CONNECTION BETWEEN THE RATE CONSTANTS OF CROSS AND SYMMETRICAL ELECTRON-TRANSFER REACTIONS

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UDC 541.124

To calculate the rate constants (k_{AB}) of electron-transfer reactions between dissimilar ions (cross reactions)

$$AL_m^{ox} + BL_m^{red} \rightarrow AL_m^{red} + BL_m^{ox} \qquad (*)$$

(where the symbols $AL_m^{ox, red}$ and $BL_m^{ox, red}$ denote complex ions in the oxidized and reduced forms) the approximate cross ratio [1] is used often:

$$k_{AB} = (k_A k_B K_{AB} f_M)^{1/2}, \qquad (1a)$$

$$\lg f_M = \lg K_{AB})^2/4 \lg(k_A k_B/Z_M^2). \qquad (1b)$$

In formulas (1a) and (1b), k_A and k_B are the rate constants of the symmetrical electron-transfer reactions between AL_m^{ox} and AL_m^{red} and between BL_m^{ox} and BL_m^{red}, respectively, K_{AB} is the equilibrium constant of reaction (*), and Z_M is the preexponential factor of the rate constant ($\sim 10^{11}$ sec^{-1} [1]). Relation (1a) is, strictly speaking, applicable only with the following limitations: 1) if the Coulomb interactions between the ions are insignificant or can be neglected; 2) if it is possible to neglect the effect of the change in the frequency of the intramolecular vibrations on passing from the reduced form to the oxidized form; and 3) if there is additivity of the reorganization field energies, i.e., those of the solvent and the inner coordination sphere ($E^t = E_s + E_{in}^r$) for the cross and symmetrical reactions†

$$E^t_{AB} = (E^t_A + E^t_B)/2.$$

Since reactions are known from the literature [2] in which the calculation of the k_{AB} by formulas (1a) and (1b) leads to a contradiction with experiment (by 5-6 orders of magnitude), it appeared of interest to obtain the cross relation under more general assumptions: when the Coulomb effects are not small and when a change takes place in the frequency of the skeletal metal–ligand vibrations (the characteristic frequency of the fluctuations of the polarization of the solvent is considered to be constant).

According to the quantum theory of the kinetics of chemical reactions, the observed free energy of activation ($\Delta F^{\neq}$) of the cross reaction (*) is [3]

$$\Delta F^{\neq}_{AB} = -kT \ln\left(\varkappa_{AB} \frac{\hbar\omega_{AB}}{kT} \Delta V_{AB}\right) + \Delta F^*_{AB} + U^r_{AB}, \qquad (2)$$

where $\varkappa_{AB}$ is a transmission coefficient; ω_{AB} is the effective frequency of fluctuations of the whole classical subsystem, i.e., the solvent and the classical intramolecular degrees of freedom; ΔV_{AB} is the reaction volume; U^r_{AB} is the energy of Coulomb interaction between AL_m^{ox} and BL_m^{red} for the initial state; and ΔF_{AB}^* is the component of the free energy of activation defined as the distance in the term of the initial state‡ (U_i) reckoned from the minimum (I_i) of the term to the saddle point ($\{\xi_k^*\}$), i.e.,

†Condition 3) is not completely independent but is determined to a certain extent by condition 2).

‡In agreement with the basic postulates of the quantum theory, the terms of the system are functions only of the classical coordinates; for criteria of quantum and classical conditions, see [3].

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. (Presented by Academician A. N. Frumkin, November 21, 1973.) Translated from Doklady Akademii Nauk SSSR, Vol. 215, No. 3, pp. 620-623, March, 1974. Original article submitted November 11, 1973.

$$\Delta F_{AB}^{*}=U_i(\{\xi_k^{*}\})-I_i. \tag{3}$$

The full set of coordinates $\{\xi_k\}$ describing the system under consideration includes the normal coordinates of the solvent $\{\eta_k\}$ and the coordinates Q_A and Q_B of the reacting complexes.† Let us denote by η_k^0, Q_A^0, and Q_B^0 the displacement along the corresponding coordinates in passing from the initial to the final states, and by ω_k, Ω_{A_1}, and Ω_{A_2}, Ω_{B_1}, and Ω_{B_2} the frequencies of the normal vibrations along the coordinate of the solvent η_k and the coordinate of the complexes AL_m and BL_m (the indices 1 and 2 relate, respectively, to the oxidized and reduced forms of the complex ion). Then, in the transition state for the reaction (*) the cooreinates η_k^*, Q_A^* and Q_B^* are

$$\eta_k^{*}=\alpha\eta_k^{0}, \tag{4a}$$

$$Q_A^{*}=\alpha\Omega_{A_2}^2Q_A^0/[(1-\alpha)\Omega_{A_1}^2+\alpha\Omega_{A_2}^2]\equiv\alpha Q_A^0/[(1-\alpha)\gamma_A+\alpha], \tag{4b}$$

$$Q_B^{*}=\alpha\Omega_{B_1}^2Q_B^0/[(1-\alpha)\Omega_{B_2}^2+\alpha\Omega_{B_1}^2]\equiv\alpha\gamma_BQ_B^0/[1-\alpha+\alpha\gamma_B], \tag{4c}$$

where

$$\gamma_A=\Omega_{A_1}^2/\Omega_{A_2}^2, \qquad \gamma_B=\Omega_{B_1}^2/\Omega_{B_2}^2. \tag{5}$$

By substituting (4a)-(4c) in expression (6) for the term of the initial state

$$U_i=\frac{1}{2}\sum\omega_k^2\eta_k^2+\frac{1}{2}\Omega_{A_1}^2Q_A^2+\frac{1}{2}\Omega_{B_2}^2Q_B^2+I_i, \tag{6}$$

we obtain

$$\Delta F_{AB}^{*}=\alpha^2E_s^{AB}+\frac{1}{2}\Omega_{A_1}^2\alpha^2Q_A^{02}/[(1-\alpha)\gamma_A+\alpha]^2+\frac{1}{2}\Omega_{B_2}^2\gamma_B^2\alpha^2Q_B^{02}/[1-\alpha+\alpha\gamma_B]^2, \tag{7}$$

where E_s^{AB} is the energy of the reorganization of the solvent [3] in reaction (*).

The symmetry coefficient α introduced into (4a)-(4c) and (7) is defined as the derivative $\partial(\Delta F^{\neq})/\partial(\Delta F_0)$ (where ΔF_0 is the free energy of reaction (*) and can be found by solving the equation $U_i[\xi_k^{*}(\alpha)]=U_f[\xi_k^{*}(\alpha)]$.

On considering the symmetrical reactions in a similar manner, it is not difficult to show that

$$\Delta F_A^{\neq}=E_A^{*}/4+U_A+\frac{1}{2}\Omega_{A_1}^2Q_A^{02}/(1+\gamma_A)-kT\ln\left(\varkappa_A\frac{\hbar\omega_A}{kT}\Delta V_A\right), \tag{8}$$

$$\Delta F_B^{\neq}=E_B^{*}/4+U_B+\frac{1}{2}\Omega_{B_1}^2Q_A^{02}/(1+\gamma_B)-kT\ln\left(\varkappa_B\frac{\hbar\omega_B}{kT}\Delta V_B\right), \tag{9}$$

where E_A^S and E_B^S are the energies of reorganization of the solvent and U_A and U_B are the energies of Coulomb interaction for the corresponding symmetrical processes.

By substituting (8) and (9) in (7), using (2), and passing from free energies to the equivalent expressions for the rate constants, we obtain

$$k_{AB}=k_A^ak_B^b(Z_{AB}/Z_A^aZ_B^b)\exp\left[\frac{(aE_A+bE_B^{*})/4-\alpha^2E_{AB}^{*}}{kT}\right]\exp\left[\frac{aU_A+bU_B-U_{AB}^{r}}{kT}\right], \tag{10}$$

where Z_{AB} denotes the value of $\varkappa_{AB}\frac{\omega_{AB}}{2\pi}\Delta V_{AB}$ and Z_A and Z_B have analogous meanings, and a and b denote, respectively, $\alpha^2(1+\gamma_A)/[(1-\alpha)\gamma_A+\alpha]^2$ and $\alpha^2\gamma_B(1+\gamma_B)/[1-\alpha+\alpha\gamma_B]$.

†In the approximation of a symmetrical deformation of the inner spheres it is possible to limit oneself to a consideration of the symmetrical metal–ligand vibrations alone.

TABLE 1. Experimental Values of the Rate Constants of the Symmetrical and Cross Electron-Transfer Reactions between the Complex Ions A $(H_2O)_6^{3,2+}$ and B $(H_2O)_6^{3,2+}$

A	B	$\lg k_A$ [5]	$\lg k_B$	$\lg K_{AB}$ [6]	$\lg k_{AB}$	$\lg k_{AB}^0$	$\lg f^{exp}$ *	α_M	α
Co(III)	Mn(II)	0,7	−4,0 [6]	+5,2	2,1 [4]	1,7	2,3	0,94 †	0,43
	Fe(II)	0,7	0,65 [5]	+18,4	2,4 [4]	9,9	−15	−0,3	0,45
	V(II)	0,7	−2,0 [5]	35,2	6,0 [2]	16,9	−22	−0,13	0,31
	Cr(II)	0,7	−4,7 [7]	37,7	4,1 [2]	16,8	−25,4	−0,17	0,35

* $\log f^{exp} = 2\ (\log k_{AB} - \log k_{AB}^0)$.

† The calculation of the total energy of reorganization from formula (12) using this value of α_M leads to a negative value of E_{AB}^t.

Expression (10) is the cross relation for electron-transfer reactions accompanied by the reorganization of the inner coordination sphere. In the special case of rigid spheres, it passes into the relation (1a), (1b). In actual fact, let us consider those reactions between ions in which $\gamma_{A,B} = 1$ (i.e., $a = b = 2\alpha^2$) and neglect the Coulomb interaction between the ions ($U_A = U_B = U_{AB}^r = 0$). Then, assuming that the transfer of an electron in unsymmetrical and symmetrical reactions takes place at the same distance R, and also that $\varkappa_{AB}=\varkappa_A=\varkappa_B$ and $\omega_{AB}=\omega_A=\omega_B$ (i.e., $Z_{AB} = Z_A = Z_B = Z$) and adopting the condition of additivity for E^t [$E_{AB}^t = (E_A^t + E_B^t)/2$], we obtain the cross relation in the form

$$k_{AB}=(k_Ak_B)^{2\alpha^2}Z^{1-4\alpha^2}, \tag{11}$$

which is identical with (1a), (1b) if one considers that under the assumptions mentioned above

$$\alpha=1/2+\Delta F_0/2E_{AB}^t. \tag{12}$$

The cross relation (10) can be rewritten in more convenient form for the case in which the change in the frequency of the vibrations of the inner coordination sphere is not too great, i.e., when $\gamma = 1 + \Delta\gamma$, $\Delta\gamma \ll 1$. It is obvious that this case is the most important in practice, since the change in the frequency Ω usually does not exceed 40-50%. Furthermore, we shall assume that AL_m and BL_m have the same charges in the oxidized and reduced forms, i.e., $U_A = U_B = U_{AB}^r = U$. With this limitation, expression (10) changes into the simpler relation (13)

$$k_{AB}=(k_Ak_B)^{2\alpha^2}Z^{1-4\alpha^2}\exp\left[(4\alpha^2-1)U/kT\right], \tag{13}$$

in which, in contrast to (11), the coefficient α is no longer defined according to (12) but must be found from a solution of the equation $U_i[\xi^*(\alpha)] = U_f[\xi^*(\alpha)]$ or it can be considered as an empirical parameter.

Let us now compare (1a), (1b), and (13). For this, let us rewrite (1a), (1b), in identical fashion as

$$\lg k_{AB}=\lg k_{AB}^0+1/2\lg f_M, \tag{14}$$

$$\lg f_M=(\alpha_M-1/2)\lg K_{AB}, \tag{15}$$

where

$$k_{AB}^0=(k_Ak_BK_{AB})^{1/2}. \tag{16}$$

If the value of $\log f_M$ is considered as an experimental value (determined from the difference between $\log k_{AB}$ for the unsymmetrical reaction and $\log k_{AB}^0$), then (15) can be used to find α_M

$$\alpha_M=1/2+\lg f^{exp}/\lg K_{AB}. \tag{17}$$

Expression (13) can also be represented in the form (14), but with the factor f given by

$$\lg f=(4\alpha^2-1)\left[\lg\left(k_Ak_B/Z^2\right)+2U/kT\right]-\lg K_{AB} \tag{18}$$

[it is obvious that (18) passes into (15) on the assumptions that $\Delta\gamma = 0$, $U = 0$, and $E_{AB}^S = (E_A^S + E_B^S)/2$]. According to (18), the coefficient α is given by

$$\alpha = \frac{1}{2}\left\{1+\lg(f^{\exp}K_{AB}) \Big/ \left[\frac{2U}{2{,}3kT}+\lg(k_Ak_B/Z^2)\right]\right\}^{1/2}. \quad (19)$$

Let us consider a group of reactions for which the calculation of the rate constant of the cross reaction k_{AB} by formulas (14) and (15) [or (1a) and (1b), which are equivalent to them] leads to values 5-6 orders of magnitude higher than the experimental figures (Table 1).

As estimates according to formula (17) using the experimental value of log f show (see Table 1), for these systems the coefficient α_M proves to be negative, which contradicts the definition of α given in the theory [1, 3], according to which the value of α is located in the range between zero and unity. Nevertheless, calculation by formula (19) leads to reasonable values of the symmetry coefficient α. The rate constants k_{AB} of the cross reactions calculated from formula (13) with such values of α agree with the experimental values. An important conclusion follows directly from this: for the systems collected in Table 1 the assumptions of the additivity of the energies of reorganization and of the small role of the effects of Coulomb interaction and of the invariability of the frequency of the intramolecular vibrations are incorrect. It is just the neglect of these effects that leads to the considerable discrepancy between the theoretical and experimental rate constants of the cross reactions.

According to (13), between the rate constants (k_{AN} and k_{BN}) of two series of redox reactions in each of which AL_m^{ox} and BL_m^{ox} react with one and the same set of ions NL_m^{red}, there must be a correlation of the type of

$$\lg k_{AN} = (\alpha_A/\alpha_B)^2 \lg k_{BN} + C.$$

It is obvious that, generally speaking, the tangent of the angle of slope of the graph of log k_{AN} versus log k_{BN} differs from unity and depends on the symmetry coefficients α_A and α_B in each of the series. Only in the particular case where $\alpha_A = \alpha_B$, which corresponds to relation (1a), is the correlation under consideration characterized by a slope of 45°.

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