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Theory of the Self-Exchange Electron Transfer in the Dioxygen/Superoxide System in Water

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Theoretical investigation of the rate constant and activation energy of the charge-transfer reaction in water is performed. Equations for these kinetic characteristics of the reaction obtained in the framework of quantum mechanical theory are presented. The equations take into account a quantum character of the O−O vibration and the fact that the dielectric spectrum of water has an absorption in the quantum frequency range. Parameters of these equations, such as the reactants' interaction free energy in water, $U(R)$, electron coupling matrix element, V_{fi}, and reorganization energies are calculated in terms of appropriate models for several mutual geometries of the reactants. For each of these geometries, the distance dependence of the parameters is investigated and used for numerical estimation of the rate constant and activation energy. Results of the theoretical analysis are in a reasonable agreement with experimental data.

1. Introduction

Dioxygen and its anions O_2^- and O_2^{2-} play a key role in many important direct and catalytic redox processes in the gas phase, on metal and semiconductor surfaces, and in solutions.[1,2] Superoxide and peroxide anions have been observed by many experimental techniques and, in particular, on well-defined surfaces (see ref 2 and references therein). These particles are of crucial importance in biochemical processes. This accounts for the great interest in the study of redox reactions involving the dioxygen molecule and its anion O_2^-, and a large number of theoretical and experimental studies have been devoted to this problem.[2−10]

An approximate estimation of the rate constant of the self-exchange redox reaction in solvent

$$O_2 + O_2^- \rightarrow O_2^- + O_2 \qquad (1)$$

has been made using the Marcus cross-relationship and experimental rate constants of cross-reactions for various oxidants.[3,4] The estimation gave values that differed by as much as 15 orders of magnitude. This led to the statement[3,4] that the cross-relationship is inapplicable to the O_2/O_2^- system. Also, some important characteristics of reaction 1, such as electron matrix element[8,9] and intramolecular reorganization energy,[10] have been calculated. However, to the best our knowledge, an accurate theoretical analysis of reaction 1 in solvent has not been fulfilled yet.

In view of the importance of the system under discussion, in the present work we perform accurate calculations of the rate constant and the corresponding activation characteristics of reaction 1 in water. Our general theoretical method is based on the theory of nonadiabatic electron transfer originating from the works of Dogonadze (for a review of historical aspects and recent development, see refs 11 and 12).

The rest of our paper is organized as follows. In section 2 we discuss the physical features of the system, which are then used to formulate a theoretical model. Equations for the rate constant and activation energy obtained in terms of the model by the application of the general theory for nonadiabatic reactions in solution to the considered system are presented. In section 3 the estimations of the parameters of these equations are performed. Section 4 presents the results of calculations of the rate constant and activation energy of the reaction for three configurations of the approaching reactants O_2 and O_2^-. The paper is concluded by showing the most significant results of our theoretical analysis.

2. General Relationships

2.1. Characteristics of the Reacting System. The following main features of the reacting system were taken into account in the model.

1. Experimental data[13] support that the O−O bond length in the oxygen molecule is shorter than that in the superoxide by 0.14 Å. This difference (∼10%) is rather significant in order to affect the rate constant. On the other hand, it is not very large so that a possible anharmonicity of molecular potentials may be neglected (for comparison, the bond extension in the Cl_2/Cl_2^- reaction is 0.57 Å [14]).

2. The O−O vibrational frequencies in dioxygen and superoxide are 1580 and 1073 cm^{-1},[13] respectively. According to criteria of quantum mechanical or classical behavior of a degree of freedom,[11,12] these vibrations have to be considered in terms of a quantum mechanical model. To reveal the importance of quantum mechanical effects, we will compare the results obtained in the quantum mechanical and classical description of the O−O bond.

3. In some liquids, including water, the dielectric absorption spectrum extends to the frequency range $\omega \gg \mathbf{k}T/\hbar$.[11] The

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reorganization of the inertial solvent polarization affects then both the activation barrier and the preexponential factor of the rate constant. The former is related to a reorganization of the classical part of the solvent polarization ($\omega \ll \mathbf{k}T/\hbar$), whereas the latter is connected with a tunnel reorganization of its high-frequency part ($\omega \gg \mathbf{k}T/\hbar$) and is proportional to $\exp(-\sigma_s)$, where σ_s is the tunnel factor for the solvent polarization.[12]

2.2. Reaction Rate Constant. The rate constant of the self-exchange reaction O_2/O_2^- is considerably below the diffusion limit.[6] Therefore, the spatial distribution of the reactants O_2 and O_2^- in the solvent may be described in terms of an equilibrium distribution function $\Phi(\vec{R})$. The rate constant k may be calculated then as a local transition probability per unit time, $k(\vec{R})$, at a given distance $\vec{R}$ between reactants averaged over all distances with the distribution function $\Phi(\vec{R})$, i.e.,

$$k = \int \Phi(\vec{R})\, k(\vec{R})\, \mathrm{d}\mathbf{R} \tag{2}$$

A classical Boltzmann distribution $Q^{-1} \exp[-U(\vec{R})/(\mathbf{k}T)]$ may be used for $\Phi(\vec{R})$, since the mutual motion of the reactants is classical. Here, $U(\vec{R})$ is the interaction (free) energy for the reactants located in a configuration $\vec{R}$ with respect to each other and Q is the normalization factor.

Equation 2 involves the integration over the inter-reactant distance R and over the angles. Thus, the transition probability $k(\vec{R})$ must be calculated at an arbitrary mutual orientation of the reactants in order to perform exact calculations of the reaction rate constant. This is a rather complicated problem, since a large number of mutual configurations of the reactants has to be considered. Instead, we shall perform the upper and lower estimations of the rate constant using the values of the transition probability for several characteristic configurations and performing the integration over angles as if we had spherically symmetric systems. In other words, we shall calculate the rate constant for these configurations as

$$k \approx 4\pi \int_0^\infty k(R)\, R^2\, \mathrm{d}R \equiv \int_0^\infty y(R)\, \mathrm{d}R \tag{3}$$

where $y = 4\pi\, k(R)\, R^2$. More exact estimation of the rate constant may be obtained using some interpolation scheme between these limits.

(a) Nonadiabatic Regime. If the electron matrix element $V_{if}(R)$ coupling the donor and acceptor states is sufficiently small (for the criterion see eq 13 below), the reaction is nonadiabatic and one may use general equations for the transition probability obtained in the framework of the model of harmonic vibrations.[12] For the system under consideration, which involves two harmonic intramolecular modes and inertial polarization of the solvent, these equations take the following form:

$$k_{nad}(R) = \frac{(V_{fi}(R))^2 \exp[-\sigma_s]}{\mathbf{k}T\hbar}\left[\frac{2\pi}{|B''|}\right]^{1/2} f(\omega_1,\omega_2) \exp[-B_{nad}(R)] \tag{4}$$

where the factor $f(\omega_2,\omega_2)$ is related to the frequency change of the intramolecular modes of the reactants

$$f = \frac{4t^{1/2}}{(\tanh(x/2) + t^{1/2}\tanh(y/2))(\coth(x/2) + t^{1/2}\coth(y/2))} \tag{5}$$

and $x = \hbar\omega_i/(2\mathbf{k}T)$, $y = \hbar\omega_f/(2\mathbf{k}T)$, $t = (\omega_f)^2/(\omega_i)^2$; ω_i and ω_f are the initial and final vibration frequencies of the O−O oscillation (i.e., in molecule O_2 and in its anion O_2^-, respectively). The exponent B_{nad} in eq 4 is equal to

$$B_{nad}(R) = \frac{E_s^{cl}(R)/4 + 2\varphi_{qm}\left(\frac{1}{2}\right) t^{1/2} E_r^{in} + U(R)}{\mathbf{k}T} \tag{6}$$

where

$$\varphi_{qm}\left(\frac{1}{2}\right) = [x \coth(y/2) + y \coth(x/2)]^{-1} \tag{7}$$

Intramolecular reorganization energy E_r^{in} is due to the extension of the O−O bond in the dioxygen molecule, and in the harmonic approximation, it is equal to

$$E_r^{in} = \mu(\omega_i)^2(\Delta R_0)^2/2 \tag{8}$$

where μ is the effective mass of O−O vibration and ΔR_0 is the difference of the equilibrium bond lengths in the O_2^- anion and in the O_2 molecule at a given inter-reactant distance R.

The solvent tunnel factor σ_s in eq 4 (see section 2.1) is given by

$$\sigma_s = \frac{E_s^{qu}}{\hbar\Omega_s^{qu}} \tag{9}$$

where Ω_s^{qu} is the characteristic fluctuation frequency for the quantum part of the solvent polarization. E_s^{cl} and E_s^{qu} in eqs 6−9 are the classical and quantum solvent reorganization energies for reaction 1 in water[11,12] (see eqs 33 and 34 below). These quantities are important characteristics of the theory, and some models were developed to estimate the reorganization energy. The problem of the estimation of the solvent reorganization energy is discussed in detail in the next section.

The second derivative of B_{nad} over the symmetry factor in eq 4 has the form

$$|B''| = \frac{2E_s^{cl}}{\mathbf{k}T} + \frac{2t^{1/2}E_r^{in}}{\mathbf{k}T}|\varphi_{qm}{}''({}^1/_2)| \tag{10}$$

where

$$\varphi''_{qm}\left(\frac{1}{2}\right) = -xy\left\{\frac{x \sinh x + y \sinh y}{[x \sinh(x/2)\cosh(y/2) + y \sinh(y/2)\cosh(x/2)]^2} + \frac{2(x^2 - y^2)\cosh(x/2)\cosh(y/2)[\sinh^2(x/2) - \sinh^2(y/2)]}{[x \sinh(x/2)\cosh(y/2) + y \sinh(y/2)\cosh(x/2)]^3}\right\} \tag{11}$$

The argument in both the function φ_{qm} and its derivative φ''_{qm} denotes a symmetry factor[12] that is ${}^1/_2$ for the self-exchange reactions, i.e., for those with zero reaction free energy, in particular for reaction 1.

V_{fi} is the electron matrix element that according to ref 12 is determined as

$$V_{fi} = \frac{\langle\Psi_f|\hat{H}'|\Psi_i\rangle - \langle\Psi_f|\Psi_i\rangle\langle\Psi_i|\hat{H}'|\Psi_i\rangle}{1 - |\langle\Psi_f|\Psi_i\rangle|^2} \tag{12}$$

where Ψ_i and Ψ_f are the many-electron wave functions for reactants and products. Operator $\hat{H}'$ in eq 12 is responsible for the electron transfer. This operator and the electron wave functions should be calculated at *the transitional configuration for nuclei and for an inertial polarization of the solvent*.

The reaction is nonadiabatic if the following inequality is fulfilled:

$$4\pi\gamma \equiv \frac{(2\pi)^{3/2}(V_{\mathrm{fi}})^2 \exp[-\sigma]}{\mathbf{k}T(\hbar\omega_{\mathrm{eff}})\sqrt{|B''|}} \ll 1 \qquad (13)$$

where σ is the tunnel factor for the whole quantum subsystem and ω_{eff} is the effective frequency for the motion along the atomic coordinates. The quantum subsystem includes a *quantum part of the inertial solvent polarization*. The reorganization of the latter determines the tunnel factor σ_s (eq 9). The O−O vibration frequency has an intermediate value; therefore, this degree of freedom is neither really quantum nor classical. This fact is exploited below in two aspects. First, we obtain an upper estimate for the quantity $4\pi\gamma$, replacing σ in eq 13 by σ_s. Second, it allows us to separate approximately the O−O normal mode from high-frequency solvent polarization. In fact, for water we use a model based on refs 15 and 16 in which the classical ($\omega \ll \mathbf{k}T/\hbar$) and quantum ($\omega \gg \mathbf{k}T/\hbar$) dielectric absorption bands are separated by a transparency zone, with the O−O vibration frequency within this zone.

The effective frequency ω_{eff} in eq 13 for the liquid with a Debye frequency spectrum may be estimated as[17]

$$\omega_{\mathrm{eff}} = \pi\left(\frac{E_s^{\mathrm{tot}}}{2V_{\mathrm{if}}}\right)^{3/2} \tau_L^{\ -1} \qquad (14)$$

where $E_s^{\mathrm{tot}} = E_s^{\mathrm{cl}} + E_s^{\mathrm{qu}}$ is the total reorganization energy of the inertial solvent polarization (see eq 36 below) and τ_L is the longitudinal relaxation time equals to[18]

$$\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$$

where ϵ_∞ and ϵ_0 are the high-frequency and static dielectric constants of the solvent and τ_D is the Debye relaxation time. For water, τ_L is of the order of 10^{-13} s^{-1} as follows from the estimation according to this equation with the numerical values (ref 19) for the dielectric constants and τ_D.

Equation 14 was derived for the case of large splitting, $2V_{\mathrm{fi}}$, of the free energy surfaces. In principle, it may result in ω_{eff} values somewhat larger than the classical limit $4\mathbf{k}T/\hbar$. This may be justified to some extent for strongly adiabatic reactions, since the conditions for overbarrier transitions are shifted toward quantum vibrational frequencies in view of the large distortion of the shape of the potential barrier. For nonadiabatic reactions the rate constant is independent of ω_{eff} (see below). However, the nonadiabaticity criterion must be restricted by $4\mathbf{k}T/\hbar$.

The quantity γ in eq 13 is the so-called Landau−Zener parameter, which determines the probability P_{LZ} of the state rearrangement of the quantum subsystem (the electron and the quantum vibrational modes), while the classical subsystem passes through the transitional configuration with thermal velocity, i.e.,

$$P_{\mathrm{LZ}} = \frac{1 - \exp(-2\pi\gamma)}{1 - \frac{1}{2}\exp(-2\pi\gamma)} \qquad (15)$$

This quantity may be called quantum transmission coefficient $\kappa(R)$ of rate constant, similar to the electron transmission coefficient in ref 12. In terms of $\kappa(R)$, the rate constant may be rewritten in the following general form:

$$k_{\mathrm{nad}}(R) = \frac{\omega_{\mathrm{eff}}}{2\pi}\,\kappa(R)\exp\left[-\frac{G_a}{\mathbf{k}T}\right]$$

where G_a is the free activation energy. This approximate formula describes correctly two limit cases of nonadiabatic and adiabatic reactions. For nonadiabatic reactions $\kappa < 1$ and is proportional to γ. In this case, the rate constant is independent of ω_{eff}.

(b) Adiabatic Regime. If the inequality opposite to eq 13 holds, the reaction is adiabatic. For adiabatic reactions the quantum transmission coefficient in the last equation is equal to 1. We shall not further discuss this regime, since, as it will be seen from the estimations below, the Landau−Zener probability, eq 15, is small in the whole region of the inter-reactant distances giving the major contribution to the reaction rate constant.

(c) Classical Approximation for the O−O Vibration in the Nonadiabatic Regime. This limit may be obtained if the hyperbolic functions in eqs 5, 7, and 11 are replaced by their arguments. Equation 4 then takes the form

$$k_{\mathrm{nad}}^{c}(R) = A_{\mathrm{nad}}^{c}(R)\exp[-B_{\mathrm{nad}}^{c}(R)] \qquad (16)$$

where

$$B_{\mathrm{nad}}^{\mathrm{c}}(R) = \frac{E_s^{\mathrm{cl}}/4 + \frac{t}{1+t}E_r^{\mathrm{in}} + U(R)}{\mathbf{k}T} \qquad (17)$$

$$A_{\mathrm{nad}}^{\mathrm{c}} = \frac{[V_{\mathrm{if}}(R)]^2\exp(-\sigma_s)}{\mathbf{k}T\hbar}\left[\frac{2\pi\mathbf{k}T}{|B_{\mathrm{nad}}''^{\mathrm{c}}|}\right]^{1/2}\left[\frac{2t^{1/2}}{1+t}\right] \qquad (18)$$

$$|B_{\mathrm{nad}}''^{\mathrm{c}}| = \frac{2E_s^{\mathrm{cl}} + 32t^2E_r^{\mathrm{in}}}{(1+t)^3} \qquad (19)$$

2.3. Activation Energy. For k'_{nad} and k''_{nad} calculated at temperatures T_1 and T_2, respectively, the Arrhenius activation energy may be expressed as

$$E_{\mathrm{Arr}} = 2.3026\,\frac{T_1T_2}{T_1 - T_2}\mathbf{k}\log\left(\frac{k'_{\mathrm{nad}}}{k''_{\mathrm{nad}}}\right) \qquad (20)$$

3. Model Estimations of Parameters of the Theory

3.1. Interaction Free Energy, *U*(*R*). The semiempirical UHF/PM3 method implemented in program SIBIQ2.4 by Voityuk[22] was used to calculate *U(R)*. Solvent effects in Voityuk codes is described in terms of the polarized continuum model theory developed by Miertus, Scrocco, and Tomasi.[23] The PM3 method seems to be more preferable for our system compared to other methods using the neglect of diatomic differential overlap (NDDO) approximation, AM1, and MNDO (modified neglect of diatomic overlap), since it gives better results for both the molecule O_2 and its anion (Tables 1 and 2).

The quantity $U(R)$ is determined as the difference between free energies of the reactants O_2 and O_2^- in water at a distance R, $G_f(R)$, and at infinite distance, $G_f(\infty)$, i.e.,

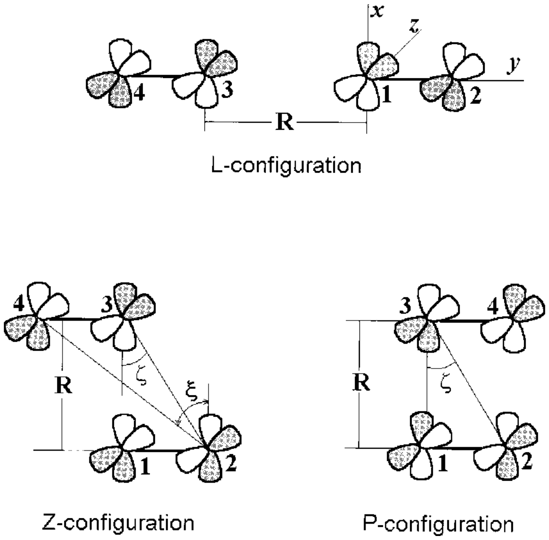
$$U(R) = G_f(R) - G_f(\infty) \qquad (21)$$

The bond lengths in O_2 and O_2^- were optimized at fixed intermolecular distances R for the three mutual reactant orientations shown in Figure 1. The calculated free energies G_f are given in Table 3. In the range of distances R from 2.5 to 3.3 Å the values of $U(R)$ for the considered configurations are fitted very well by exponential functions plotted in Figure 2. From

TABLE 1: Structure and Energetic Characteristics of the O_2 and O_2^- in the Gas Phase

	method	ΔH_f	EA_{ad}[a]	R(O−O)
O_2, triplet	PM3	−4.17	9.1	1.169
	MNDO	−16.0	3.2	1.134
	AM1	−27.7	−4.9	1.085
	CASSCF+MRCI[10]		9.0	1.219
	QCSD/aug-cc-pvDZ[20]			1.211
	QCISD/aug-cc-pvDZ[20]			1.212
	HF/6-311+G*[9]			1.155
	MP2(full)6-311+G*[9]			1.222
	HF/Dunning−Huzinaga/dif(s,p)/pol(d)[2]			1.20
	SD-CI/Dunning−Huzinaga/dif(s,p)+pol(d)[2]			1.27
	expt[13]	0	10.4	1.207
O_2^-, doublet	PM3	−13.3		1.259
	MNDO	−19.2		1.193
	AM1	−22.8		1.174
	CASSCF+MRCI[10]			1.362
	QCSD/aug-cc-pvDZ[20]			1.352
	QCISD/aug-cc-pvDZ[20]			1.353
	HF/6-311+G*[9]			1.285
	MP2(full)6-311+G*[9]			1.356
	HF/Dunning−Huzinaga/dif(s,p)/pol(d)[2]			1.33
	SD-CI/Dunning−Huzinaga/dif(s,p)+/pol(d)[2]			1.42
	expt[13]			1.342

[a] $EA_{ad} = \Delta H_f(O_2) - \Delta H_f(O_2^-)$. ΔH_f and EA_{ad} are in kcal/mol and R in Å.



L-configuration

Z-configuration

P-configuration

Figure 1. Mutual orientations of reactants O_2 and O_2^- in charge-transfer reaction.

TABLE 2: Free Energy of Solvation of the Ion O_2^- in Water (kcal/mol)

PM3	MNDO	AM1	expt[21]
−90.7	−91.4	−91.7	−85

these data one can see that the interaction becomes repulsive at $R < 3.3$ Å. For the P configuration the interaction free energy increases more steeply when R decreases because of the more compact structure of this configuration. At $R \approx 3.5-4$ Å the interaction between O_2 and O_2^- is of an attractive type, and a very weakly bonded complex is formed. Therefore, an additional contribution to the energy of the reaction will exist at $R < 3$ Å owing to the repulsion between the reactants.

3.2. Electron Matrix Element. The Condon approximation[11,12] usually used to calculate V_{fi} was applied in the present work. Within this approximation, the dependence of $\hat{H}'$ and of the wave functions on the solvent polarization is neglected in calculations of the Franck−Condon factors, i.e., in the process of obtaining the transitional configuration. The non-Condon effects on the matrix element due to solvent have been studied in ref 24. It was shown that these effects are of importance for electron transfer to long distances, and apparently, it is not the case considered in our paper. Therefore, neglecting the solvent effect under estimation of the matrix elements for our system seems to be justified. The explicit form of $\hat{H}'$ is not important at the present point. In general, this operator may be written as the sum of one-electron and two-electron terms, i.e.,

TABLE 3: Free Energies G_f of Formation of the O_2/O_2^- System in Water Solvent[a]

	G_f		
R	L configuration	Z configuration	P configuration
2.5	−105.3	−104.4	−100.6
2.6	−105.9	−105.7	−101.7
2.7	−107.7	−107.0	−104.3
2.8	−107.8	−107.2	−105.2
2.9	−108.1	−108.1	−105.9
3	−108.2	−108.1	−105.8
3.3	−108.8	−108.1	−108.3
3.5	−108.7	−109.4	−108.4
4	−108.4	−109.3	−108.7
5	−108.2	−109.8	−108.3
6	−108.0	−109.2	−108.3
∞	−108.6	−108.6	−108.6

[a] Free energies in kcal/mol, R in Å.

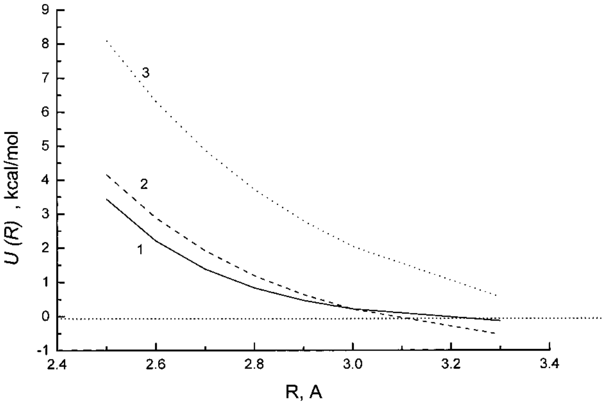


Figure 2. Distance dependence of free energy of interaction between O_2 and O_2^- in water: (1) L configuration; (2) Z configuration; (3) P configuration.

$$\hat{H}' = \sum_{k=1}^{N} h(k) + \sum_{k<l}^{N} g(k,l) \tag{22}$$

where N is the total number of electrons in the system.

First, we construct the wave functions Ψ_i and Ψ_f describing reactants ($O_2 + O_2^-$) and products ($O_2^- + O_2$) of the reaction. It is assumed that the electron transfer occurs by the outer-sphere mechanism, and therefore, the distance between reactants is longer compared to the intramolecular bond length. The wave functions Ψ_i and Ψ_f are expressed then as products of the wave functions of independent fragments O_2 and O_2^-, i.e.,

$$\Psi_i = \varphi_l^i \varphi_r^i, \qquad \Psi_f = \varphi_l^f \varphi_r^f \tag{23}$$

Here, subscripts/superscripts (l/i) and (r/i) correspond to the left and right reactant in the left-hand side of eq 1, and (l/f) and (r/f) correspond to the left and right reactant in the right-hand side of the equation. In the framework of Hartree–Fock method the valence electron wave functions φ_l^i and φ_r^i represent the 12- and 13-electron determinants composed of initial one-electron molecular orbitals a_n. Similarly, the functions φ_r^f and φ_l^f are composed of the final molecular orbitals b_m.

In terms of NDDO approximation the matrix element of eq 12 written with the use of functions in eq 23 reduces to a simpler form

$$V_{fi} = \langle \Psi_f | \hat{H}' | \Psi_i \rangle \tag{24}$$

due to the orthogonality of the wave functions Ψ_i and Ψ_f. Furthermore, the matrix element in this approximation involves one-electron two-center terms of the type $\langle b_m^l | h | a_m^r \rangle$ only, where a_n^l and b_m^r are the molecular orbitals localized on the left and right reactant, respectively (see also ref 25). We can further simplify eq 24 using the method of *corresponding orbital transformation*.[26] As a result, we obtain an expression for V_{fi} in the following form

$$V_{fi} = \langle \bar{b}_A^l | h | \bar{a}_D^r \rangle \prod_{j \neq D,A} \bar{S}_{jj} \tag{25}$$

where $\bar{a}_D^r$ and $\bar{b}_A^l$ are the transformed molecular orbitals of the donor (O_2^-) and acceptor (O_2) between which the electron transfer takes place, and $\bar{S}_{jj} = \langle \bar{b}_j^l | \bar{a}_j^r \rangle$. Our calculations show that $\prod \bar{S}_{jj} \approx 1$ for the reaction under consideration and the orbitals $\bar{a}_D^r$ and $\bar{b}_A^l$ are approximately the same as a_D^r and b_A^l. Therefore, we have

$$V_{fi} \approx \langle b_A^l | h | a_D^r \rangle \tag{26}$$

The MOs a_D^r and b_A^l are antibonding π orbitals composed of $2p_x$ and $2p_z$ atomic orbitals of oxygen directed perpendicular to the molecular y axis O–O, i.e.,

$$a_D^r = \frac{1}{2}(px_1 - px_2 + pz_1 - pz_2) \tag{27}$$

$$b_A^l = \frac{1}{2}(px_3 - px_4 + pz_3 - pz_4) \tag{28}$$

where numbers 1 and 2 denote atoms in the right reactant and numbers 3 and 4 in the left one. For numerical estimations, three mutual orientations of the reactants O_2^- and O_2 shown in Figure 1 were considered.

TABLE 4: Distance Dependence of Electron Matrix Element $|V_{if}|$ for O_2/O_2^- System[a]

	$\lvert V_{if} \rvert$		
R	L configuration	Z configuration	P configuration
2.5	0.568	0.810	2.735
2.6	0.393	0.576	1.964
2.7	0.275	0.407	1.401
2.8	0.193	0.285	1.991
2.9	0.134	0.200	0.692
3.0	0.093	0.139	0.474
3.1	0.066	0.094	0.315
3.2	0.047	0.062	0.199
3.3	0.033	0.040	0.115

[a] V_{if} in kcal/mol; R in Å (see Figure 3).

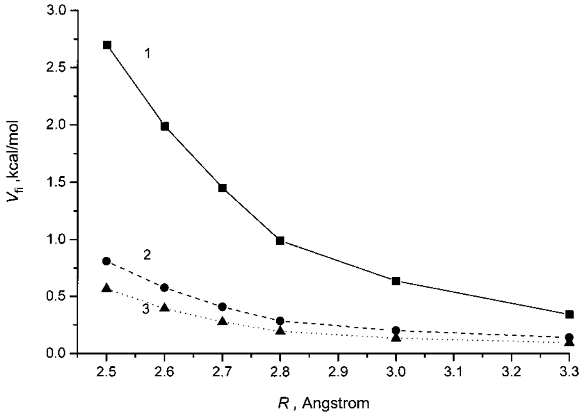


Figure 3. Distance dependencies of matrix element: (1) L configuration; (2) Z configuration; (3) P configuration.

As in all semiempirical methods, the integrals of eq 26 are calculated according to the Mulliken approximation

$$\langle \chi_i | h | \chi_j \rangle = (\beta_i + \beta_j) s_{ij}/2 \tag{29}$$

where β_i and β_j are the resonance parameters of centers i and j, and s_{ij} is the overlap integral between atomic functions. In the PM3 method, the parameter β for the 2p electron of the oxygen atom is equal to -571 kcal/mol.[27] Taking into account eqs 26–29, one can obtain the following approximate expression of the matrix element for L-orientation of the reactants:

$$V_{fi}^{L} = \frac{1}{2}\beta_O^{2p}\{|s_{13}^{\pi\pi}| - |s_{23}^{\pi\pi}| - |s_{14}^{\pi\pi}| + |s_{24}^{\pi\pi}|\} \tag{30}$$

where $s_{ij}^{\pi\pi}$ is the integral of $\pi-\pi$ type between p functions of oxygen.

For Z and P orientations we find

$$V_{fi}^{Z} = \frac{1}{4}\beta_O^{2p}\{|s_{13}^{\sigma\sigma}| - |s_{13}^{\pi\pi}| - 2|s_{23}^{\sigma\sigma}|\cos^2\zeta + 2|s_{23}^{\pi\pi}|(1 + \sin^2\zeta) + |s_{24}^{\sigma\sigma}|\cos^2\xi - |s_{24}^{\pi\pi}|\sin^2\xi\} \tag{31}$$

$$V_{fi}^{P} = \frac{1}{2}\beta_O^{2p}\{-|s_{13}^{\sigma\sigma}| + |s_{13}^{\pi\pi}| - |s_{23}^{\pi\pi}|(1 + \sin^2\zeta) + |s_{23}^{\sigma\sigma}|\cos^2\zeta|\} \tag{32}$$

where ξ and ζ are the angles identified in Figure 1.

Results of calculations according to eqs 30–32 at different distances R are shown in Table 4 and Figure 3. The dependencies of the matrix element on R plotted in Figure 3 are fitted well by exponential functions $B_0 + B\exp(-\lambda R)$ with λ = 3.6486, 3.3467, and 3.1585 Å^{-1} and B = 0.5388, 0.7877, and 2.6493 kcal/mol for L, Z, and P configurations, respectively.

These large values of the decay factor λ seem to be typical for the direct overlap of donor and acceptor orbitals (electron transfer to a short distances). They are in line with the values of λ (2.4−3.2 Å^{-1}) calculated by semiempirical and ab initio methods in refs 28−33 for other systems with the direct overlap. In contrast to that, long electron transfers (usually mediated by bridge groups) are characterized by lower values of the decay factor $\lambda \leq 1$ Å^{-1} (see review in ref 38).

One can see that the value of the electron matrix element at a given R is highest for the P configuration. It is due to the overlaps of $\sigma-\sigma$ type for two pairs of atoms. Our semiempirical values of the matrix element are significantly smaller than those calculated by the ab initio method in ref 8, which are largely overestimated, and agree reasonably with ab initio calculations[9] involving electron correlation.

3.3. Energies of the Solvent Reorganization. The classical and quantum reorganization energies of the solvent in the equations for the rate constant are determined as follows:[33−35]

$$E_s^{cl} = \Delta G_{solv}(\epsilon_m) - \Delta G_{solv}(\epsilon_0) \tag{33}$$

$$E_s^{qu} = \Delta G_{solv}(\epsilon_\infty) - \Delta G_{solv}(\epsilon_m) \tag{34}$$

$\Delta G_{solv}(\epsilon_k)$ here is the solvation energy of *an effective dipole* corresponding to the transfer of one electron from donor to acceptor in a solvent with dielectric constant ϵ_k. For the reaction under consideration it is the solvation energy of the reaction complex with the charge distribution

$$[O^{-1/2}-O^{-1/2}\cdots\cdots O^{1/2}-O^{1/2}] \tag{35}$$

In fact, eqs 33 and 34 assume a certain model for the solvent polarization in which the dielectric absorption bands are separated by the transparency zones.[12] The quantities ϵ_∞ and ϵ_0 are then the optical (high frequency) and static dielectric constants, respectively, and ϵ_m is the dielectric constant in the transparency zone separating the classical ($\omega < 4\mathbf{k}T/\hbar$) and quantum ($\omega > 4\mathbf{k}T/\hbar$) absorption bands. The values of ϵ_∞ and ϵ_0 for water are 1.78 and 78, respectively. However, the absorption bands overlap, and therefore, ϵ_m is an effective quantity that may be estimated using the following approximate procedure. The rigorous calculations[12] of the electron-transfer rate in a uniform local dielectric, using the continuous dielectric spectrum of water, resulted in the expression for the transition probability, which involves classical and quantum reorganization energies of the inertial polarization

$$E_s^{cl} \approx 0.8E_s^{tot}, \qquad E_s^{qu} \approx 0.2E_s^{tot} \tag{36}$$

where

$$E_s^{tot} = \frac{1}{8\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\int d^3r\, D^2(r)$$

Comparison of eqs 33 and 34 with eq 36 for the case of a uniform dielectric gives an estimate $\epsilon_m = 2.237$. This value is used below for the calculation of the solvent reorganization parameters in the presence of cavities in the dielectric.

A cavity model taking into account the nonspherical form of the reactants O_2 and O_2^- should be used for the calculation of the solvent reorganization parameters in terms of eqs 33 and 34. We employ some of the cavity models previously developed in refs 38−42. For L and Z configurations the model of prolate ellipsoidal cavity ("sausage" cavity) formed by solvent molecules seems to be relevant, while for the P configuration we used the model of an oblate spheroid.

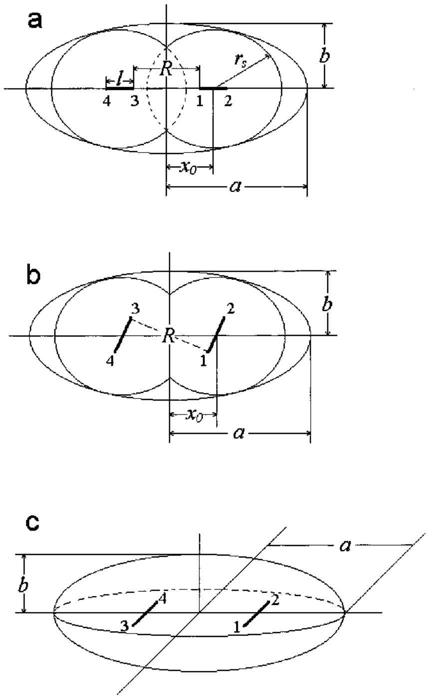


Figure 4. Models of prolate (a, b) and oblate (c) ellipsoids. (a) L configuration: $\delta = a/b = 2$; $x_0 = R/2 + l/2$; $b = [r_s^2 + x_0^2/(\delta^2 - 1)]^{1/2}$; $q_1 = q_2 = |e|/2$; $q_3 = q_4 = -|e|/2$. (b) Z configuration: $x_0 = {}^1/_2[R^2 + l^2]^{1/2}$; $\delta = 2$; $q_1 = q_2 = |e|/2$; $q_3 = q_4 = -|e|/2$. (c) P configuration: $a = R/2 + r_s$; $b = r_s = 2.035$ Å. a and b are semiaxes of ellipsoid.

The problem of the estimation of the semiaxes, a and b, of the spheroid cavity, in which the reactants forming the reaction complex are situated, is rather ambiguous. First, we consider the estimation of axes lengths of the sausage cavity for the L configuration (see Figure 4a). Let us assume that the reactants represent effective spheres tangential to the surface of an ellipsoid at an arbitrary distance R between the reactants. This distance may be smaller or greater than the sum of van der Waals radii $r_{vdw}(O)$ of contacting oxygen atoms 1 and 3. The effective radius of such a sphere may be assumed to be equal to $r_s = l/2 + r_{vdw}(O) = 2.035$ Å (where l is the O−O bond length). Then, using the tangency condition for the sphere and ellipsoid, the semiaxes for a given form of ellipsoid characterized by the relation $\delta = a/b$ may be estimated. Now, the reorganization energies E_s^{cl} and E_s^{qu} may be calculated using the formulas of ref 41 based on general eqs 33 and 34. The obtained results with $\delta = 2$ for the charge distribution (eq 35) are given in the second and third columns of Table 5. It is worth noting that the variation of δ from 1.8 to 2.2 results in a rather small variation of the solvent reorganization energies.

For the Z configuration (Figure 4b) the procedure of estimation of the sausage cavity geometrical parameters is similar to that for the L configuration, and the corresponding solvent reorganization energies are listed in the fourth and fifth columns of Table 5. In the case of the P configuration (Figure 4c) the semiaxes of the oblate ellipsoid, a and b, were estimated to be equal to $a = R/2 + r_s$ and $b = r_s$. The results of calculations for the cavity of this form according to formulas from ref 42 are given in the two last columns of Table 5.

3.4. Intramolecular Reorganization Energy. Since both vibration frequencies and equilibrium lengths of the oxygen and superoxide anion depend on the distance R and the mutual

TABLE 5: Solvent Reorganization Energies E_s^{cl} and E_s^{qu} for O_2/O_2^- System in Water[a]

	L configuration		P configuration		Z configuration	
R	E_s^{cl}	E_s^{qu}	E_s^{cl}	E_s^{qu}	E_s^{cl}	E_s^{qu}
2.5	28.5	6.6	21.6	4.7	24.1	5.4
2.6	29.3	6.8	22.6	4.9	25.0	5.6
2.7	30.0	7.0	23.6	5.1	25.9	5.9
2.8	30.7	7.2	24.5	5.3	26.8	6.0
2.9	31.3	7.3	25.5	5.4	27.7	6.2
3.0	33.9	7.5	25.9	5.6	28.5	6.4
3.1	32.5	7.6	27.3	5.7	29.3	6.6
3.2	33.1	7.8	28.2	5.8	30.2	6.8
3.3	33.7	7.9	29.1	5.9	30.8	7.0

[a] Energies in kcal/mol, R in Å. E_s^{cl} is the reorganization energy for classical oscillators of water, and E_s^{qu} is that for quantum ones. The reorganization energies were calculated in the cavity model (for details see text).

orientation of O_2 and O_2^-, the intramolecular reorganization energy also depends on these characteristics. However, our calculations show that in the considered range of R values between 2.5 and 3.3 Å these structure parameters change very little. For example, in the L configuration the bond length of the superoxide anion decreases by ~0.0003 Å and that of O_2 increases by ~0.001 Å when R changes from 3.3 to 2.5 Å. The corresponding variations of bond lengths in the P configuration amount to ~0.0013 and ~0.0023 Å. These increments of R obviously do not affect noticeably the intramolecular reorganization energy in the considered range of intermolecular distances and may be neglected. Therefore, the constant value of E_r^{in} is accepted in our analysis of the distance dependence of the local rate constant.

Indeed, we used the experimental structure characteristics of the reactants (see Table 1 and ref 10) for numerical calculation of the intramolecular reorganization energy according to eq 6, since the PM3 method does not provide accurate vibration frequencies and ΔR_0. The value of E_r^{in} obtained in this way is equal to 17 kcal/mol. For the experimental values[10] of the vibration frequencies (1580 cm^{-1} for the molecule and 1080 cm^{-1} for the anion), the factor t in eqs 5 and 6 and the following equations is equal to 0.4727.

4. Results for the Rate Constant Calculations

The first point of importance consists of the fact that reaction 1 is nonadiabatic in the whole region of distances R, giving a noticeable contribution to the transition probability. It follows from our calculations according to eq 15 of the Landau–Zener probability. For L and Z configurations the quantity P_{LZ} is found to be much smaller than 1 even at the minimum distances R between reactants (Figure 5a), and for the P configuration P_{LZ} decreases from ~0.4 at $R = 2.5$ Å to ~3×10^{-6} at R = 3.3 Å (Figure 5b). Therefore, the application of the nonadiabatic theory for the local rate constant calculations is justified. The results for the local rate constants $k(R)$ at distances R in the range between 2.5 and 3.3 Å obtained with the use of the above equations and parameters of the theory are plotted in Figure 6. One can see that the distance R^* between reactants, at which the electron-transfer proceeds with maximal probability, is equal to 2.7–2.9 Å depending on the mutual configuration of the reactants. This distance is approximately equal to the sum of van der Waals radii of interacting oxygen atoms (~2.8 Å); i.e., it has a reasonable value. The obtained results show that there is a contribution in the rate constant due to the repulsion of the electron shells of the reactants at this value of R^* that may amount to 3 kcal/mol for the P configuration (for the L configuration it is about 0.6–1 kcal/mol). This fact was usually not taken into account when considering the kinetics of this reaction.

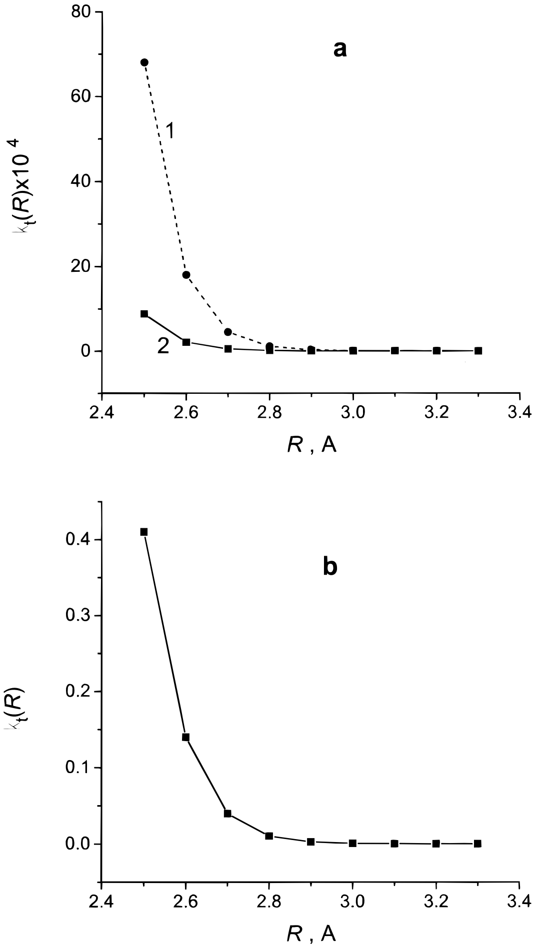


Figure 5. Distance dependence of the total transmission coefficient κ_t: (a) L configuration (curve 1) and Z configuration (curve 2); (b) P configuration.

Now, the rate constant for each configuration may be calculated according to eq 4 of the nonadiabatic theory by numerical integration of the graphics in Figure 6. It gives 28, 296, and 231 M^{-1} s^{-1} for the L, Z, and P mutual orientations of the reactants, respectively. These values are in a reasonable agreement with the experimental rate constant in water of 450 ± 160 M^{-1} s^{-1}.[6] To estimate the importance of the quantum mechanical effects, we calculated the reaction rate constant according to eqs 16–19 (Figure 7). In this case the obtained values are lower than that from quantum mechanical calculations by 1.3–1.6 orders of magnitude depending on the mutual configuration of the reactants. This difference is mainly due to the different activation energies. For example, the quantum mechanical calculations at $R = R^*$ yield the activation energies of 9.5, 8.5, and 9.6 kcal/mol for the L, Z, and P configurations, respectively. The corresponding values in the classical approximation for the O–O bond are 14.4, 13.4, and 14.5 kcal/mol.

It should be noted that the quantum mechanical behavior of the O–O bond and nonadiabatic character of the O_2/O_2^- self-exchange reaction may result in violation of the Marcus cross-relationship. The point is that the approximate Marcus relationship assumes reactants to be classical oscillators with unchanged vibration frequencies. Apparently, it is not the case for the considered system.

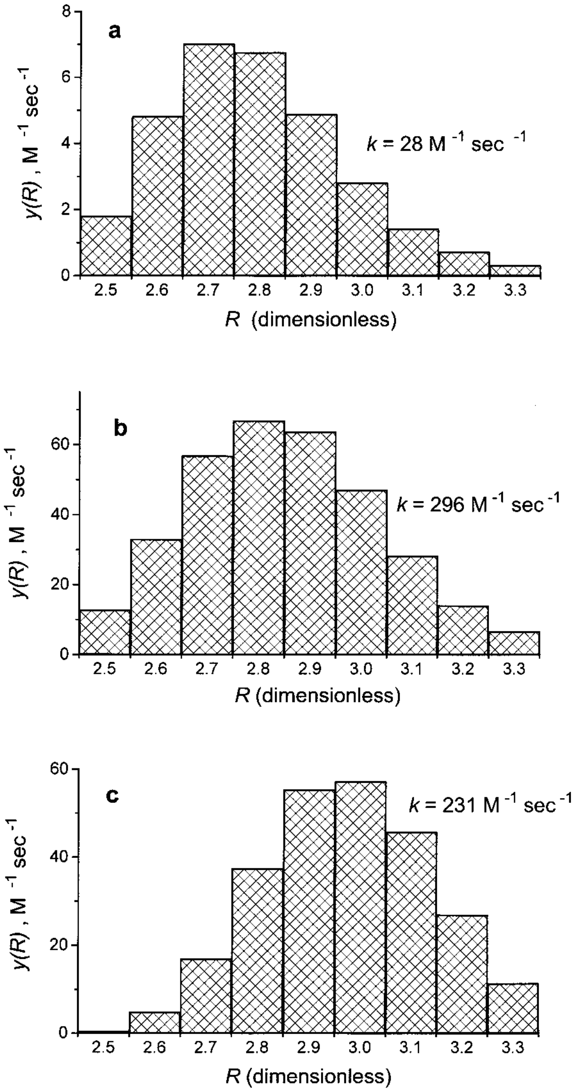


Figure 6. Distance dependence of $y = 4\pi\, k(R)\, R^2$ and average value of k: (a) L configuration; (b) Z configuration; (c) P configuration.

5. Conclusions

In this paper we present the results of calculations of the reaction rate constant and activation energy for the electron transfer in the dioxygen/superoxide anion system in water for several typical configurations of the precursor reaction complex. The aim was to take into account all factors that can affect the value of the reaction rate constant. They are the following.

The electron matrix element. It was calculated by the PM3 semiempirical method in the Condon approximation with the use of electron-localized diabatic wave functions.

Reorganization of the classical and quantum parts of the inertial solvent polarization. Models of spheroid cavity were used to calculate these quantities. The quantum part of the solvent polarization and the electron matrix element determine the rearrangement probability of the solvent quantum vibration modes and of the electron state, and the adiabatic or nonadiabatic character of the reaction. At this point the main conclusion is that the reaction is nonadiabatic at all inter-reactant distances that contribute significantly to the rate constant. The reorganization energy of the classical solvent polarization is in the range ~23−34 kcal/mol depending on the distance R and the mutual configuration of the reactants.

The intramolecular reorganization related to the change of the O−O bond lengths in both reactants upon electron transfer.

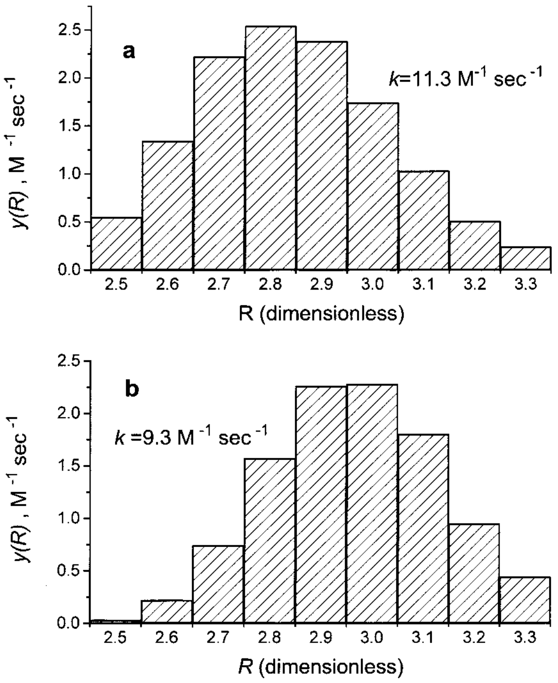


Figure 7. Distance dependence of $y = 4\pi\, k(R)\, R^2$ and average value of k in the classical approximation for O−O vibration: (a) Z configuration; (b) P configuration.

Taking into account the quantum mechanical character of the O−O vibrations leads to a considerable increase of the rate constant compared to the classical approach. The difference amounts to 1.3−1.6 orders of magnitude and is due mainly to the fact that the classical approximation overestimates the activation energy by ~4−5 kcal/mol.

The intermolecular repulsion of reactants in solvent. It gives a contribution to the activation barrier, which amounts to a few kcal/mol at $R < R^*$.

The account for all these factors allows us to obtain reasonable values of the reaction rate constant compared to the experimental ones.

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