J. Phys. Chem. A **1999,** *103,* 1239−1249

SN_2 Interactions in Substitution Reactions and Dissociative Electron Transfer

A. M. Kuznetsov[†]

The A. N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences, Leninskii Prospect 31, Building 5, 117071 Moscow, Russia

Received: May 15, 1998; In Final Form: September 23, 1998

A model of two interacting states for the SN_2-substitution reactions and dissociative electron transfer is considered. It takes into account both direct SN_2 effects which are due to the interaction between the bonded and nonbonded molecular modes and indirect SN_2 effect emerged from the Franck−Condon principle. Various SN_2 effects and the applicability of the Condon approximation are discussed. Equations for the transitional configuration and activation barrier in classical limit are derived for the adiabatic reaction with arbitrary form of the molecular potentials. A general scheme is illustrated by a simple example of the Morse/exponential molecular potentials, and simple algorithms are presented allowing one to plot the dependence of the activation barrier on the driving force using standard PC programs.

1. Introduction

The SN_2-substitution reactions in polar solvents of the type

$$X^- + BY \rightarrow BX + Y^- \tag{1}$$

as well as the dissociative electron transfer (ET) reactions

$$X^- + BY \rightarrow X + B + Y^- \tag{2}$$

belong to one broad class of charge transfer processes in condensed media. They represent an extreme limit of ET reactions accompanied by a change of the intramolecular structure of the reactants. The attempts at theoretical description of the latter began soon after the theory of simple outer-sphere ET reactions was put forward.[1−4] Small changes of the intramolecular bond lengths were approached in harmonic approximation.[1,2] This allowed one to develop a theory for both classical[1] and quantum mechanical[2] behavior of the intramolecular vibrations for arbitrary number of the intramolecular degrees of freedom. The harmonic approximation is insufficient when the intramolecular reorganization is large. The theory was extended to the systems in which only one intramolecular chemical bond undergoes a large change of its length in the course of the electron transfer.[3,4] A rather general equation for the activation free energy barrier of a nonadiabatic reaction was given, in particular, in the classical limit for the intramolecular degrees of freedom[3,4]

$$F_a = [E_r + \Delta F - \Delta j]^2/4E_r + E_a(\Delta j) \tag{3}$$

where E_r is the reorganization energy of the inertial solvent polarization and intramolecular harmonic vibrational degrees of freedom, Δj the effective partial driving force for the anharmonic intramolecular degree of freedom, ΔF is the free energy of transition (the driving force for the whole process), and E_a is the activation barrier along the anharmonic intramolecular degree of freedom calculated as the energy of the crossing point Q^* of the intramolecular diabatic potential energy curves $u_i(Q)$ and $u_f(Q)$ at a given value of the partial driving force Δj along this degree of freedom

$$u_i(Q) = u_f(Q) + \Delta j \tag{4}$$

The value of Δj is determined by eq 5 (see a more detailed discussion in Appendix A)

$$\frac{1}{2} + \frac{\Delta F - \Delta j}{2E_r} = \frac{\partial E_a}{\partial \Delta j} = \alpha_l(\Delta j) \tag{5}$$

The second equality in eq 5 is in fact the definition of the partial symmetry factor α_l, for the intramolecular degree of freedom at arbitrary Δj value as a quantity characterizing the rate of variation of the activation barrier along this degree of freedom with the change of the corresponding partial driving force. This coincides with the symmetry factor α of the whole process at Δj value determined by eq 5. It was noted in ref 4 that if α_l for the intramolecular degree of freedom is constant, the same is true for the symmetry factor of the whole process α in spite of the parabolic form of the solvent diabatic free energy surfaces. Equation 5 shows the importance of α for the free energy relationships. This is important quantity also in other aspects. It is related with the geometrical symmetry of the transition state and with the symmetry of the distribution of the electron density at the transitional configuration (see Appendices A and C).

Equation 3 is valid for rather general case of the reorganization of one anharmonic intramolecular chemical bond including the limit when this bond is broken due to the electron transfer. More detailed forms of the activation barrier were obtained later with the use of specific intramolecular potentials.[5−7] In particular, sine-like potentials were used in ref 5 for the rotational intramolecular reorganization, and Morse/exponential potential (with the same parameters of anharmonicity and "dissociation" energy for the bonded and nonbonded states) for the dissociative ET in ref 6. Different rather simple equations were suggested recently in ref 7 for the case of arbitrary forms of the molecular potentials in the classical limit. In the first works on quantum mechanical theory of substitution reactions in solutions, a limiting case was considered which corresponds in fact to the neglect of the direct SN_2 interaction.[8] This resulted in rather

---

[†] E-mail: theor@servl.phyche.ac.ru. Fax: (007) (095) 955 08 46.

10.1021/jp9822539 CCC: $18.00

simple expressions for the activation barrier involving a number of parameters.[8]

Numerical calculation for a number of systems (see, e.g. ref 9, where the motion along two reactive modes was first considered for SN_2 reactions, and a recent one, ref 10) made possible a detailed general analysis taking into account both the SN_2 interactions and possible different role of the solvent polarization in the course of the reaction.[11,12] Recently, these systems were discussed[13] much in line with general physical approach of refs 11 and 12 but with the use of simple Morse/exponential model for the molecular potentials similar to that of Saveant.[6] In addition, only a part of the SN_2 interactions was taken into account in ref 13; in particular, the direct interaction between the two molecular degrees of freedom was ignored. (The refs 12 and 13 involve many references to other earlier theoretical models of SN_2-substitution reactions. In particular, pioneering works[14−18] and ref 19 should be mentioned where (semi)empirical approach was extensively developed).

Simple models used in refs 6 and 13 give attractive analytical expressions for the activation barrier. However, the molecular potentials obtained from quantum chemical calculations have in general a more complicated shape. The aim of the present paper is to derive more general equations which, being rather simple, would be applicable to the molecular potentials of rather arbitrary shape, including in particular Morse/exponential functions with different parameters of the potentials for the bonded and nonbonded states. This work is closely related to the studies by Kuznetsov[11,12] and Marcus[13] and the reader is referred to those for the details of the basic model and discussion of advantages and shortcomings of the two-states model (especially ref 13 for the latter; see also Appendix B).

The goals of the present paper are (1) to derive main equations determining the kinetic parameters and characteristics of the transition state, (2) to present a simple scheme for the numerical calculation of the free energy relationships, and (3) to give a systematic analysis of the role of various types of SN_2 interactions and approximations used in earlier studies. Therefore a numerical example in section 6 serves mainly for the purposes of illustration rather than as an example of detailed analysis of a concrete system, although the parameters used are rather typical for some reaction classes.

The paper is organized as follows. Section 2 summarizes the main features of the model for SN_2 reactions. The basic equations for the activation barrier and transitional configuration in the classical limit are derived in section 3. A Condon approximation is considered in section 4. Various SN_2 effects are discussed in section 5. Section 6 involves a simple example of the application of the general scheme to particular molecular potentials. Section 7 concludes the paper.

2. Summary of the Model for SN_2 Reactions

A substitution reaction (1) in a polar solvent is considered in this section in a two-interacting-states model. It is assumed that all three atomic groups X, B, and Y are located in a line in the course of the transition (linear complex) and their intramolecular structure is unchanged. We shall ignore the vibrational entropy contribution referring to ref 13 and will focus on the configurational Gibbs free energy barrier for the transition from the reactants' "encounter complex" R to the products' "encounter complex" P.

The two-state model[11−13] will be used below with the introduction of the diabatic Gibbs free energy surfaces. The reaction is assumed to proceed in the adiabatic regime, i.e., the electron resonance integral V_e is sufficiently large. The criteria may be found in refs 4 and 20. In most cases the fulfillment of the inequality

$$V_e > k_B T \tag{6}$$

is sufficient.

According to refs 11 and 12, the diabatic Gibbs free energy surfaces of the initial (i ≡ R) and final (f ≡ P) states in the two-state model may be written as follows:

$$U_i(x,y,q_k) = U_R^S(q_k,x) + U_R(x,y)$$
$$U_f(x,y,q_k) = U_P^S(q_k,y) + U_P(x,y) + \Delta F \tag{7}$$

where $U_R^S(q_k,x)$ and $U_P^S(q_k,y)$ are the Gibbs free energy surfaces for the inertial solvent polarization in the initial, R, and final, P, states, $U_R(x,y)$ and $U_P(x,y)$ are the molecular potentials, and ΔF is the free energy of the transition (the driving force). Here x and y are the distances between the groups X and B, and B and Y, respectively. x varies from $-\infty$ to 0 and y from 0 to ∞, and the equilibrium free energy of the initial state is chosen to be zero, all the energy difference between the final and initial equilibrium states being included in ΔF.

The inertial polarization will be described in the framework of the effective Hamiltonian method[4,20] as a set of harmonic oscillators with dimensionless normal coordinates q_k and frequencies ω_k. (Introduced in ref 21, this method became widely known due to works by Caldeira and Leggett.[22]) Since the charge is located in the initial state on the group X, and in the final state on the group Y, the equilibrium polarization values in these states depend on x and y, respectively, and $U_R^S(q_k,x)$ and $U_P^S(q_k,x)$ may be written as follows:

$$U_R^S(q_k,x) = {}^1/_2\sum_k \hbar\omega_k[q_k - q_{k0}^R(x)]^2$$
$$U_P^S(q_k,y) = {}^1/_2\sum_k \hbar\omega_k[q_k - q_{k0}^P(y)]^2 \tag{8}$$

where the equilibrium coordinates of the effective oscillators depend on x and y. The equilibrium solvation free energies of the reaction complex

$$F_R^S(q_k,x) = -{}^1/_2\sum_k \hbar\omega_k[q_{k0}^R(x)]^2 \tag{9}$$

$$F_P^S(q_k,y) = -{}^1/_2\sum_k \hbar\omega_k[q_{k0}^P(y)]^2 \tag{10}$$

are included in molecular potentials (see eq 11 below).

Throughout the paper we assume that the molecular potentials are known either from quantum mechanical calculations or from some model considerations (see, e.g. ref 10 and 14−19). If we neglect the direct interaction between the nonbonded and bonded modes, they may be written in the form

$$U_R^0(x,y) = V_X^0(x) + F_R^S(q_k,x) + u_{BY}^0(y - y_0)$$
$$U_P^0(x,y) = V_Y^0(y) + F_R^S(q_k,y) + u_{BX}^0(x - x_0) \tag{11}$$

where the first terms on the right-hand side are the interactions of the nonbonded groups with the corresponding "rigid" molecule, and the last terms are the intramolecular potentials of the isolated molecules with x_0 and y_0 as the equilibrium bond lengths. This is the approximation used in fact in refs 8 and 13. The direct interaction of the nonbonded and bonded modes produces two effects:[11,12] (1) "polarization" of the molecule by the nonbonded group resulting in a dependence of the equilibrium chemical bond length on the coordinate of the nonbonded group, $y_R(x)$ and $x_P(y)$, and (2) a decrease of the energy by a quantity δV_X (and δV_Y) as compared to that for the case of "rigid" molecule resulting in a softening of the potentials $V_X(x)$ and $V_Y(y)$:

$$\begin{aligned} U_R(x,y) &= V_X(x) + u_{BY}(y - y_R(x)) \\ U_P(x,y) &= V_Y(y) + u_{BX}(x - x_P(y)) \end{aligned} \tag{12}$$

where $V_X(x)$ and $V_Y(y)$ include now both the equilibrium solvation free energies $F_R^S(q_k,x)$ and $F_P^S(q_k,y)$ and the terms δV_X and δV_Y. The latter can be represented in an analytical form if the harmonic approximation is used for the intramolecular vibrations.[11,12]

The softening of the potentials $V_X(x)$ and $V_Y(y)$ due to the direct interaction of the x- and y-modes results in a lowering of the activation barrier and will be called "quasi-equilibrium" SN_2 effect. The model described by eqs 7, 8, and 12 has been suggested in refs 11 and 12 and will be used below in a general scheme.

The adiabatic Gibbs free energy surfaces are constructed from eqs 7 in the usual way

$$U = {}^1/_2[U_i + U_f \pm \{(U_i - U_f)^2 + 4V_e^{\,2}\}^{1/2}] \tag{13}$$

where the sign minus refers to the lower and the sign plus to upper adiabatic free energy surface.

The electron resonance integral V_e depends on the positions of the incoming and outgoing groups. A simple factorized exponential form has been suggested in ref 11

$$V_e = V_0 e^{-\gamma_x\epsilon_x(x-x_0)-\gamma_y\epsilon_y(y-y_0)} \tag{14}$$

where the orbital exponents $\gamma_x\epsilon_x$ and $\gamma_y\epsilon_y$ are in general different. The dimensionless factors ϵ_x and ϵ_y are introduced here for the sake of convenience in view of application of the model to specific molecular potentials (see section 6 where the Morse-like molecular potentials are used with γ_x and γ_y characterizing the rate of their variation). In fact, we shall use a more specific form

$$V_e = V_0 e^{-\gamma_x\epsilon_x(x-x_P(y))-\gamma_y\epsilon_y(y-y_R(x))} \tag{15}$$

The effect which is due to the dependence of V_e on x and y will be referred to as the non-Condon SN_2 effect. The values of the parameters V_0, $\gamma_x\epsilon_x$ and $\gamma_y\epsilon_y$ can be found in principle from quantum chemical calculations.

The model in its present form is more appropriate for strongly polar solvents. With some modifications it can be extended to low-polar or nonpolar solvents. In particular, the effect of ion pairing must be included into consideration.

3. Activation Barrier in the Classical Limit

The activation barrier in the classical limit is determined by the saddle point on the lower adiabatic free energy surface (eq 13). The equations for the saddle point have the form (see Appendix B)

$$\begin{aligned} (1-\alpha)\frac{\partial U_i}{\partial x} + \alpha\,\frac{\partial U_f}{\partial x} &= 2\frac{\partial V_e}{\partial x}[\alpha(1-\alpha)]^{1/2} \\ (1-\alpha)\frac{\partial U_i}{\partial y} + \alpha\,\frac{\partial U_f}{\partial y} &= 2\frac{\partial V_e}{\partial y}[\alpha(1-\alpha)]^{1/2} \end{aligned} \tag{16}$$

$$U_i - U_f = \frac{(2\alpha - 1)V_e}{[\alpha(1-\alpha)]^{1/2}} \tag{17}$$

where the symmetry factor α is determined as follows

$$\alpha = \frac{\partial U_i/\partial q_k}{\partial U_i/\partial q_k - \partial U_f/\partial q_k} \tag{18}$$

The symmetry factor defined by eq 18 characterizes the geometrical symmetry of the transitional configuration for the solvent polarization and harmonic intramolecular degrees of freedom, being the ratio of the slopes of the diabatic free energy surfaces along these reactive modes. However, the latter is not the case for the molecular coordinates x and y due to the presence of the terms in the right-hand side of eqs 16. Due to this fact, the symmetry factor introduced does not characterize anymore the variation of the activation free energy as a function of the free energy of the transition for the adiabatic reaction (see eqs 43 and 44 below and Appendix C).

Equation 18 in fact determines the values of the normal coordinates of the effective oscillators for the medium polarization at the saddle point at a given α whereas eqs 16 determine the values of x and y, and the symmetry factor may be found from eq 17. With the aid of eqs 7 and 8 eqs 16 can be transformed as follows (see Appendix B)

$$\begin{aligned} &(1-\alpha)\frac{\partial V_X}{\partial x} - \alpha(1-\alpha)\frac{\partial E_r(x,y)}{\partial x} + (1-\alpha)\frac{\partial u_{BY}}{\partial x} + \alpha\frac{\partial u_{BX}}{\partial x} = \\ &\qquad 2\frac{\partial V_e}{\partial x}[\alpha(1-\alpha)]^{1/2} \\ &(1-\alpha)\frac{\partial u_{BY}}{\partial y} - \alpha(1-\alpha)\frac{\partial E_r(x,y)}{\partial y} + \alpha\frac{\partial u_{BX}}{\partial y} + \alpha\frac{\partial V_Y}{\partial y} = \\ &\qquad 2\frac{\partial V_e}{\partial y}[\alpha(1-\alpha)]^{1/2} \end{aligned} \tag{19}$$

where we used the relationships

$$\begin{aligned} \frac{\partial U_R^S(q_k,x)}{\partial x} &= -\alpha\frac{\partial E_r(x,y)}{\partial x} \\ \frac{\partial U_P^S(q_k,y)}{\partial y} &= -(1-\alpha)\frac{\partial E_r(x,y)}{\partial y} \end{aligned} \tag{20}$$

which follow from the definition of the reorganization energy for the solvent polarization[11]

$$E_r(x,y) = {}^1/_2\sum_k \hbar\omega_k[q_{k0}^R(x) - q_{k0}^P(y)]^2 \tag{21}$$

with the use of eqs 8 and 18. Note that the reorganization energy depends here on the positions of the groups X and Y.[11] This dependence is rather weak as compared to that for the other terms in eqs 19, and the terms involving the reorganization energy in eqs 19 will be omitted in what follows. However, this dependence should be taken into account in general in equations for the symmetry factor (eq 17) and for the activation barrier. The latter can be written as follows (Appendix B)

$$F_a^{\text{forward}} = U_i(x^s,y^s,q_k^s) - \delta F_a = U_i(x^s,y^s,q_k^s) - V_e(x^s,y^s)\left[\frac{\alpha}{1-\alpha}\right]^{1/2} \qquad (22)$$

where the superscript s denotes the values of the coordinates at the saddle point, and the free energy of the initial equilibrium state is chosen to be zero (see eq 7). This expression differs from an approximate form used in refs 4 and 23 by a more exact calculation of the saddle point and the symmetry factor. This form is convenient for the forward reaction. The corresponding expression for the backward reaction has the form

$$F_a^{\text{backward}} = U_f - V_e\left[\frac{1-\alpha}{\alpha}\right]^{1/2} - \Delta F \qquad (23)$$

Using eqs 7, 8, and 12 we can transform eq 22 to the final form

$$F_a^{\text{forward}} = \alpha^2 E_r(x^s,y^s) + V_X(x^s) + u_{BY}(y^s - y_R(x^s)) - V_e(x^s,y^s)\left[\frac{\alpha}{1-\alpha}\right]^{1/2} \qquad (24)$$

In a similar way eq 17 can be transformed as follows (Appendix B)

$$\Delta F = (2\alpha - 1)E_r(x,y) + V_X(x) - V_Y(y) + u_{BY}(y - y_R(x)) - u_{BX}(x - x_P(y)) + \frac{(2\alpha-1)V_e(x,y)}{[\alpha(1-\alpha)]^{1/2}} \qquad (25)$$

Finally, omitting the terms involving the solvent reorganization energy in eqs 19, we obtain approximately

$$(1-\alpha)\frac{\partial V_X}{\partial x} + (1-\alpha)\frac{\partial u_{BY}}{\partial x} + \alpha\frac{\partial u_{BX}}{\partial x} = 2\frac{\partial V_e}{\partial x}[\alpha(1-\alpha)]^{1/2}$$

$$(1-\alpha)\frac{\partial u_{BY}}{\partial y} + \alpha\frac{\partial u_{BX}}{\partial y} + \alpha\frac{\partial V_Y}{\partial y} = 2\frac{\partial V_e}{\partial y}[\alpha(1-\alpha)]^{1/2} \qquad (26)$$

The presence of the terms in the right-hand side of eq 26 involving the x- and y-derivatives of the electron matrix element is responsible for the non-Condon SN_2 effect.

Equations 25 and 26 represent a complete set of equations for the determination of the transitional configuration for so far arbitrary molecular potentials. In fact the solution of only two equations (26) is sufficient if we want to plot the activation free energy (eq 24) as a function of the free energy of the transition ΔF. Equations 24−26 give then a parametric dependence of the activation free energy on the free energy of the transition with α as running variable. The calculational procedure is as follows. We fix α and solve eqs 26 for x^s and y^s. Then using eqs 24 and 25 we calculate F_a and ΔF. More simple algorithms can be elaborated for some specific molecular potentials and standard programs available for PC can be used (see section 6).

4. Condon Approximation

Condon approximation in the nonadiabatic reactions corresponds to the neglect of the dependence of the electron matrix element on the vibrational coordinates while calculating the Franck−Condon factors. This does not mean that the dependence of the electron matrix element on the coordinates of nuclear modes is entirely neglected. The electron matrix element is calculated then at the transitional configuration (which in classical limit corresponds to the saddle point on the free energy surfaces) and this value is used for the calculation of the transition probability. It may differ significantly from the values of the electron matrix element at the initial or final equilibrium configurations. A change of the position of the saddle point (either due to the variation of the driving force or in the reaction series) produces then the variation of the electron matrix element. A similar approximation for the adiabatic reaction consists of the neglect of the terms in the right-hand side of eqs 26 (whereas the dependence of the electron matrix element on the position of the saddle point in eqs 24 and 25, i.e., $V_e(x^s,y^s)$, is kept)

$$(1-\alpha)\frac{\partial V_X}{\partial x} + (1-\alpha)\frac{\partial u_{BY}}{\partial x} + \alpha\frac{\partial u_{BX}}{\partial x} = 0$$

$$(1-\alpha)\frac{\partial u_{BY}}{\partial y} + \alpha\frac{\partial u_{BX}}{\partial y} + \alpha\frac{\partial V_Y}{\partial y} = 0 \qquad (27)$$

Th symmetry factor α can be then excluded from eqs *27* and we end up with one equation relating x and y. Thus the solution of the latter is sufficient if we want to plot the activation energy as a function of the free energy of the transition with x or y as running variable. Doing so, one has to control the fulfillment of eq 6. If it is violated, the reaction switches to the nonadiabatic regime and the electron resonance integral is moved from the activation energy to the preexponential factor.

Note that in Condon approximation the meaning of the symmetry factor is the same both for the solvent coordinates q_k and for the molecular coordinates x and y as the ratio of the slopes of the diabatic free energy surfaces.

5. SN_2 Interactions in the Substitution Reactions and Dissociative Electron Transfer

5.1. Substitution Reactions. If the molecular potentials are rather steep as compared to the x,y dependence of the electron resonance integral, the Condon approximation may be quite sufficient for the substitution reactions since the transitional configuration is then rather close to the equilibrium bond lengths in the molecules XB and BY. Note, however, that although the non-Condon SN_2 effect in Condon approximation is excluded from eqs 27 for the saddle point, the value of the electron matrix element at this point is used in the expression for the activation energy. Therefore, if the position of the saddle point varies in the series of reactions, the value of the electron resonance integral will also vary within the Condon approximation. Moreover eqs 27 still involve other SN_2 effects.

Generally speaking, the SN_2 interactions are reflected in eqs 27 (as well as in general eqs 26) in the fact that eqs 27 represent a set of coupled equations for x and y. The coupling of eqs 27 is caused by two factors: (1) the dependence of the chemical bond lengths of bonded groups on the position of the nonbonded groups and (2) the presence of the symmetry factor α in both equations. (Additional coupling of eqs 26 is due to the electron matrix element in the right-hand side.)

The first factor is the reason for two SN_2 effects: (i) quasi-equilibrium SN_2 effect manifested in the lowering of the activation barrier due to mutual polarization of the reaction partners in the initial and final states while the transitional configuration is determined by the self-consistently determined equilibrium bond lengths, and (ii) nonequilibrium SN$_2$ effect resulting in a self-consistently determined transitional configuration which differs from the self-consistent equilibrium bond lengths (see below).

The second factor (related with α) is the reason for the SN$_2$ effect which may exist even in the absence of the first two. It may be called the Franck–Condon SN$_2$ effect. The reason for this notion is as follows. The symmetry factor coupling the first and second equation in eq 27 obeys eq 25. The latter for nonadiabatic reactions reduces to the Franck–Condon condition $U_i = U_f$ (see also eq 17).

Equations 27 can be analyzed in a general form for some limiting cases. First, we note that the dependence of u_{BX} on y and u_{BY} on x is due to the corresponding dependence of the equilibrium length of the chemical bond of the bonded group. If the potentials V_X and V_Y for the nonbonded groups are soft as compared to u_{BX} and u_{BY}, the first term in the first equation and the last term in the second equation in eqs 27 may be omitted and eqs 27 can be reduced to

$$\frac{\partial u_{BX}}{\partial x} = 0; \quad \frac{\partial u_{BY}}{\partial y} = 0 \tag{28}$$

i.e., to two coupled equations[11]

$$x = x_P(y); \quad y = y_R(x) \tag{29}$$

The transitional configuration is thus determined by the equilibrium lengths of the chemical bonds X–B and B–Y. However, these bond lengths are not equal in general to those in isolated molecules (x_0 and y_0) but must be calculated self-consistently with due account of the interaction with the reaction partner.

The vibrations of the chemical bonds X–B and B–Y are not excited in this limit (i.e., $u_{BY}(y^s - y_R(x^s)) = 0$ in eq 24) and only non-Condon SN$_2$ effect and quasi-equilibrium SN$_2$ effect operate. If the latter may be neglected (i.e., $x^s \approx x_0$; $y^s \approx y_0$), we arrive at a particular case considered in ref 8.

A simple model illustration for eqs 29 is obtained in the case of the exponential form for the dependence of the equilibrium bond length of the bonded group on the position of the nonbonded group suggested in ref 11

$$x_P(y) = x_0 + \lambda_x b_x e^{-(y-y_0)/\lambda_x}$$

$$y_R(x) = y_0 + \lambda_y b_y e^{-(x-x_0)/\lambda_y} \tag{30}$$

Assuming that $x - x_0$ and $y - y_0$ are small near the transitional configuration, we obtain the solution of eqs 29 as follows

$$x^s - x_0 = \{x_P(y_0) - x_0 - b_x[y_R(x_0) - y_0]\}/(1 - b_x b_y)$$

$$y^s - y_0 = \{y_R(x_0) - y_0 - b_y[x_P(y_0) - x_0]\}/(1 - b_x b_y) \tag{31}$$

If other terms in eqs 27 may not be neglected (e.g., due to a steep form of the repulsive potentials of the nonbonded groups), their solution will differ from eq 29

$$x^s < x_P(y^s); \quad y^s > y_R(x^s) \tag{32}$$

All the terms in the activation barrier (24) are then nonzero. Equations 32 mean that the transitional configuration corresponds to elongated chemical bond of the bonded group Y as compared to the equilibrium configuration $y_R(x^s)$ at a given position x^s of the incoming group. On the other hand, the incoming group approaches the molecule to the distance x^s exceeding the equilibrium length $x_P(y^s)$ of the chemical bond to be formed at a given position y^s of the outgoing group. The vibrations of the chemical bond to be broken and the chemical bond to be formed are thus excited. Since x^s and y^s are determined self-consistently with due account of the interaction of both molecular modes, we have nonequilibrium SN$_2$ effect, and since the transitional configuration depends in general on α, the Franck–Condon SN$_2$ effect also takes place. It should be emphasized that these effects do not exclude the existence of the quasi-equilibrium SN$_2$ effect since the chemical bonds are elongated as compared to their equilibrium configurations in the presence of the reaction partner (eq 29).

5.2. Dissociative Electron Transfer. Equations derived in Condon approximation in section 3 are formally the same also for the dissociative electron transfer (eq 2). The physical situation, however, is different here from the substitution reactions in that the electron transfer does not lead to the formation of the chemical bond B–X. This is reflected in the shape of the potential u_{BX} which is also repulsive here. The solution of eqs 27 for y^s gives the values not far from y_0. Therefore, the Condon approximation may be sufficient with respect to the dependence of V_e on y. However, the first equation in (27) demonstrates the inapplicability of the Condon approximation with respect to its x dependence since the solutions for x^s in Condon approximation give usually large values. This may be easily seen if the repulsive potentials for the X group in the initial and final states are identical, $u_{BX} \equiv V_X$, and the quasi-equilibrium SN$_2$ effect can be neglected (i.e., the second term in the first equation in (27) may be omitted). This equation is then reduced to

$$\partial V_X/\partial x = 0 \tag{33}$$

with the solution $x \rightarrow -\infty$.

This means that the x dependence of V_e may not be ignored and the first equation in (27) is inapplicable. Instead, we have to calculate the transition probability at any fixed x value and then to average it with the distribution function $\sim\exp(-V_X/k_BT)$ as in ordinary electron transfer reactions. For the adiabatic reactions this averaging leads to a minimum value of the activation free energy

$$\frac{d}{dx}\left[\alpha^2 E_r(x,y^s(x)) + V_X + u_{BY}(y^s(x) - y_R(x)) - V_e(x,y^s(x))\left(\frac{\alpha(x)}{1-\alpha(x)}\right)^{1/2}\right] = 0 \tag{34}$$

The SN$_2$ interactions are taken into account in eq 34 in that all the quantities involved depend on x. The potentials of the B–X interaction appear here as usual work terms (see e.g. eq 25) and may be straightforwardly introduced into equations of ref 7.

6. Simple Example

For the purpose of illustration of the application of the above scheme we consider below a simple example of the Morse/exponential functions for the molecular potentials. A detailed analysis of specific systems would require a special study. Therefore, that analysis and other examples of molecular potentials will be given in a separate paper. However, in the discussion below we shall refer to the systems such as X^-/CH_3Y (with Cl, Br, and I as X and Y) or X^-/t-BuY (where t-Bu is $(CH_3)_sC$) for which some calculations in solutions exist.[24−26] For example, the molecular potentials for t-BuY and t-BuY$^-$ were calculated in dimethylformamide by PM3 quantum chemical method in refs 24 and 25. The effect of the polar solvent was taken into account in the continuum approximation using Chudinov et al. modification[27] of the self-consistent reaction field theory.[28] It was found in particular that the potentials for stable molecule can be approximated by the Morse curves with D in the range between 1.5 and 3.5 eV. The repulsive potential for the anion t-BuY$^-$ may be approximated by the exponential functions in the case of Y = Cl and Br. However, the parameters of these curves are significantly different from those describing the corresponding Morse potentials. The exponential fit is much worse for Y = I. Qualitatively similar results were obtained for alkyl halides.[26] For example, the preexponential factor in the repulsive potential for CH_3Cl^- was estimated as 34.8 kcal/mol as compared to the dissociation energy of the neutral molecule 78 kcal/mol.[26] The calculation of the outer-sphere reorganization energy E_r is rather complicated here as compared to the electron transfer between simple spherical ions due to a complicated shape of the solvent cavity surrounding the reaction complex. It can be estimated with the use of the calculational methods of Tomasi et al.[28,29] and Basilevskii et al.[27,30,31] which are specially developed for the calculation of the solvent contribution in such complicated geometry. For the reactions under discussion E_r should not be large. The theory predicts even very small (practically zero) values[12] which agree with calculations for some systems.[23,31,32] Therefore in all calculations we accepted the value 0.3 eV for E_r.

Similar to refs 6 and 13 for the purpose of illustration we shall assume that the dissociation energies and anharmonicity parameters for the atomic groups in bonded and nonbonded states are identical, i.e.

$$U_R(x,y) = D_x e^{-2\gamma_x[x-x_P(y)]} + D_y(1 - e^{-\gamma_y[y-y_R(x)]})^2$$

$$U_P(x,y) = D_y e^{-2\gamma_y[y-y_R(x)]} + D_x(1 - e^{-\gamma_x[x-x_P(y)]})^2 \quad (35)$$

For this model the dimensionless parameters ϵ_x and ϵ_y in eqs 14 and 15 determine the rate of the variation of the electron matrix element as compared to that of the molecular potentials.

The model of eqs 35 differs from that of Saveant−Marcus[6,13] only in the fact that the equilibrium bond lengths are allowed to depend on the position of the nonbonded groups. Since the repulsion potentials in this model depend on both coordinates, we have to use general eqs 16 and 17. Introducing new notations

$$X(x,y) = e^{-\gamma_x[x-x_P(y)]}; \quad Y(x,y) = e^{-\gamma_y[y-y_R(x)]} \quad (36)$$

we can transform these equations as follows

$$D_xX^2 - \alpha D_xX = [\alpha(1-\alpha)]^{1/2}V_0\epsilon_xX^{\epsilon_x}Y^{\epsilon_y}$$

$$D_yY^2 - (1-\alpha)D_yY = \frac{\epsilon_y}{\epsilon_x}D_x(X-\alpha)X \quad (37)$$

$$\Delta F = (2\alpha - 1)E_r(X,Y) + D_y(1-2Y) - D_x(1-2X) + \frac{(2\alpha-1)}{[\alpha(1-\alpha)]^{1/2}}V_0X^{\epsilon_x}Y^{\epsilon_y} \quad (38)$$

The equation for the activation free energy takes the form

$$F_a = \alpha^2E_r(X,Y) + D_xX^2 + D_y(1-Y)^2 - \left[\frac{\alpha}{1-\alpha}\right]^{1/2}V_0X^{\epsilon_x}Y^{\epsilon_y} \quad (39)$$

It is worth noting that the dependence of the equilibrium bond lengths on x and y do not appear here explicitly and is hidden in X and Y. Therefore, the values of X and Y at the transitional configuration (being different from 1) take into account also nonequilibrium SN_2 effect, non-Condon effect, and Franck−Condon SN_2 effect.

Substituting the solution for Y from the second equation of eqs 37

$$Y = \frac{1}{2}\left[1 - \alpha + \left\{(1-\alpha)^2 + 4\frac{D_x\epsilon_y}{D_y\epsilon_x}(X-\alpha)X\right\}^{1/2}\right] \quad (40)$$

into the first equation in (37) we end up with one equation for X

$$D_xX^2 - D_x\alpha X = [\alpha(1-\alpha)]^{1/2}V_0\epsilon_xX^{\epsilon_x}\left\{\frac{1}{2}\left[1 - \alpha + \left((1-\alpha)^2 + 4\frac{D_x\epsilon_y}{D_y\epsilon_x}(X-\alpha)X\right)^{1/2}\right]\right\}^{\epsilon_y} \quad (41)$$

which can be solved at each α.

Condon approximation corresponds to the neglect of the terms in the right-hand sides of eqs 37 and gives

$$X = \alpha; \quad Y = 1 - \alpha \quad (42)$$

Equations 38 and 39 take then the form

$$\Delta F = (2\alpha - 1)[D_x + D_y + E_r(\alpha,1-\alpha)] + V_0\frac{2\alpha-1}{[\alpha(1-\alpha)]^{1/2}}\alpha^{\epsilon_x}(1-\alpha)^{\epsilon_y} \quad (43)$$

$$F_a = \alpha^2[D_x + D_y + E_r(\alpha,1-\alpha)] - V_0\left[\frac{\alpha}{1-\alpha}\right]^{1/2}\alpha^{\epsilon_x}(1-\alpha)^{\epsilon_y} \quad (44)$$

$$V_e = V_0\alpha^{\epsilon_x}(1-\alpha)^{\epsilon_y} \quad (45)$$

The main goals of the use of the Condon approximation here are to see how large may be deviations of the results by eqs 42−45 from the exact ones (by eqs 38−41) and to compare the above results with those of ref 13 which in the notation of the present paper can be written as follows

$$\Delta F = (2\alpha - 1)[D_x + D_y + E_r(\alpha,1-\alpha)] \quad (46)$$

$$F_a = \alpha^2[D_x + D_y + E_r(\alpha,1-\alpha)] - V_0\alpha^{\epsilon_x}(1-\alpha)^{\epsilon_y} \quad (47)$$

with $\epsilon_x = \epsilon_y$.

The approximation corresponding to eqs 46 and 47 will be referred to below as a crude Condon approximation. Comparison of eqs 46−47 and eqs 43−44 shows that the difference consists of the form of the last term in eqs 44 and 47 and the absence of the last term in eq 46 as compared to eq 43. It should be emphasized that both Condon approximation and crude Condon approximation take into account the deviation of α from $^1/_2$ and therefore the variation of the electron matrix element with the driving force (via the variation of the position of the saddle point). Note that the derivative of F_a over ΔF is reduced to α

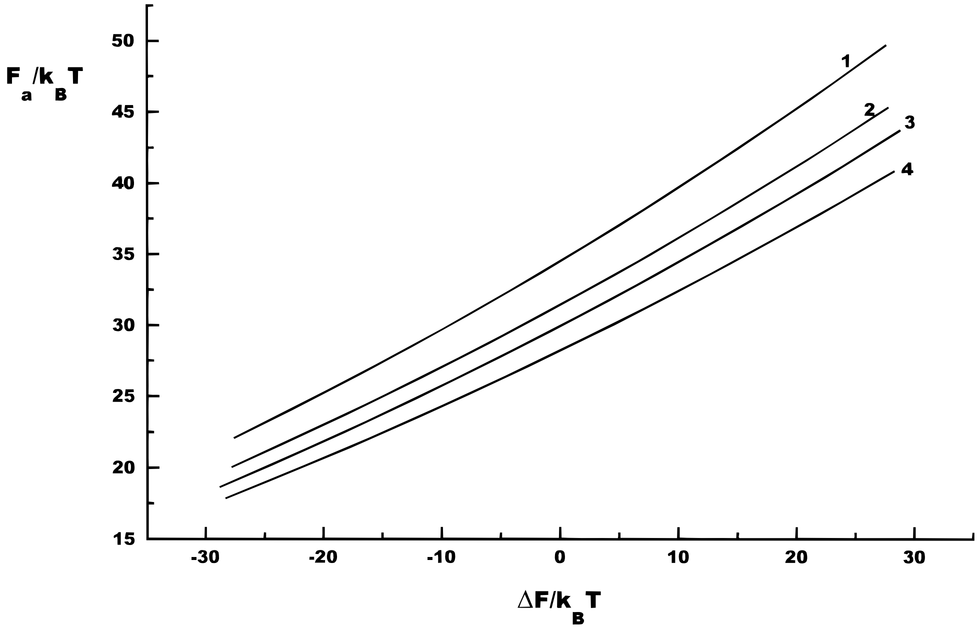

Figure 1. Dependence of the activation free energy on the driving force (in the units of $k_BT = 0.025$ eV). Calculations according to eqs 38−41. For all curves $E_r = 0.3$ eV. (1) $V_0 = 0$ eV, $\epsilon_x = \epsilon_y = 0.5$, $D_x = D_y = 1.5$ eV; (2) 0.15 eV, 0.5, 1.5 eV; (3) 0.15 eV, 0.2, 1.5 eV; (4) 0.3 eV, 0.5, 1.5 eV.

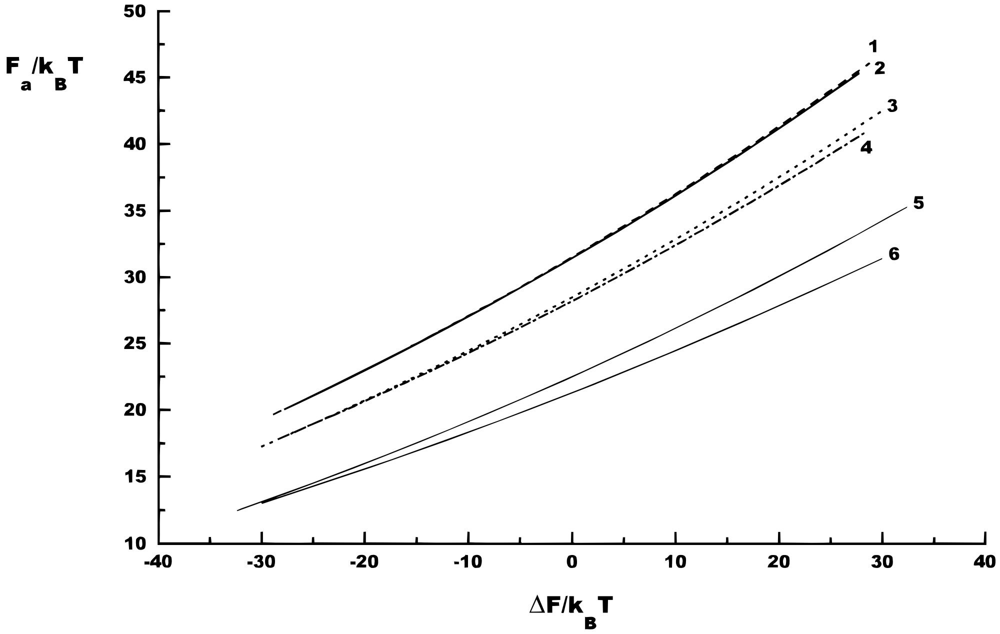

Figure 2. Comparison of exact calculation (eqs 38−41, curves 2, 4, and 6) with that in Condon approximation (eqs 42−45, curves 1, 3, and 5). (1) $V_0 = 0.15$ eV, $\epsilon_x = \epsilon_y = 0.5$, $D_x = D_y = 1.5$ eV; (2) 0.15 eV, 0.5, 1.5 eV; (3) 0.3 eV, 0.5, 1.5 eV; (4) 0.3 eV, 0.5, 1.5 eV; (5) 0.6 eV, 0.5, 1.5 eV; (6) 0.6 eV, 0.5, 1.5 eV.

only if the last terms in eqs 43, 44, and 47 and the dependence of the reorganization energy on α is neglected. The results of calculations of the activation energy as a function of ΔF according to eqs 38−41 in comparison with the results of the Condon approximation (eqs 42−45) and crude Condon approximation (eqs 46−47) are shown in Figures 1−3. The corresponding variations of the electron matrix element are shown in Figure 4. Figure 5 shows the variation of the term δF_a responsible for the lowering of the activation barrier due to resonance splitting of the free energy surfaces. It should be emphasized that the parameters of the Morse/exponential curves were kept constant under the variation of the driving force ΔF. The value 1.5 eV for D was chosen to be in the range between the values of the preexponential factor and dissociation energies for the systems of this type. The values of the dimensionless parameters ϵ_x and ϵ_y were chosen to be usually smaller than 1 since one may expect that the electron matrix element varies slower than the molecular potentials. Their change from 0.2 to 0.5 allowed one to see the effect of different rate of the variation of electron matrix element on the kinetic parameters. The values of V_0 chosen provide the adiabatic regime at equilibrium lengths of chemical bonds. Recent estimates[32] show that the electronic coupling is not large (~0.2 eV). However, higher values (~0.5 eV) obtained for some similar systems are feasible. Exact values of the parameters can be obtained in principle from quantum chemical calculations. It is worth emphasizing that both model potentials and those obtained in semiempirical[9,14−18,19] or ab initio calculations[10] as well as various values of the electron

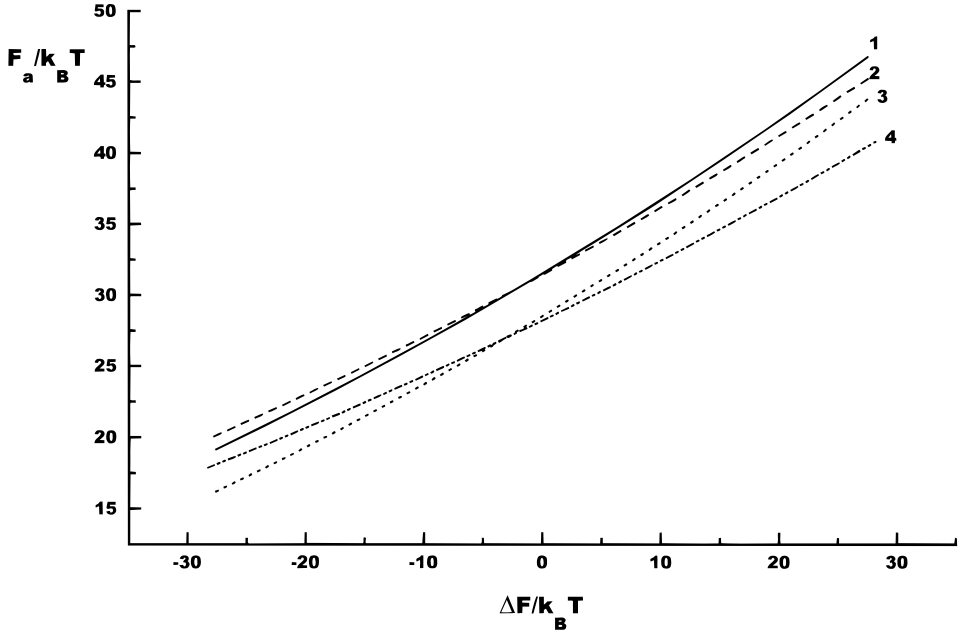

Figure 3. Comparison of exact calculation (eqs 38−41, curves 2 and 4) with that in crude Condon approximation (eqs 46−47, curves 1 and 3). (1) $V_0 = 0.15$ eV, $\epsilon_x = \epsilon_y = 0.5$, $D_x = D_y = 1.5$ eV; (2) 0.15 eV, 0.5, 1.5 eV; (3) 0.3 eV, 0.5, 1.5 eV; (4) 0.3 eV, 0.5, 1.5 eV.

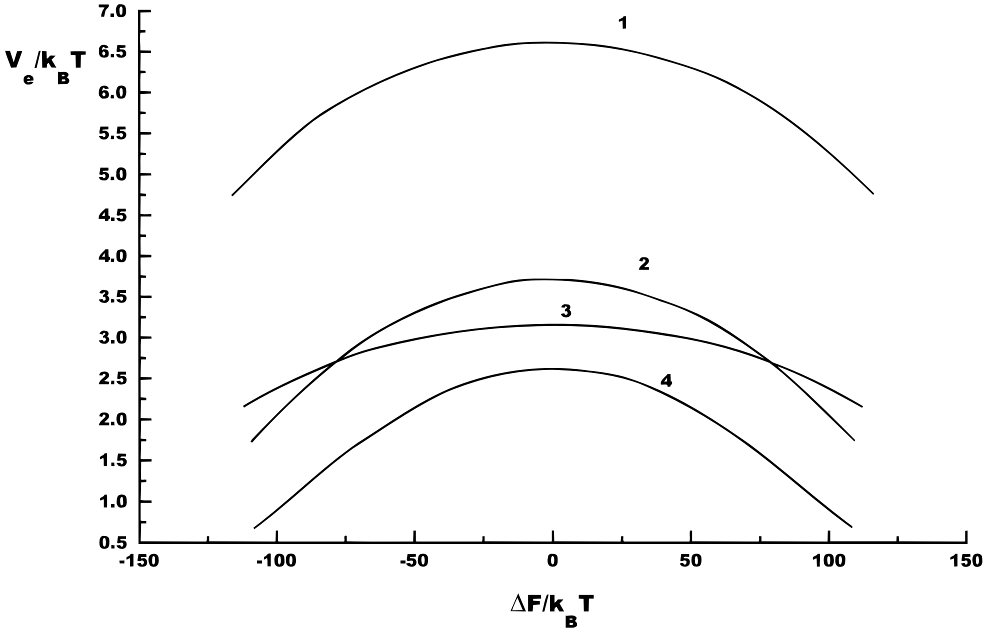

Figure 4. Dependence of the electron matrix element at the transitional configuration on the driving force. (1) $V_0 = 0.3$ eV, $\epsilon_x = \epsilon_y = 0.5$, $D_x = D_y = 1.5$ eV; (2) 0.3 eV, 1, 1.5 eV; (3) 0.15 eV, 0.5, 1.5 eV; (4) 0.375 eV, 1.5, 1.5 eV.

matrix element may be used in the calculational scheme suggested in the present paper. The values of V_0 chosen in the calculations below are aimed to show the qualitative tendencies rather than to give exact estimates for a concrete system. Figures 1 and 5 show that the resonance splitting of the free energy surfaces leads to a considerable decrease of the activation barrier (see curves 2−4 in Figure 1, as compared to curve 1, and curves in Figure 5). For the system with identical groups X and Y (but different driving forces) the exact results are rather close to those obtained in Condon approximation (i.e., with the neglect of the terms in the right-hand sides of eqs 37) (see Figure 2). However, crude Condon approximation (see eqs 46 and 47) leads to larger deviations from the exact results (Figure 3). Figure 4 shows the variation of the electron matrix element in the broad range of the free energy of the transition ΔF. It may be seen that a noticeable drop of electron matrix element takes place only in the region of large absolute values of ΔF. However, even in this region it does not usually cross the critical value $V_e = k_BT$ separating adiabatic and nonadiabatic regions and reaction remains adiabatic (curve 4 represents an exception corresponding to a rather strong dependence of the electron matrix element on the nuclear coordinates, $\epsilon_x = \epsilon_y = 1.5$). The variation of electron matrix element in the ΔF range corresponding to Figures 1−3 and 5 is rather small. The examination of Figure 4 shows then that the major variation of the term δF_a responsible for the resonance lowering of the activation barrier is due to the variation of the square root factor depending on the symmetry factor (see the last term in the right-hand side of eqs 22 and 39).

It is worth noting that the variation of electron matrix element (curves 1−3 in Figure 4) in the $\Delta F/k_BT$ interval between −30 and 30 does not exceed 5% whereas the activation barrier

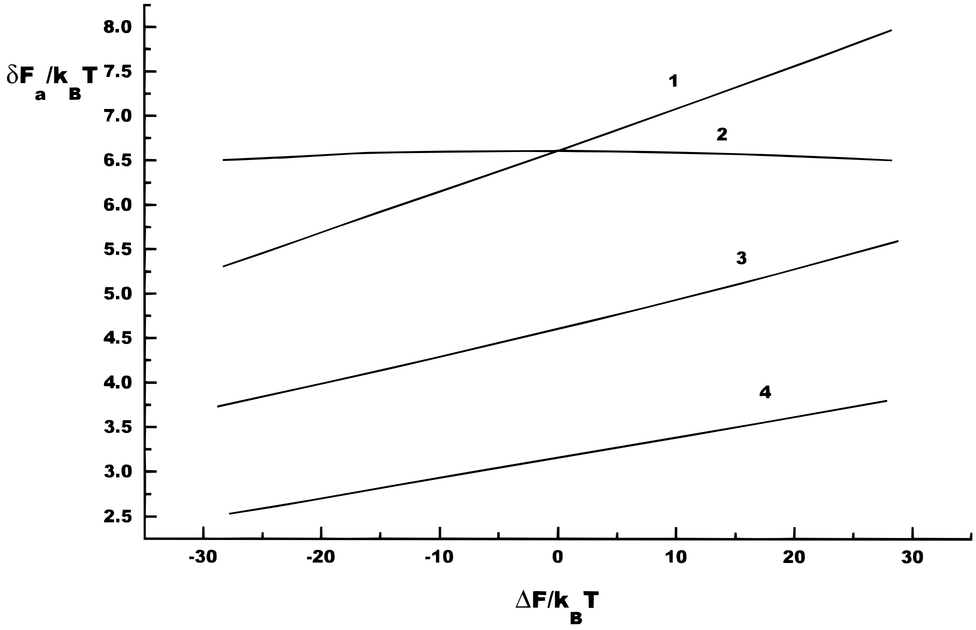

Figure 5. Dependence of the term δF_a responsible for the resonance lowering of the activation barrier on the driving force (see eq 22). (1) $V_0 = 0.3$ eV, $\epsilon_x = \epsilon_y = 0.5$, $D_x = D_y = 1.5$ eV; (2) 0.3 eV, 0.5, 1.5 eV (the calculation with $\delta F_a = V_e(x^s,y^s)$, see eqs 45 and 47); (3) 0.15 eV, 0.2, 1.5 eV; (4) 0.15 eV, 0.5, 1.5 eV.

(curves 1−4 in Figure 2) varies by the factor 2 in the same interval. This shows that the scales of the variation of the nuclear factors and the electron matrix element are quite different and explains rather close agreement of the exact results and those obtained in Condon approximation. However, the agreement is poorer for larger V_0 values (curves 5 and 6 in Figure 2).

It should be emphasized that these results are obtained for the “symmetric” systems (with identical groups X and Y but different ΔF values). However, we may expect that the qualitative conclusions will not be much altered for other systems. The latter will be considered in a separate paper.

7. Conclusions

In this paper we presented a model for the adiabatic SN$_2$ substitution reactions and dissociative electron transfer. The main results of the paper are eqs 24−26 (or in a more general form eqs 16−19, 22, and 23) which allow one to find the transitional configuration and to calculate the dependence of the activation free energy on the driving force for rather general form of the molecular potentials. The calculational algorithm is simple since it allows use of standard PC programs to plot the curves in parametric form and to solve the algebraic equations. The symmetry factor may serve as a universal running variable. In some cases it is more convenient for this role to be played by the value of one of molecular coordinates at the transitional configuration. The model takes into account the reorganization of the polar solvent and the interaction between the molecular modes which is responsible for direct SN$_2$ effects.

It is shown that various SN$_2$ effects may in general exist. Usually they are interrelated. Four types of SN$_2$ effects are distinguished: (1) non-Condon, (2) quasi-equilibrium, (3) nonequilibrium, and (4) Franck−Condon effects. The first three effects are the direct SN$_2$ effects. The last one is indirect and emerges from a general Franck−Condon principle. The model allows one to see the influence of various effects on the activation energy of the reaction.

It is emphasized that the Condon approximation, being sometimes quite satisfactory for the SN$_2$ reactions, is inapplicable to dissociative electron transfer.

We shall present the application of the suggested model to various types of molecular potentials elsewhere.

Acknowledgment. The financial support of the Russian Foundation for Basic Research (Grant 97-03-32010a) is gratefully acknowledged.

Appendix A. The Symmetry Factor for a Nonadiabatic Reaction

If the diabatic free energy surfaces of the initial and final states are represented as a sum of terms corresponding to different reactive modes

$$U_i = \sum_k u_{ik}(q_k); \quad U_f = \sum_k u_{fk}(q_k) + \Delta F \tag{A1}$$

with the equilibrium free energy of the initial state taken as zero, the activation free energy may be also represented as a sum of contributions from different reactive modes

$$F_a = \sum_k u_{ik}(q_k^s) \tag{A2}$$

where q_k^s are the values of the coordinates at the saddle point on the crossing of the diabatic free energy surfaces.

Using the Lagrange multiplier α the saddle point can be found from the equations

$$\frac{\partial}{\partial q_k}[U_i + \alpha(U_f - U_i)] = 0 \quad \text{or} \quad (1-\alpha)\frac{\partial U_i}{\partial q_k} + \alpha\frac{\partial U_f}{\partial q_k} = 0 \tag{A3}$$

which give for α

$$\alpha = \frac{\dfrac{\partial U_i}{\partial q_k}}{\dfrac{\partial U_i}{\partial q_k} - \dfrac{\partial U_f}{\partial q_k}} \tag{A4}$$

The quantity α is thus related with the slopes of the free energy surfaces at the saddle point and therefore characterizes the geometrical symmetry of the transition state. It determines also the symmetry of the distribution of the electron density at the transitional configuration (see Appendix C). Moreover, it can be shown that for nonadiabatic reaction α characterizes also the rate of variation of the activation free energy as a function of the free energy of the transition ΔF[20]

$$\alpha = \mathrm{d}F_{\mathrm{a}}/\mathrm{d}\Delta F \tag{A5}$$

On the other hand, every term of the sum of eq A2 can be calculated as the free energy at the crossing of the initial and final energy profiles along corresponding reactive mode q_k with a certain partial driving force Δj_k determining their mutual position

$$u_{\mathrm{i}k}(q_k^{\mathrm{s}}) = F_{\mathrm{a}k}(\Delta j_k) \tag{A6}$$

The free energy of the transition ΔF determines only mutual position of the whole multidimensional free energy surfaces U_{i} and U_{f}. Therefore, in principle we may consider various sets of Δj_k values provided their sum is equal to ΔF. For example, if Δj is the partial driving force for an anharmonic molecular mode, then the driving force for all other reactive modes is $\Delta F - \Delta j$. The expression for the activation free energy of a set of harmonic modes with the driving force $\Delta F - \Delta j$ is known and expressed by the first term in the right-hand side of eq 3. Various Δj values correspond to various points on the crossing of the initial and final diabatic free energy surfaces and therefore to different values of the whole activation barrier. The true activation free energy corresponds to minimum value of the activation barrier with respect to different Δj values. This condition leads to eq 5.

Similar to eq A5, we may introduce the partial symmetry factors α_k for each reactive mode

$$\alpha_k = \mathrm{d}F_{k\mathrm{a}}/\mathrm{d}\Delta j_k \tag{A7}$$

These quantities will obey equations similar to eq A4 but they will be in general different at arbitrary values of Δj_k. Only when the crossings of the corresponding potential profiles occur at the saddle point, all α_k will be identical and equal to the symmetry factor α of the whole transition. It is worth noting that for the nonadiabatic reaction the symmetry factor a characterizes both the symmetry of the transitional configuration for all reactive modes (eq A4) and the rate of the variation of the activation free energy. This is different for the adiabatic reactions (see sections 3 and 6 and Appendix C).

Appendix B. Transition State for the Adiabatic Reaction

The transition state for the adiabatic reaction is determined as the saddle point on the adiabatic free energy surface (eq 13). Differentiating eq 13 over coordinates of the inertial solvent polarization q_k we obtain

$$\frac{\partial U_{\mathrm{i}}}{\partial q_k} + \frac{\partial U_{\mathrm{f}}}{\partial q_k} - \frac{\left(\frac{\partial U_{\mathrm{i}}}{\partial q_k} - \frac{\partial U_{\mathrm{f}}}{\partial q_k}\right)(U_{\mathrm{i}} - U_{\mathrm{f}})}{[(U_{\mathrm{i}} - U_{\mathrm{f}})^2 + 4V_{\mathrm{e}}^2]^{1/2}} = 0 \tag{B1}$$

If we introduce the symmetry factor according to eq 18, eq B1 can be transformed to

$$(2\alpha - 1)[(U_{\mathrm{i}} - U_{\mathrm{f}})^2 + 4V_{\mathrm{e}}^2]^{1/2} = U_{\mathrm{i}} - U_{\mathrm{f}} \tag{B2}$$

Solving this equation with respect to $U_{\mathrm{i}} - U_{\mathrm{f}}$, we obtain eq 17 and

$$[(U_{\mathrm{i}} - U_{\mathrm{f}})^2 + 4V_{\mathrm{e}}^2]^{1/2} = \frac{V_{\mathrm{e}}}{[\alpha(1-\alpha)]^{1/2}} \tag{B3}$$

Differentiation of eq 13 with respect to x gives

$$\frac{\partial U_{\mathrm{i}}}{\partial x} + \frac{\partial U_{\mathrm{f}}}{\partial x} - \frac{1}{[(U_{\mathrm{i}} - U_{\mathrm{f}})^2 + 4V_{\mathrm{e}}^2]^{1/2}} \times \left[\left(\frac{\partial U_{\mathrm{i}}}{\partial x} - \frac{\partial U_{\mathrm{f}}}{\partial x}\right)(U_{\mathrm{i}} - U_{\mathrm{f}}) + 2\frac{\partial V_{\mathrm{e}}^2}{\partial x}\right] = 0 \tag{B4}$$

A similar equation is obtained after the differentiation over y. With the use of eqs 17, 18, and B3, these equations can be transformed to eqs 16. Further transformations of eqs 16 to eqs 19 and 20 are straightforward with the use of the definition of the diabatic free energy surfaces. For example, the derivative $\partial U_{\mathrm{R}}^{\mathrm{S}}(q_k,x)/\partial x$ with the use of eq 8 is equal to

$$\frac{\partial U_{\mathrm{R}}^{\mathrm{S}}(q_k,x)}{\partial x} = -\sum_k \hbar\omega_k[q_k - q_{k0}^{\mathrm{R}}(x)]\frac{\partial q_{k0}^{\mathrm{R}}(x)}{\partial x} \tag{B5}$$

Equations 8 and 18 give the values of the solvent coordinates as functions of α, x, and y

$$q_k^{\mathrm{s}} = (1-\alpha)q_{k0}^{\mathrm{R}}(x) + \alpha q_{k0}^{\mathrm{P}}(y) \tag{B6}$$

which after insertion into eq B5 gives

$$\frac{\partial U_{\mathrm{R}}^{\mathrm{S}}(q_k,x)}{\partial x} = \alpha\sum_k \hbar\omega_k[q_{k0}^{\mathrm{P}}(y) - q_{k0}^{\mathrm{R}}(x)]\frac{\partial q_{k0}^{\mathrm{R}}(x)}{\partial x} \tag{B7}$$

Using the definition of the reorganization energy (eq 21), it may be easily seen that eq B7 is equivalent to the first equation in eqs 20.

The expression for the activation free energy (eq 22) can be obtained from the definition

$$F_{\mathrm{a}} = U(x^{\mathrm{s}},y^{\mathrm{s}},q_k^{\mathrm{s}}) \tag{B8}$$

with the use of eq B3. Equation 17 is transformed to eq 25 simply with the use of the definition of the diabatic free energy surfaces U_{i} and U_{f} (eqs 7–12).

Appendix C. The Symmetry Factor for the Adiabatic Reactions

In the classical limit the symmetry factor for nonadiabatic reaction was introduced according to eq A4 as the ratio of the slopes of the diabatic free energy surfaces for all reactive modes. For the adiabatic reactions similar definition of α refers only to the harmonic reactive modes (eq 18). The equations for the molecular coordinates x and y (eqs 16) are different from eq 18 and are reduced to the latter only in Condon approximation. Thus, in Condon approximation the meaning of the symmetry factor as the quantity characterizing the geometrical symmetry of the transition state is the same for both adiabatic and nonadiabatic reactions. It can be shown that in both cases the symmetry factor characterizes also the distribution of the electron density in the reaction complex at the transitional configuration as this was first discussed by Hush.[33] In the two-state model the electron wave function ψ may be represented as a linear combination of the diabatic states ψ_i and ψ_f with the coefficients C_i and C_f depending on the nuclear coordinates

$$\psi = C_i\psi_i + C_f\psi_f \qquad \text{(C1)}$$

Solution of the Schrödinger equation gives for the coefficients[34]

$$C_i = \left\{\frac{1}{2}\left[1 - \frac{U_i - U_f}{\{(U_i - U_f)^2 + 4V_e^{\,2}\}^{1/2}}\right]\right\}^{1/2}$$

$$C_f = -\left\{\frac{1}{2}\left[1 + \frac{U_i - U_f}{\{(U_i - U_f)^2 + 4V_e^{\,2}\}^{1/2}}\right]\right\}^{1/2} \qquad \text{(C2)}$$

The solution of eq 17 for α gives $\alpha = C_f^2$. This meaning of α is the same for both adiabatic and nonadiabatic reactions. As for the free energy relationships, in the case of the adiabatic reactions the symmetry factor plays, however, an auxiliary role since it does not characterize directly the variation of the activation barrier with ΔF (see eqs 43 and 44 as an example).

References and Notes

(1) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(2) Dogonadze, R. R.; Kuznetsov, A. M. *Elektrokhimiya* **1967**, *3*, 1324.

(3) Vorotyntsev, M. A.; Kats, V. M.; Kuznetsov, A. M. *Elektrokhimiya* **1971**, *7*, 597.

(4) Dogonadze, R. R.; Kuznetsov, A. M. *Itogi Nauki I Tekhniki, Series Physical Chemistry, Kinetics*; VINITI: Moscow, 1973; Vol. 2.

(5) German, E. D.; Kuznetsov, A. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 77.

(6) Saveant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

(7) German, E. D.; Kuznetsov, A. M. *J. Phys. Chem.* **1994**, *98*, 6120.

(8) (a) German, E. D.; Dogonadze, R. R. *Int. J. Chem. Kinet.* **1994**, *6*, 457,467. (b) German, E. D.; Dogonadze, R. R. *Dokl. Akad. Nauk SSSR* **1973**, *210*, 377.

(9) (a) Bergsma, J. P.; Gertner, B. J.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1987**, *86*, 1356. (b) Gertner, B. J.; Bergsma, J. P.; Wilson, K. R.; Lee, S.; Hynes, J. T. *J. Chem. Phys.* **1987**, *86*, 1372.

(10) Pomelli, C. S.; Tomasi, J. *J. Phys. Chem.* **1997**, *101*, 3561.

(11) Kuznetsov, A. M. *Elektrokhimiya* **1986**, *22*, 401.

(12) Kuznetsov, A. M. *J. Phys. Chem.* **1990**, *94*, 8664.

(13) Marcus, R. A. *J. Phys. Chem. A* **1997**, *101*, 4072.

(14) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692.

(15) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.

(16) Shaik, S. S. *Nouv. J. Chim.* **1982**, *6*, 159.

(17) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187, 1129.

(18) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 2708.

(19) Churg, A. K.; Weiss, R. M.; Warshel, A.; Takano. *J. Phys. Chem.* **1983**, *87*, 1683. Warshel, A. *J. Phys. Chem.* **1982**, *86*, 2218.

(20) Kuznetsov, A. M. *Charge Transfer in Physics, Chemistry and Biology*; Gordon & Breach: Reading, MA, 1995.

(21) Dogonadze, R. R.; Kuznetsov, A. M. *Elektrokhimiya* **1971**, *7*, 763.

(22) Caldeira, A. O.; Leggett, A. J. *Ann. Phys. N.Y.* **1983**, *149*, 374.

(23) Dogonadze, R. R.; German, E. D.; Kuznetsov, A. M.; Moiseev, I. I.; Vargaftik, M. N. *J. Coord. Chem.* **1977**, *6*, 141.

(24) Tikhomirov, V. A.; German, E. D.; Kuznetsov, A. M. *Chem. Phys.* **1995**, *191*, 25.

(25) German, E. D.; Kuznetsov, A. M.; Tikhomirov, V. A. *J. Electroanal. Chem.* **1997**, *420*, 235.

(26) German, E. D.; Kuznetsov, A. M.; Tikhomirov, V. A. *J. Phys. Chem.* **1995**, *99*, 9095.

(27) Chudinov, G. E.; Napolov, D. V.; Basilevsky, M. V. *Chem. Phys.* **1992**, *160*, 41.

(28) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

(29) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(30) Basilevskii, M. V.; Parsons, D. F. *J. Chem. Phys.* **1996**, *105*, 3734.

(31) Basilevsky, M. V.; Chudinov, G. E.; Rostov, I. V.; Yi-Ping, L.; Newton, M. D. *J. Mol. Struct. (Theochem)* **1996**, *371*, 191.

(32) German, E. D., private communication.

(33) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

(34) Landau, L. D.; Lifshits, E. M. *Quantum Mechanics:* Pergamon: Oxford, U.K., 1965.