CALCULATION OF THE RATE CONSTANTS FOR ELECTRON EXCHANGE BETWEEN AQUOCOMPLEXES

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In [1, 2] a general method for theoretical calculation of the rate constants of electron exchange between complex ions in a polar liquid was proposed. According to [1, 2], in order to calculate the kinetic parameters for specific electron exchange reactions, one must obtain data on the equilibrium configurations and normal vibration frequencies of the reacting complexes both in the oxidized and reduced forms. However, at the present time the necessary data (both experimental and theoretical) for these parameters do not exist. Thus, for practical calculations of rate constants, Marcus proposed the so-called cross-relationship relating the rate constants k_A and k_B for the symmetrical reactions:

$$AL_m^{ox} + A^*L_m^{red} \rightarrow AL_m^{red} + A^*L_m^{ox}, \tag{1a}$$

$$BL_m^{ox} + B^*L_m^{red} \rightarrow BL_m^{red} + B^*L_m^{ox}, \tag{1b}$$

to the rate constants for the unsymmetrical reaction

$$AL_m^{ox} + BL_m^{red} \rightarrow AL_m^{red} + BL_m^{ox}. \tag{1c}$$

In the limits of the assumptions chosen by Marcus, this relationship has the form

$$k_{AB} = (k_A k_B K_{AB} f M)^{1/2} \tag{2a}$$

$$f_M = (\lg K_{AB})^2 / 4 \lg \{k_A k_B Z M^{-2}\}, \tag{2b}$$

where K_{AB} is the equilibrium constant for reaction (1c) and ZM is the frequency factor in the rate constant which is taken to be the same for all reactions (1a)-(1c) ($Z \simeq 10^{11}$ sec^{-1}).

Electron exchange rate constants for unsymmetrical reactions calculated using Eqs. (2a) and (2b) differ in several cases from the experimental values by several orders of magnitude). Thus, it is of interest to analyze the fundamental approximations used in deriving (2a) and (2b). In [3], only one of all the normal coordinates of the complexes was considered, namely, that describing the centrally symmetric vibration of the ligands with respect to the metal ion. For complexes in which the Jahn–Teller effect is not significant, this assumption is completely correct. Moreover, in deriving (2a) and (2b) it was assumed that the total reorganization energy* for all classical subsystems, i.e., the reorganization energy of the medium and intramolecular degrees of freedom of the reactants, for the unsymmetrical reaction (1c) is equal to half the sum of the reorganization energies for the symmetrical reactions (1a) and (1b). The assumption made in [3] that one may replace frequencies differing (approximately 1.5 to 2 times) from the centrally symmetrical ligand vibrations for the oxidized and reduced forms

*We note that according to [1, 2, 6], the reorganization energy of the system in the course of the reaction is determined as the work necessary to carry the system from the equilibrium configuration of the initial state to the equilibrium configuration of the final state under the condition that the system is always located on the potential energy surface of the initial state. The reorganization energy is greater or equal to the activation energy for the process (equality holds only for reactions for which the activation energy is equal to the heat of reaction).

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of the complex by one effective frequency ω also seems to be important to us. Moreover, it should be noted that the role of Coulombic repulsion of the reactants in the activation energy is not taken into consideration in Eqs. (2a) and (2b).

The cross-relationship, free from the assumptions cited above, was obtained in [7], according to which

$$k_{AB}=k_A^a k_B^b (Z_{AB}/Z_A^a Z_B^b) \exp\frac{aE_{sA}+bF_{sB}-\alpha E_{sAB}}{kT} \exp\frac{aU_A+bU_B-U_{AB}}{kT} \quad (3)$$

The terms found in this formula have the following physical meaning: The preexponential term

$$Z=\varkappa\frac{\omega}{2\pi}\Delta V\cdot\frac{kT}{h} \quad (4)$$

contains the transmission coefficient $\varkappa$, the reaction volume [8] ΔV, and the effective fluctuational frequency of all classical subsystems [9] ω; E_S is the reorganization energy of the polar medium in the course of the reaction; V is the Coulombic interaction energy of the reactants.* The symmetry factor α is determined by the relationship between the slopes of the potential energy curves near the transition state [6, 9]. For the symmetrical reactions (1a) and (1b) the symmetry factor is equal to 1/2, but for unsymmetrical reactions (1c) the value of α [in Eq. (3)] is found by solving the following equation [7]:

$$f(\alpha)=(2\alpha-1)E_s+E_A\frac{\alpha^2-(1-\alpha)^2\gamma_A}{[(1-\alpha)\gamma_A+\alpha]^2}+E_B\frac{\alpha^2\gamma_B-(1-\alpha)^2}{[1-\alpha+\alpha\gamma_B]^2}-\Delta F_0=0, \quad (5)$$

where F_0 is the free energy of reaction (1c); E_S and E_1, E_2 are the reorganization energies of the polar medium and the complex ions AL_m and BL_m, respectively; γ_A and γ_B are the ratios of the force constants for the centrally symmetric vibrations of the ligands of the corresponding complexes (AL_m and BL_m) in the oxidized and reduced forms. Finally, the quantities a and b in Eq. (3) are given by the equations

$$a=\alpha^2(1+\gamma_A)/[(1-\alpha)\gamma_A+\alpha]^2, \quad (6a)$$

$$b=\alpha^2\gamma_B(1+\gamma_B)/[1-\alpha+\alpha\gamma_B]^2. \quad (6b)$$

Formula (3), as can easily be shown, simplifies to the Marcus cross-relationships (2a) and (2b) if one uses the assumption made in [3]. In order to determine the correctness of these assumptions, we calculated rate constants for the unsymmetrical electron transfer reaction between different aquo-complexes. The results of the calculations using Eqs. (2a), (2b), and (3) are presented in Table 1. The kinetic parameters in Eq. (3) were calculated within the limits of Marcus theory. In particular, the formula [1] used for the reorganization energy was

$$E_s=c(1/2r_a+1/2r_b-1/R), \quad (7)$$

and the repulsive potential was approximated by the simple Coulombic law

$$U=z_1z_2e^2/\varepsilon R, \quad (8)$$

the ionic radii (r_a, r_b), the distances between the reactants, and the constant c being given the same values as were used in [5] in a study of symmetrical electron exchange reactions. The values of the parameters E_S and U calculated using these data for all reactions in Table 1 are 36 kcal·mole^{-1} and 3.6 kcal·mole^{-1}, respectively. We also used the data of [5] in order to determine the parameters which characterize reorganization of the inner coordination sphere of the complexes. In particular, the value of γ was taken to be the same and equal to 1.5 for all reactions investigated, and the reorganization energies E_1 and E_2 for the different reactions presented in Table 1 were found to lie in the range 10-20 kcal/mole.

As is apparent from Table 1, the rate constants calculated by Eqs. (2a), (2b), and (3) are significantly different from one another (by 0.4 to 2.3 orders), Eq. (3) giving the correct tendency for theoretical and experimental values to approach one another because of the more exact calculation of the factor α. However, it should be emphasized that the disagreement between experimental rate constants and those calculated by

*In sufficiently concentrated solutions, the quantity exp (−U/kT) should be replaced by the binary correlation function which gives the probability for approach of the reacting particles to a given distance.

TABLE 1

Reaction*	$\lg k_A$	$\lg k_B$	$\lg k_{AB}$	$\lg k_{AB}^{\dagger}$ †	$\lg k_{AB}^{\ddagger}$ ‡	$\log k_{AB}^{exp}$
$Co(H_2O)_6^{3+}+Mn(H_2O)_6^{2+}$	0,7	0,65	5,2	3,1	2,6	2,1
$Co(H_2O)_6^{3+}+Fe(H_2O)_6^{2+}$	0,7	0,6	18,4	7,8	6,6	2,4
$Co(H_2O)_6^{3+}+V(H_2O)_6^{2+}$	0,7	—2,0	35,2	10,4	8,5	5,9
$Co(H_2O)_6^{3+}+Cr(H_2O)_6^{2+}$	0,7	—4,7	37,7	10,0	8,7	4,1
$Mn(H_2O)_6^{2+}+Fe(H_2O)_6^{2+}$	0,65	0,6	13,1	5,8	5	
$Mn(H_2O)_6^{2+}+V(H_2O)_6^{2+}$	0,65	—2,0	13,0	9,5	7,5	
$Mn(H_2O)_6^{2+}+Cr(H_2O)_6^{2+}$	0,65	—4,7	32,4	9,2	7,9	
$Fe(H_2O)_6^{2+}+V(H_2O)_6^{2+}$	0,6	—2,0	16,8	6,2	5	5
$Fe(H_2O)_6^{2+}+Cr(H_2O)_6^{2+}$	0,6	—4,7	19,3	5,9	5,3	3,9
$V(H_2O)_6^{2+}+Cr(H_2O)_6^{2+}$	—2,0	—4,7	2,5	0,75	—2,5	

*Experimental data for rate of equilibrium constants were taken from [12].

† Values of k_{AB} calculated according to Eqs. (2a), (2b).

‡ Values of k_{AB} calculated according to Eq. (3).

Eq. (3) is still sufficiently large (0.6 to 4.2 orders of magnitude). This can be related to the fact that we used a rather crude model in this paper to estimate the basic kinetic parameters of the reaction, in order to illustrate the quantitative differences which can arise within the limits of the same physical model when the approximate Eqs. (2a) and (2b) are used instead of the exact expression (3). In order to obtain satisfactory agreement with experiment in calculating rate constants for electron exchange in unsymmetrical reactions using Eq. (3), it is most important that one use instead of Eqs. (7) and (8) the more exact expressions derived in [10, 11], in which the presence of a solvent structure near the ions, which results in an effective lowering of the dielectric constant of the medium at small distances, is taken into account. According to the results of these studies, consideration of structural effects in polar liquids results in a lowering of the reorganization energy and an increase in the electrostatic repulsion in comparison with Eqs. (7) and (8). As can be seen from analysis of Eq. (3), this effect should result in a further lowering of the electron transfer rate constants, with respect to that obtained by Eqs. (2a) and (2b).

Investigation of electron transfer processes points out the important role of Coulombic repulsion of the reactants and the effect of normal vibration frequency change in the systems examined. In these cases Eqs. (2a) and (2b) are not appropriate for calculating the rate constants of cross reactions.

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