Nonadiabatic Redox Reactions in Solution: A Model of Two Classical Morse Potentials and Its Comparison with Harmonic Approximation

Ernst D. German* and Alexander M. Kuznetsov

The A. N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences, Lininskii prospect 31, 117 071 Moscow, Russia

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Equations for the activation free energy $\Delta F^{\#}$ and preexponential factor of the rate constant of the redox reaction $X_2 + e \rightarrow X_2^-$ in solution characterized by a considerable elongation of the chemical bond X−X are obtained. Intramolecular potential energies describing the stretching vibrations along the X−X bond in the molecule and its anion are approximated by Morse functions. The dependencies of $\Delta F^{\#}$ and other characteristics of the transition configuration on the free energy of the reaction are compared with those obtained in harmonic approximation.

1. Introduction

Electron-transfer (ET) reactions are often accompanied by a change of the intramolecular structure of reactants. In the case when these changes are small, a harmonic approximation may be satisfactorily used for the description of the structural changes in ET kinetics in solutions. These reactions will be referred to below as the reactions of the type A. In the framework of the classical Marcus−Hush theory,[1,2] the harmonic approximation leads to the well-known quadratic expression for the activation barrier

$$\Delta F^{\#}_{\mathrm{M-H}} = (E_s + E_r + \Delta F)^2/4(E_s + E_r) \qquad (1)$$

where ΔF is the free energy of the transition and E_s and E_r are the solvent and intramolecular reorganization energies. It is of importance that the frequencies of all classical oscillators were assumed to be unchanged before and after ET when deriving eq 1.

The reorganization energy E_r in eq 1 is equal to

$$E_r = \sum_k (\mu_k \omega_k^2/2)(q_{kf}^0 - q_{ki}^0)^2 \qquad (2)$$

where, μ_k and ω_k are the effective mass and frequency of the kth normal vibration, and q_{ki}^0 and q_{kf}^0 are the equilibrium values of the normal coordinates before and after transition, and the summation is performed over the degrees of freedom participating in the transition.

The reorganization energy E_r along with E_s is an important parameter of the Marcus−Hush theory. A number of papers were published recently which concern the methods of the calculation of the reorganization energy E_r.[3−10]

We note that the nonparabolic form of the potential curves of the chemical bonds of the donor and acceptor species was used for the calculation of E_r in all cited works except refs 4 and 5. For that form of curves, if ET is accompanied by a considerable change of the reactants structure, E_r calculated in harmonic approximation seems to be inappropriate for use in eq 1. This point is illustrated by Figure 1, which shows (for one degree of freedom participating in the transition) a noticeable difference between the reorganization energies calculated with the use of harmonic and anharmonic potentials.

On the other hand, to be exact, anharmonic intramolecular potentials should be used to derive an equation for the activation energy of ET reactions characterized by a significant extension (compression) of chemical bonds of reactants (products) (i.e., in this case one has to go beyond the harmonic approximation). The reactions of this class will be referred to below as the reactions of type B.

A general method was suggested in ref 11 which allows one to consider both classical and quantum mechanical behavior of the chemical bond in an electron-transfer reaction. A simpler approach for the classical limit is developed in the present paper. The results are compared quantitatively with the harmonic approximation. In this connection, a special attention is paid to the relation between the methods used for the calculation of E_r and the models in which the ET kinetics is described.

2. Systems

In the present paper we shall restrict ourselves by the reactions of the type

$$\mathrm{A(solv)} + \mathrm{N^-(solv)} \rightarrow \mathrm{A^-(solv)} + \mathrm{N(solv)} \qquad (3)$$

in polar solvent where it is assumed that (1) the intramolecular state of the electron donor N^- is unchanged in the course of the reaction, (2) only one chemical bond or normal vibration in the electron acceptor A undergoes a reorganization in the course of the electron transfer, and (3) the motions along all nuclear degrees of freedom are classical. As an example of electron acceptors of this type we would refer to diatomic halogen molecules X_2, which are often used as oxidants in organic reactions,[12] and to polyhalogen methane molecules CX_4 or CF_3X (where X = Cl, Br, and I). The reduction of the latter results in the formation of the radical anions of C_{3v} symmetry with one C−X bond considerably elongated.[13−15] The typical examples of electron donors with rigid structure are ions of polycyclic aromatic molecules or electrodes (in electrochemical reactions). Note that if the intramolecular structure of the

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* Corresponding author. Present address: 11/17 Burla str., 32812 Haifa, Israel. E-mail: c1447543@techst02.technion.ac.il.

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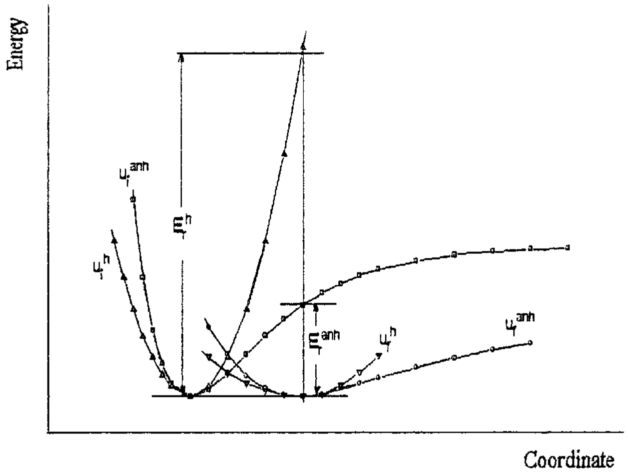

Figure 1. Scheme illustrating the definition of the reorganization energies E_r^h and E_r^{anh} in harmonic approximation (curves u_i^h and u_f^h) and for anharmonic potentials (curves u_i^{anh} and u_f^{anh}), respectively. $E_r^h \gg E_r^{anh}$ if the distance between the minima of the potential curves is rather large.

electron donor is also slightly disturbed by the ET, this effect can be easily incorporated into the theory within developed formalism given that the harmonic approximation is applicable to the nuclear vibrations of the electron donor.

In what follows, we shall consider for the sake of definiteness ET reactions between donor N^- and diatomic molecules X_2 as electron acceptor

$$X_2(\text{solv}) + N^-(\text{solv}) \rightarrow X_2^-(\text{solv}) + N(\text{solv}) \tag{4}$$

keeping in mind that all the results will be equally valid for a more general reaction class (eq 3).

3. Model

It is assumed below that the reaction is nonadiabatic. This means that the diabatic free energy surfaces of the initial and final states, U_i and U_f, may be conveniently used for the calculation of the reaction rate constant. Two components of the reacting system (along with the electron) undergo the reorganization in the course of the reaction. They are the inertial solvent polarization $\boldsymbol{P}$ and the length R of a chemical bond X$-$X. Thus, the diabatic free energy surface of the initial state $U_i(\boldsymbol{P}, R)$ represents the Gibbs free energy of the system involved in the left-hand side of eq 4 as a function of the solvent polarization $\boldsymbol{P}$ and the intramolecular coordinate R. Similarly the diabatic free energy surface of the final state $U_f(\boldsymbol{P}, R)$ represents the Gibbs free energy of the system involved in the right-hand side of eq 4. Neglecting the interaction between the small intramolecular vibrations and the fluctuations of the solvent polarization, we may split the diabatic free energy surfaces into two components, $U^S(\boldsymbol{P})$ and $u(R)$, describing separately the state of the solvent polarization and the state of the chemical bond

$$U_i(\boldsymbol{P}, R) = U_i^S(\boldsymbol{P}) + u_i(R) + I_i \tag{5}$$

$$U_f(\boldsymbol{P}, R) = U_f^S(\boldsymbol{P}) + u_f(R) + I_f \tag{6}$$

where I_i and I_f are the minimum values on the free energy surfaces of eqs 5 and 6, respectively.

The effective Hamiltonian method[11,16,17] will be used for the description of the inertial polarization. The method exploits a well-known fact that the behavior of a linear system (i.e., the system with linear response to an external field) may be mapped onto the behavior of a set of harmonic oscillators with an appropriate choice of their parameters. The inertial polarization is, therefore, represented as a set of effective oscillators, and the corresponding components of the free energy surfaces have the form

$$U_i^S(\boldsymbol{P}) = {}^1\!/_2\sum_k \hbar\omega_k(y_k - y_{ki}^0)^2 \tag{7}$$

$$U_f^S(\boldsymbol{P}) = {}^1\!/_2\sum_k \hbar\omega_k(y_k - y_{kf}^0)^2 \tag{8}$$

where y_{ki}^0 and y_{kf}^0 are the initial and final equilibrium values of the coordinates of the effective oscillators. They correspond to different initial and final equilibrium values of the solvent polarization, which depend on the charge distribution in the electron donor and acceptor in the initial and final states.

The potential energies of the X$-$X chemical bond in the molecule X_2 and its anion X_2^-, u_i and u_f, are approximated by Morse functions similar to those of ref 18, where the gas phase molecules of this type were considered

$$u_i^m(R) = D_i(\exp[-\alpha(R - R_i^0)] - 1)^2 \tag{9}$$

$$u_f^m(R) = D_f(\exp[-\beta(R - R_f^0)] - 1)^2 \tag{10}$$

where

$$\alpha = (\mu\Omega_i^2/2D_i)^{1/2} \tag{11}$$

$$\beta = (\mu\Omega_f^2/2D_f)^{1/2} \tag{12}$$

The subscripts i and f label the neutral molecule and anion, respectively, μ is the effective mass of the stretching vibrations, R_i^0 and R_f^0 are the equilibrium bond lengths in the neutral molecule and anion, D_i is the dissociation energy of the neutral molecule for two atoms and D_f is the energy of dissociation of the anion with the formation of the atom X and anion X^- in the solvent, and Ω_i and Ω_f are the corresponding vibrational frequencies. It is convenient for what follows to place the origin of the coordinates at the point of the minimum of the initial multidimensional free energy surface characterizing the reactants ($X_2 + N^-$) and the solvent, i.e., to put $y_{ki}^0 = 0$; $R_i^0 = 0$. The diabatic free energy surfaces take then the form

$$U_i(R, \{y_k\}) = D_i[\exp(-\alpha R) - 1]^2 + {}^1\!/_2\sum_k \hbar\omega_k y_k^2 \tag{13}$$

$$U_f(R, \{y_k\}) = D_f[\exp(-\beta\{R - \Delta R_0\}) - 1]^2 + {}^1\!/_2\sum_k \hbar\omega_k(y_k - \Delta y_k^0)^2 + \Delta F \tag{14}$$

where $\Delta R_0 = R_f^0 - R_i^0 \equiv R_f^0$, $\Delta y_k^0 = y_{kf}^0 - y_{ki}^0$, and ΔF is *the free energy of the transition in the reaction complex.* The introduction of ΔF as a separate term means, in particular, that the values of the solvent and inner-molecular components of the free energy surfaces at their points of minimum are chosen to be zero. It should be emphasized that the free energy of the transition ΔF involves the so-called work terms w_i and w_f,[1] which are the free energies required to bring the reactants and reaction products from infinity to the reaction complex position, respectively, so that

$$\Delta F = \Delta F_0 + w_{\mathrm{f}} - w_{\mathrm{i}} \tag{15}$$

where ΔF_0 is the reaction free energy. We note also that the characteristics of both reacting species affect the value of the free energy of the transition ΔF.

4. Rate Constant: The Activation Free Energy and the Preexponential Factor in the Model of Morse Potentials

The rate constant of the nonadiabatic reaction can be calculated in a standard way with the use of the Fermi golden rule.[11] For the model described, in classical limit, the expressions for the activation free energy and the preexponential factor have the form (see Appendix A)

$$\Delta F_{\mathrm{m}}^{\#} = (1-\hat{z})^2\left\{\frac{E_{\mathrm{r}}^{\mathrm{m}}}{(1-\gamma^{-1/t})^2} + \frac{E_{\mathrm{s}}}{1-\hat{z}+(tD_{\mathrm{f}}/D_{\mathrm{i}})(\gamma^2\hat{z}^{2t-1}-\gamma\hat{z}^{t-1})}\right\} \tag{16}$$

$$A_{\mathrm{m}} = \frac{2\pi V_{\mathrm{if}}^2\delta}{\hbar}\left\{\frac{\alpha^2 D_{\mathrm{i}}[(1-\hat{\theta})\alpha^2 D_{\mathrm{i}}(2\hat{z}^2-\hat{z})+\hat{\theta}\beta^2 D_{\mathrm{f}}(2\gamma^2\hat{z}^{2t}-\gamma\hat{z}^t)]^{-1}}{4\pi k_{\mathrm{B}}T[E_{\mathrm{s}}+\{2\alpha D_{\mathrm{i}}(1-\hat{z})\hat{z}-2\beta D_{\mathrm{f}}(\gamma\hat{z}^t-\gamma^2\hat{z}^{2t})\}]\left(\frac{\mathrm{d}\hat{R}}{\mathrm{d}\theta}\right)_{\hat{\theta}}}\right\} \tag{17}$$

where a cap above z and θ denotes that these quantities are taken at the transitional configuration; γ and t are defined in Appendix A. V_{if} in eq 17 is the electron resonance integral, δ is the reaction volume, $z = \exp(-\alpha R)$, and the intramolecular energy $E_{\mathrm{r}}^{\mathrm{m}}$ is defined as follows

$$E_{\mathrm{r}}^{\mathrm{m}} = u_{\mathrm{i}}^{\mathrm{m}}(R_{\mathrm{f}}^0) - u_{\mathrm{i}}^{\mathrm{m}}(0) = D_{\mathrm{i}}(1-\gamma^{-1/t})^2 \tag{18}$$

The set of equations for $\hat{z}$ and $\hat{\theta}$ at the transitional configuration has the form

$$\hat{\theta} = \frac{\hat{z}-\hat{z}^2}{\hat{z}-\hat{z}^2+(tD_{\mathrm{f}}/D_{\mathrm{i}})(\gamma^2\hat{z}^{2t}-\gamma\hat{z}^t)} \tag{19}$$

$$\hat{\theta} = \frac{1}{2} + \frac{\Delta F}{2E_{\mathrm{s}}} + \frac{D_{\mathrm{f}}(\gamma\hat{z}^t-1)^2 - D_{\mathrm{i}}(\hat{z}-1)^2}{2E_{\mathrm{s}}} \tag{20}$$

5. Harmonic Approximation

It is of interest to compare the results obtained in the model of Morse potentials with those in harmonic approximation when the potential energies u_{i} and u_{f} are the parabolic functions

$$u_{\mathrm{i}}^{\mathrm{h}}(R) = \mu\Omega_{\mathrm{i}}^2R^2/2 \tag{21}$$

$$u_{\mathrm{f}}^{\mathrm{h}}(R) = \mu\Omega_{\mathrm{f}}^2(R-\Delta R_0)^2/2 \tag{22}$$

Then the quantities $\Delta F^{\#}$ and A are equal to (see Appendix B)

$$\Delta F_{\mathrm{h}}^{\#} = \hat{\theta}(1-\hat{\theta})\left\{\left[\frac{\nu}{1-\hat{\theta}+\nu\hat{\theta}}\right]^2 E_{\mathrm{r}}^{\mathrm{h}} + E_{\mathrm{s}}\right\} + \hat{\theta}\Delta F \tag{23}$$

where $\nu = (\Omega_{\mathrm{f}}/\Omega_{\mathrm{i}})^2$ and the intramolecular reorganization energy

$$A_{\mathrm{h}} = \frac{2\pi V_{\mathrm{if}}^2\delta}{\hbar}\left\{\frac{(1-\hat{\theta}+\nu\hat{\theta})^{-1}}{4\pi k_{\mathrm{B}}T\left(E_{\mathrm{s}}+2E_{\mathrm{r}}^{\mathrm{h}}\left[\frac{\hat{R}}{\Delta R_0}+\nu\left(1-\frac{\hat{R}}{\Delta R_0}\right)\right]\frac{\nu(2-\hat{\theta})}{(1-\hat{\theta}+\nu\hat{\theta})^2}\right)}\right\}^{1/2} \tag{24}$$

in harmonic approximation is defined as follows

$$E_{\mathrm{r}}^{\mathrm{h}} = {}^1\!/_2\,\mu\Omega_{\mathrm{i}}^2(\Delta R_0)^2 \tag{25}$$

The value of the bond stretching coordinate R at the transitional configuration is expressed through θ as follows

$$\hat{R} = \frac{\nu\hat{\theta}\Delta R_0}{1-\hat{\theta}+\nu\hat{\theta}} \tag{26}$$

and $\hat{\theta}$ is the solution of the equation

$$\hat{\theta} + \frac{[\nu\hat{\theta}^2-(1-\hat{\theta})^2]p}{[1-\hat{\theta}+\nu\hat{\theta}]^2} - q = 0 \tag{27}$$

where $\Delta R_0 = R_{\mathrm{f}}^0 - R_{\mathrm{i}}^0 \equiv R_{\mathrm{f}}^0$ and p and q are defined in Appendix B. We note that eq 23 is identical to eq 1 at $\nu = 1$.

6. Results and Discussion

Reaction 4 is considered in this section as an example for numerical comparison between the harmonic and Morse approximations of intramolecular potentials. For our calculations to correspond to a certain real situation, we used here for numerical estimations the characteristics of the Cl−Cl chemical bond in a Cl_2 molecule and its anion Cl_2^-. The characteristics for the Cl_2 in gas phase are given in ref 18. We can expect that they are the same in solution since the solvation effect on the molecule is known to be negligible. The dissociation energy and vibration frequency for the anion Cl_2^- in condensed phase were taken from ref 19, and according to this reference these characteristics are close to those in the gas phase.

Thus, the energy D_{i} of the dissociation of the Cl_2 molecule for two chlorine atoms and the frequency of the valence vibrations Ω_{i} were taken equal to 58 kcal/mol and 559 cm^{-1}, respectively.[18] The length of the Cl−Cl bond in the anion Cl_2^- is larger than that in the neutral molecule by about 0.63 Å,[18] which is the distance ΔR_0 between the minima of the corresponding potential curves. The dissociation energy D_{f} of the anion for the chlorine atom and the anion Cl^- and the frequency Ω_{f} may be taken as 30 kcal/mol and 260 cm^{-1}.[19] Therefore, the considered reaction belongs to type B. It is characterized by the very different Morse and harmonic intramolecular reorganization energies $E_{\mathrm{r}}^{\mathrm{m}}$ and $E_{\mathrm{r}}^{\mathrm{h}}$, which being estimated by eqs 18 and 25 with the above parameters values are equal to 30 and 94 kcal/mol, respectively.

Since the source of the electrons for the electrochemical reaction is the electrode, the free energy of the transition ΔF depends on the electrode potential.

The order of magnitude of the solvent reorganization energy E_{s} in water was estimated with the use of the ellipsoidal cavity model.[20] The Cl_2 molecule in the reaction complex was assumed to be located in the position normal to the electrode surface, and a distance between the surface and the nearest Cl atom to be equal to the van der Waals radius of the latter. The negative charge (−1e) accepted by the molecule Cl_2 was

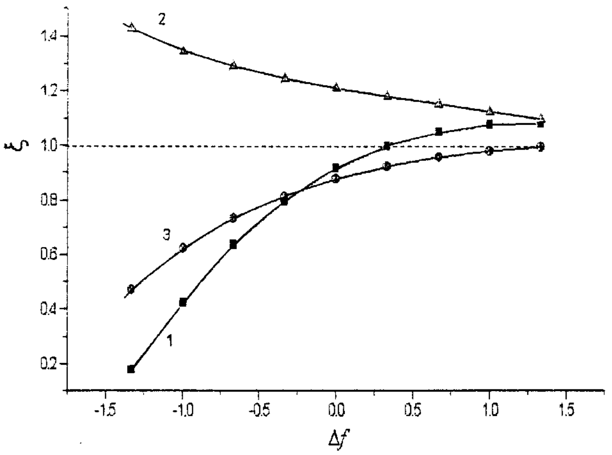

Figure 2. Dependencies of $\xi_1 = \Delta F^{\#}_{h}/\Delta F^{\#}_{m}$, $\xi_2 = \Delta F^{\#}_{M-H}(2)/\Delta F^{\#}_{m}$, and $\xi_3 = \Delta F^{\#}_{M-H}(3)/\Delta F^{\#}_{m}$ on Δf (curves 1, 2, and 3). The subscripts h, M−H, and m correspond to the harmonic, Marcus−Hush, and Morse models; $\Delta f = \Delta F/E_s$, ΔF and E_s are the free energy of the transition and the solvent reorganization energy, and $\Delta F^{\#}_{M-H}(2)$ and $\Delta F^{\#}_{M-H}(3)$ are the values calculated with the use of the average reorganization energies given by eqs 28 and 29 in the text, respectively.

assumed to be uniformly distributed between two Cl atoms. The semiaxes of the ellipsoid, whose lengths depend on the Cl−Cl distance (~2 Å) and van der Waals radius of Cl (1.88 Å), were estimated as 5.6 and 1.8 Å, respectively. This model gives $E_s \sim 30$ kcal/mol.

Results of comparison of the activation free energies calculated in various models are presented in terms of the quantities $\xi_1 = \Delta F^{\#}_{h}/\Delta F^{\#}_{m}$, $\xi_2 = \Delta F^{\#}_{M-H}(2)/\Delta F^{\#}_{m}$, and $\xi_3 = \Delta F^{\#}_{M-H}(3)/\Delta F^{\#}_{m}$ shown in Figure 2 where subscripts h, m, and M−H denote the harmonic, Morse and Marcus−Hush model, respectively. Curve 1 represents ξ_1 as a function of the dimensionless free energy of the transition $\Delta f = \Delta F/E_s$. It is seen that $\xi_1 < 1$ at $\Delta f < 0$, i.e., the activation barrier $\Delta F^{\#}_{h}$ calculated in the exact harmonic model (eqs 23−27) is lower than the barrier $\Delta F^{\#}_{m}$ calculated in the Morse model (eqs 16−20), in spite of the fact that the intramolecular harmonic reorganization energy E^{h}_{r} is three times as large as the Morse reorganization energy E^{m}_{r}. For example, $\Delta F^{\#}_{m} \sim 2.5\, \Delta F^{\#}_{h}$ at $\Delta f = -1$. At $\Delta f > 0$ the difference between $\Delta F^{\#}_{m}$ and $\Delta F^{\#}_{h}$ becomes less significant than that at $\Delta f < 0$.

As for the quantities ξ_2 and ξ_3, it should be noted that eq 1 is not applicable immediately for the calculation of the activation free energy of the considered reaction, since unlike eq 23 it does not take into account the change of the intramolecular vibrational frequency. The latter is of importance since Ω_i is almost twice as large as Ω_f. In order to take account of this fact, an average reorganization energy should be used, which may be evaluated as

$$E^{h}_{r,av}(2) = \mu(\Omega_i^2 + \Omega_f^2)(\Delta R_0)^2/4 = (E^{h}_{r,i} + E^{h}_{r,f})/2 \quad (28)$$

or as

$$E^{h}_{r,av}(3) = \mu(\Delta R_0)^2(\Omega_i^2\, \Omega_f^2)/(\Omega_i^2 + \Omega_f^2) = 2(E^{h}_{r,i}\, E^{h}_{r,f})/(E^{h}_{r,i} + E^{h}_{r,f}) \quad (29)$$

In particular, an equation of type 29 has been used for the calculation of the average reorganization energy in ref 21. The estimations of the average reorganization energies according to eqs 28 and 29 for the system under consideration give $E^{h}_{r,av}(2) = 57$ and $E^{h}_{r,av}(3) = 33$ kcal/mol, respectively. These values were used to calculate the dependencies of ξ_2 and ξ_3 on Δf according to eq 1, which are shown in Figure 2 (curves 2 and 3). It is seen that $\xi_2 > 1$, i.e., $\Delta F^{\#}_{M-H}(2) > \Delta F^{\#}_{m}$ in all investigated range of the Δf values. On the contrary $\xi_3 < 1$, i.e., $\Delta F^{\#}_{M-H}(3) < \Delta F^{\#}_{m}$ at these values of Δf. As follows from these curves, the difference in the activation free energies calculated in the Morse and the harmonic approximations may be rather significant.

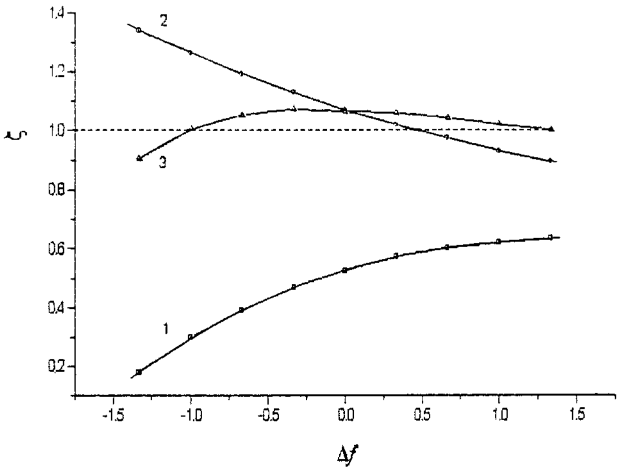

Figure 3. Dependencies of $\zeta_1 = \hat{R}_h/\hat{R}_m$, $\zeta_2 = \hat{R}_{M-H}(2)/\hat{R}_m$, and $\zeta_3 = \hat{R}_{M-H}(3)/\hat{R}_m$ on Δf (curves 1, 2, and 3); $\hat{R}_{M-H}(2)$ and $\hat{R}_{M-H}(3)$ are the values calculated with the use of the average reorganization energies given by eqs 28 and 29 in the text, respectively.

Let us compare now the transitional configuration, symmetry factor θ and bond stretching $\hat{R}$ calculated in the harmonic approximation with the use of eqs 1 and 26 and in the Morse model (eqs 19 and 20). The results of calculations of the bond stretching are represented in terms of quantities $\zeta_1 = \hat{R}/\hat{R}_m$, $\zeta_2(2) = \hat{R}_{M-H}(2)/\hat{R}_m$, and $\zeta_3(2) = \hat{R}_{M-H}(3)/\hat{R}_m$ in Figure 3. This figure shows that the exact harmonic model (eqs 26 and 27) underestimate considerably the values of $\hat{R}$ as compared with the Morse model. The difference amounts to a factor of 2−5 depending on the Δf value. The simple Marcus−Hush harmonic approximation leads to values of $\hat{R}_{M-H}$ that are different from $\hat{R}_m$ only at Δf far below zero (e.g., $\xi_2 \sim 1.4$ at $\Delta f = -1.3$).

The dependence of the symmetry factor θ on Δf in the Morse model of the intramolecular potentials is qualitatively different from that obtained in the exact harmonic model and in the Marcus−Hush model (Figure 4). Figure 4 shows that unlike eq 1 which leads to a linear dependence of θ_{M-H} on Δf (curves 3 and 4), the θ vs Δf plots are curvilinear in the Morse and exact harmonic models, the curvature being positive for the Morse model (curve 1) and negative for the exact harmonic model (curve 2).

Concluding we note that the main results of the paper are represented by eqs 16, 17, 19, and 20 for the Morse model of the intramolecular potentials and by eqs 23, 24, 26, and 27 for the model of harmonic vibrations with the frequency change. Two points should be noted:

1. The numerical calculations performed demonstrate a significant difference between the harmonic approximation (eqs 23−27) and the more realistic model for the intramolecular potentials (eqs 16−20). The effect is expected to be more pronounced if we pass from reaction 4 to a redox reaction in which the geometrical structure of an electron donor N^- is also changed. It should be noted, however, that the Morse function approaches the real potential around equilibrium and at very large distances. In the intermediate region the Morse curve is more smooth than the exact one.[22] Therefore, if the crossing

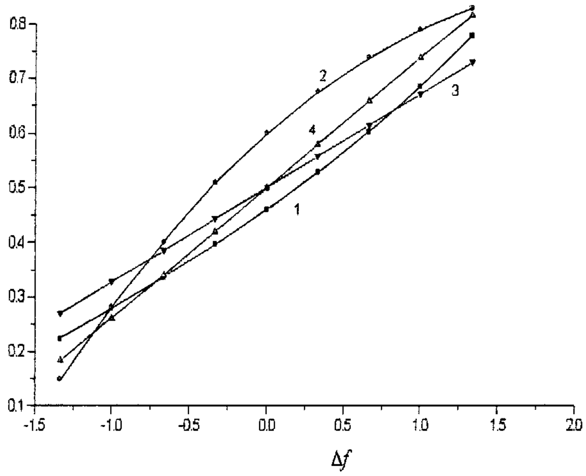

Figure 4. Dependencies of θ_{M-H} on Δf in the Morse and harmonic approximations (curves 1 and 2), and in the Marcus–Hush approximation (curves 3 and 4 corresponding to the reorganization energies calculated according to eqs 28 and 29 in the text).

point $\hat{R}_m$ of the initial and final potential curves is far from R_i^0, the evaluations with the use of eqs 16–20 will give the upper bound of the effect only. However, for the system Cl_2/Cl_2^- considered in this paper the values of $\hat{R}_m$ are close to R_i^0, being larger by 0.12–0.5 Å than R_i^0 in the investigated interval of the reaction free energies. Thus, the curves shown in Figures 2–4 seem to describe the effects rather accurately.

2. The value of the reorganization energy E_r^h may differ considerably from E_r^m for the reactions of the B type. Moreover, the form of expressions for $\Delta F^\#$ is quite different in the harmonic and Morse models. This results in the fact, both the *numerical values* of $\Delta F^\#$ and the shapes of the $\Delta F^\#$ vs ΔF dependence are different in both approximations of the intramolecular potential. Thus, the *formal analysis* of the numerical values of the intramolecular reorganization energies, *without the reference to the concrete model*, is insufficient for the characterization of the elementary act of the B type reactions. We emphasize that the numerical value of E_r is closely related with the model used. Therefore, the reorganization energy obtained in terms of the Morse approximation of the intramolecular potentials, strictly speaking, may not be used for the estimation of $\Delta F^\#$ in the framework of equations of the harmonic approximation, if the corresponding reaction is accompanied by a considerable elongation (or shortening) of chemical bonds.

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Appendix A. Derivation of Eqs 16–20

If the intramolecular vibrations in the molecule X_2 and its anion are classical, the rate constant of the nonadiabatic ET reaction may be calculated starting from eq A1[23]

$$k = \frac{2\pi V_{if}^2\delta}{\hbar}\left[\frac{d^2u_i^m/dR^2|_{R_i^0}}{2\pi k_B T|d^2H/d\theta^2|_{\hat{\theta}}|d^2f/dR^2|_{\hat{R}(\hat{\theta})}}\right]^{1/2}\exp\left[-\frac{\Delta F^\#}{k_BT}\right] \tag{A1}$$

where

$$\Delta F^\# = \hat{\theta}^2E_s + u_i^m(\hat{R}(\hat{\theta})) - u_i^m(R_i^0) \tag{A2}$$

$$H = \theta\Delta F + \theta(1-\theta)E_s + (1-\theta)u_i^m + \theta u_f^m - u_i^m(R_i^0) \tag{A3}$$

$$f = (1-\theta)u_i^m + \theta u_f^m \tag{A4}$$

and V_{if} and δ are the electron resonance integral and reaction volume. The quantities θ and $\hat{R}$ are determined by a set of coupled equations

$$(1-\theta)\frac{dU_i(R,\{y_k\})}{dR} + \theta\frac{dU_f(R,\{y_k\})}{dR} = 0$$
$$U_i(R,\{y_k\}) = U_f(R,\{y_k\}) \tag{A5}$$

The quantity θ is the symmetry factor[23] that depends on the free energy of the transition ΔF, on the solvent reorganization energy E_s, and on the spectroscopic parameters of the chemical bond X–X in the molecule and anion. The free energy surfaces U_i and U_f are defined in eqs 13 and 14. The intramolecular potentials u_i^m and u_f^m (eqs 9 and 10) may be written in the form

$$u_i^m = D_i(z-1)^2 \tag{A6}$$

$$u_f^m = D_f(\gamma z^t - 1)^2 \tag{A7}$$

where new notations are introduced as follows

$$z = \exp(-\alpha R),\ z = 1 \text{ at } R = 0, \text{ and } z = 0 \text{ at } R \to \infty \tag{A8}$$

$$\gamma = \exp(\beta\Delta R_0) \tag{A9}$$

$$t = \beta/\alpha \tag{A10}$$

Calculation of the second derivative of the function u_i^m with respect to R at the point R_i^0 gives

$$\left.\frac{d^2u_i^m}{dR^2}\right|_{R_i^0} = 2\alpha^2D_i \tag{A11}$$

The second derivative of H with respect to θ in eq A1 is calculated with due account of the fact that the functions u_i^m and u_f^m depend on θ through $z(R)$. This gives

$$\left.\frac{d^2H}{d\theta^2}\right|_{\hat{\theta}} \approx -2E_s - 2\left(\frac{du_i^m}{dR} - \frac{du_f^m}{dR}\right)_{\hat{R}(\hat{\theta})}\left(\frac{dR}{d\theta}\right)_{\hat{\theta}} \tag{A12}$$

where first derivatives of u_i^m and u_f^m have the form

$$\frac{du_i^m}{dR} = 2\alpha D_iz(1-z) \tag{A13}$$

$$\frac{du_f^m}{dR} = 2\beta D_f(\gamma z^t - \gamma^2z^{2t}) \tag{A14}$$

The second derivative d^2f/dR^2 at the point $\hat{R}(\theta)$ is calculated with the use of eqs A4, A9, and A10 as follows

$$\left.\frac{d^2f}{dR^2}\right|_{\hat{R}(\hat{\theta})} = 2\alpha^2D_i(1-\hat{\theta})(2\hat{z}^2 - \hat{z}) + 2\beta^2D_f\hat{\theta}(2\gamma\hat{z}^{2t} - \gamma\hat{z}^t) \tag{A15}$$

Taking into account that in the coordinate system chosen $u_i^m(R_i^0) = 0$ and using eqs A1, A2, and A5−A15, we obtain eqs 16−20.

Appendix B. Derivation of Eqs 23, 24, and 27

Substituting eqs 21 and 22 for the potentials u_i^h and u_f^h in harmonic approximation into eqs A5, we obtain a set of two coupled equations for the coordinates of the saddle point $\hat{R}$ and θ in harmonic approximation

$$\hat{\theta} = \frac{\Omega_i^2 \hat{R}}{(\Omega_i^2 - \Omega_f^2)\hat{R} + \Omega_f^2 \Delta R_0} \tag{B1}$$

$$\hat{\theta} = \frac{1}{2} + \frac{\Delta F}{2E_s} + \frac{E_r^h\, \Omega_f^2[(1-\hat{\theta})^2\Omega_i^2 - \hat{\theta}^2\Omega_f^2]}{2E_s[(1-\hat{\theta})\Omega_i^2 + \hat{\theta}\Omega_f^2]^2} \tag{B2}$$

They are reduced to eqs 26 and 27 if the following notations are introduced: $\nu = (\Omega_f/\Omega_i)^2$, $p = \nu E_r^h/2E_s$, $q = {}^1/_2 + \Delta F/2E_s$, and $E_r^h = \mu\Omega_i^2(\Delta R_0)^2/2$

Taking into account the relationship between $\hat{R}$ and θ (eq B1) and explicit form of the potentials u_i^h and u_f^h (eqs 21 and 22), we obtain for the second derivative of H

$$\left.\frac{d^2H}{d\theta^2}\right|_{\hat{\theta}} = -2\left\{E_s + 2E_r^h\left[\frac{\hat{R}}{\Delta R_0} + \nu\left(1 - \frac{\hat{R}}{\Delta R_0}\right)\right]\frac{\nu(2-\hat{\theta})}{(1-\hat{\theta}+\nu\hat{\theta})^2}\right\} \tag{B3}$$

The calculation of the second derivatives of u_i^h and f (eq A4) over R gives

$$\left.\frac{d^2u_i^h}{dR^2}\right|_{R_i^0} = \mu\Omega_i^2 \tag{B4}$$

$$\left.\frac{d^2f}{dR^2}\right|_{\hat{R}(\hat{\theta})} = (1-\hat{\theta})\mu\Omega_i^2 + \hat{\theta}\mu\Omega_f^2 \tag{B5}$$

Insertion of eqs B1 and B3−B5 into eqs A1 and A2 leads to eqs 23 and 24.

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