is seen to behave as $(2/\pi)\exp(-t/\tau_L)$ when $t \gg \tau_L$. Thus, the reciprocal of the "steady-state" rate constant is τ_L. For comparison, τ_a and τ_b are seen in ref. 1 (eqns. 9.1, 9.2) to be about $0.69\tau_L$ and $0.94\tau_L$, respectively. Thus, the steady-state τ is only 6% different from τ_b in this limiting case. The difference between τ_a and τ_b, (here, about 25%) increases markedly when both λ_i/λ_o and $\Delta G^*/k_BT$ are increased from this limiting region where they are both zero, particularly when $\tau_L k_e$ is large [1]. The difference between τ_a and τ_b may then be orders of magnitude.

It was shown [1] that Kramers' well-known equation [18] for the steady-state rate constant can be obtained as a limiting case of eqn. (8), apart from the factor of two mentioned earlier, namely when $(2\lambda_0/[2\lambda_0 + \lambda_i])\Delta G^*/k_BT$ and τ_L are sufficiently large. The precise conditions are given in ref. 1. The equation, apart from a factor of two, is [1]

$$k_r^{-1} \simeq \tau_L(\Delta G^*/\pi k_BT)^{-1/2}\exp(\Delta G^*/k_BT) \tag{12}$$

We next compare eqn. (8) with a sampling of the results for τ_b in Figs. 2–4 of ref. 1. The comparison, on a logarithmic basis, is made in Table 2. (In ref. 1 $\tau_b k_e$ was obtained for $\Delta G^*/k_BT = 0, 1, 2$, for $\lambda_i/\lambda_o = 0, 0.2, 0.5, 1, 2, 5$ and for $\tau_L k_e$ varying from 10^{-2} to 10^3.) Remembering that a factor of 2 corresponds to a logarithm of 0.3, it is seen that eqn. (8) indeed gives a good description of the results, considering that $\tau_b k_e$ varies by over three orders of magnitude, and that it differs from $\tau_L k_e$ under some conditions by more than two orders of magnitude in one direction and under other conditions by two orders of magnitude in the opposite direction. Thus, the differences between the $\tau_b k_e$ calculated from eqn. (8) and that obtained in ref. 1 are relatively small (a factor of two in several instances not shown in Table 2).

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* For some purpose it is useful to have an approximation to the integral in eqn. (9). The grid of points mentioned in the text lie in the domain $0 \le \Delta G^*/k_BT \le 15$, $0 \le \lambda_i/\lambda_o \le 5$. When tested for this grid of points the expression [1] $(\pi/4x)^{1/2}(1-c^2)^{-1}\exp(x)\,\mathrm{erfc}\sqrt{c^2x}$ agreed with the value of the integral to about 30% or better. Here, x is $\Delta G^*/k_BT$ and erfc Z is the tabulated complimentary error function. For points outside the domain the expression should be tested further. (It is low at low x. With increasing x, at fixed c, it overshoots the exact value of the integral until at very large x it approaches the latter.)

TABLE 2

Comparison of values of log $\tau_b k_e$ obtained from eqn. (8) and from ref. 1

$\tau_L k_e$	ref. 1 ($\lambda_i/\lambda_o = 0$)	eqn. (8) ($\lambda_i/\lambda_o = 0$)	ref. 1 ($\lambda_i/\lambda_o = 1$)	eqn. (8) ($\lambda_i/\lambda_o = 1$)	ref. 1 ($\lambda_i/\lambda_o = 5$)	eqn. (8) ($\lambda_i/\lambda_o = 5$)
$\Delta G^*/k_BT = 0$						
10^{-2}	0.00	0.00	0.00	0.00	0.00	0.00
10^{-1}	0.03	0.03	0.00	0.00	0.00	0.00
1	0.25	0.23	0.03	0.03	0.00	0.00
10	1.00	0.90	0.23	0.23	0.02	0.03
10^2	1.98	1.85	0.84	0.90	0.14	0.23
10^3	2.97	2.84	1.72	1.85	0.67	0.90
$\Delta G^*/k_BT = 2$						
10^{-2}	0.04	0.04	0.01	0.01	0.00	0.00
10^{-1}	0.30	0.29	0.11	0.10	0.03	0.03
1	1.05	1.03	0.61	0.56	0.26	0.24
10	2.01	1.99	1.52	1.44	0.89	0.92
10^2	3.01	2.99	2.50	2.42	1.73	1.87
10^3	4.01	3.99	3.49	3.42	2.68	2.86

Moreover, the accuracy of eqn. (8) is expected to increase with increasing $\Delta G^*/k_BT$ (cf. conditions [1] for the validity of eqn. 8.3). We indeed intend to test eqn. (8) for larger values of $\Delta G^*/k_BT$ elsewhere.

Typically, it has been formulas such as Kramers' and related equations which have been applied to experimental data. However, in some cases they may have been applied under conditions for which they were not designed. Conditions for the validity of Kramers' expression are given in section VIII of ref. 1.

We conclude with some remarks on τ_L and on the application to the experimental data. The quantity τ_L is commonly written in the literature as [20] *

$$\tau_L = \tau_D \epsilon_0 / \epsilon_s \tag{13}$$

where τ_D is the usual ("constant field") dielectric relaxation time (in particular, the lowest frequency one when there are several), ϵ_s is the static dielectric constant and ϵ_0 is its "high frequency" value, interpreted by different authors in the multiple-relaxation case as the optical value (square of the refractive index) or the value on the high frequency side of the lowest frequency dispersion curve (a microwave value). We have discussed this topic elsewhere for alcohols [2] and, assuming Debye-type relaxation, it was argued that in the multiple relaxation case the optical value for ϵ_0 would be appropriate if the solvent surrounding the (organic) solute were largely in a cluster rather than a partially cluster–partially monomeric form.

On the basis of the analysis in ref. 1, i.e., without using the approximation embodied in eqn. (8), we can consider when τ_b is expected to equal to τ_L. One sees in Figs. 2–4 there, that this condition prevails only when $\Delta G^*/k_BT \simeq 0$, $\lambda_i/\lambda_o \simeq 0$

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* A related ("dipolar") τ_L has also been employed [14] and discussed [2].

and $\tau_L k_e \gg 1$. Since the occurrence of $\tau_b \simeq \tau_L$ (with ϵ_0 equal to the optical value) appears to have been established for the intramolecular electron transfers studied by Kosower and co-workers [3] (photoinduced organic intramolecular charge transfers, with some internal twisting motion) these conditions presumably apply in those experiments.

However, there are differences in the experimental literature regarding whether the charge transfer step (e.g., for dimethylaminobenzonitrile in 1-propanol) obeys a single exponential or a multiexponential law [21]. The laser pulses used were in the neighborhood of about 5–10 ps duration. By virtue of the desirability, for understanding the role of solvent dynamics, of determining whether or not the reaction is described by a single exponential, it would be highly desirable to extend such experiments by using shorter pulses, of the 1 ps or 100 fs variety. The various types of relaxation time could then be calculated from the data and compared with theoretical estimates [1].

It is clear from Figs. 2–4 of ref. 1 that for any $\Delta G^*/k_B T$ the deviation of τ_b from the equilibrium-calculated value k_e^{-1} is the greater the smaller the value of λ_i/λ_o. With this result in mind it is interesting to consider the case of solvent effects on the rates of electron transfer of metallocene redox couples, both for the electrochemical and homogeneous systems. Weaver and co-workers [5,6] pointed out that the solvent effect in this case was not well represented by the usual electron-transfer theory expression, although it was reasonably represented in some other reactions and also [6] in the optical transition for a bridged bi-ruthenium pentammine system. They attributed the discrepancy in the metallocene case to solvent dynamical effects, and showed that with some inclusion of these effects the discrepancy was reduced, though the final results still left much to be desired. The treatment used did not have available a proper inclusion of the role of λ_i/λ_o though, to be sure λ_i/λ_o is small for these reactions. Also, unlike the intramolecular vibration frequencies which contribute to $k(X)$, the best choice of the contributing frequency for the solvent is currently uncertain, an uncertainty reflected, for example, in the variety of choices for ν_{os} in ref. 5. Because of some differences [5] found in the homogeneous and electrochemical systems, however, any detailed interpretation of the experimental results may require some caution.

The electron transfers discussed above involve the transition from one potential energy surface to another. A much simpler system than this is one in which the solvent relaxation accompanies an intramolecular electron transfer on a single potential energy surface. This problem was treated in ref. [2], together with existing experimental data. The latter are very few (only one system thus far, it appears [4]). The theory for such systems [2,14] is much simpler than that [1] for the two-potential energy surfaces' problem.

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