HOMOGENEOUS ELECTRON TRANSFER PROCESSES

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The reaction rate constants of electron transfer between the octahedral aquo complexes of a number of transition metals are calculated quantum mechanically under the assumption that the attending deformation of the coordination sphere is symmetric. It is concluded from an analysis performed in the classical approximation for the metal–ligand vibrational frequencies that quantum effects are insignificant in the complexes being discussed. The results of numerical calculations are compared with experiment.

The reactions with electron transfer belong to the simplest class of redox reactions taking place in polar liquids or at the electrode–electrolyte solution interface. There is a strong resemblance in the physical mechanisms followed by the elementary act in the homogeneous and the heterogeneous case, which is due to the fact that in both cases the energy of activation is caused by the reorganization of the polar medium and by the change in the intramolecular structure of the reactants following the electronic transition. In the present work we shall limit ourselves to studying homogeneous processes with the aim of qualitatively and quantitatively analyzing the principal features of the elementary act. For the sake of simplicity we shall consider electron transfer reactions between two species which take place in a single step and are not accompanied by the rupture or formation of any chemical bonds:

$$A^{+m}+B^{+n}\rightarrow A^{+m-1}+B^{+n+1}. \tag{1}$$

Typical examples of reactions of this type are electron exchange processes between transition metal complexes.

The calculation of electron transfer rate constants reported in the present work uses, as a base, the general quantum mechanical theory of transitions between two multidimensional potential energy surfaces having the shape of paraboloids (the harmonic approximation) as outlined in [1-4]. The use of the harmonic approximation in the reactions being discussed by us is justified by the fact that the change in the metal–ligand bond lengths usually is 0.1-0.2 Å, i.e., the deviations from the equilibrium lengths are small. Quantitative comparison of the theoretical calculations with experimental data will be made for electron exchange reactions between aquo complexes of divalent and trivalent cobalt, iron, chromium, vanadium, and manganese ions. All these ions have the structure of regular octahedra (with the possible exception of Cr^{2+} and Mn^{3+} for which the Jahn–Teller effect seems to be essential), so that it will be sufficient for our purposes to only calculate centrosymmetrical vibrations in the complexes.

In the model chosen by us, the potential energy surfaces for the initial (v_i) and final (v_f) state can be written down in the form

$$v_i=\frac{1}{2}\sum_x \hbar\omega_x q_x^2+\frac{1}{2}\sum_{n=A,B}\hbar\Omega_{ni}Q_{ni}^2,$$

$$v_f=\frac{1}{2}\sum_x \hbar\omega_x (q_x-q_{x0})^2+\frac{1}{2}\sum_{n=A,B}\hbar\Omega_{nf}(Q_{nf}-Q_{n0})^2+\Delta J_0. \tag{2}$$

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Here $q_{\varkappa}$ and $\omega_{\varkappa}$ are the normal coordinates and characteristic frequencies of the effective oscillators of the medium which describe the fluctuations in the medium's polarization [5-7]; the quantities $q_{\varkappa 0}$ define the change in the medium's equilibrium polarization which occurs when an electron passes from particle A to particle B; Ω_{ni} and Ω_{nf} are the frequencies of the centrosymmetric vibrations in the complexes in the initial and final state, Q_{ni} and $Q_{n}' = \sqrt{\frac{\Omega_{nf}}{\Omega_{ni}}} Q_{ni}$ are the normal coordinates corresponding to these vibrations, and the Q_{n0} are defined by the change in metal–ligand bond length ΔR_{n0}:

$$Q_{n0} = \frac{6 M_L \Omega_n' (\Delta R_{n0})^2}{\hbar}, \tag{3}$$

where M_L is the mass of the ligand, and ΔJ_0 is the difference between the potential energy minima of the final and initial state. Presently there do not exist accurate experimental data on the vibration frequencies for all complexes to be examined in the oxidized and reduced form, but it turns out that for all those ions for which such data are available, the frequencies of the divalent ions are roughly identical and amount to $\Omega_R \cong 360\ \mathrm{cm}^{-1}$, those of the trivalent ions $\Omega_0 \cong 450\ \mathrm{cm}^{-1}$. In the following we shall adopt these frequency values for all the complexes to be examined below, and set $\Omega_{Ai} \cong \Omega_{Bf} \cong \Omega_0$ and $\Omega_{Af} \cong \Omega_{Bi} \cong \Omega_R$.

In this approximation the quantity ΔJ_0 can be identified with the reaction free energy ΔF_0.

In the model adopted by us, the probability of electron transition per unit time between two ions A and B existing at a given distance R can be written down in the form (according to quantum mechanical theory, cf., Eq. (3.35) in [5])

$$W_{if} = A \exp\left\{ -\beta\alpha\Delta F_0 - \beta\alpha(1-\alpha)E_S - \sum_{n=A,B} \left[Q_{ni}^{*2} \operatorname{th} \frac{\beta\hbar\Omega_{ni}(1-\alpha)}{2} + (Q_{nf}^{*} - Q_{n0})^2 \operatorname{th} \frac{\beta\hbar\Omega_{nf}\alpha}{2} \right] \right\}. \tag{4}$$

Here $\beta = 1/kT$, and α is the transfer coefficient (symmetry factor or Brönsted coefficient)

$$\alpha = \frac{d\Delta F^{\neq}}{d\Delta F_0}, \tag{5}$$

where $\Delta F^{\neq}$ is the free energy of activation; E_S is the energy of reorganization of the polar medium:

$$E_S = {}^1/_2 \sum_{\varkappa} \hbar\omega_{\varkappa} q_{\varkappa 0}^2, \tag{6}$$

where the summation over $\varkappa$ is conducted under the condition that $\hbar\omega_{\varkappa} \ll 2kT$, i.e., that only "classical" oscillators take part in the activation; Q_n^* is the normal coordinate of the complex in the transition state which is determined from the equation (cf., Eq. (3.39) in [5])

$$Q_{ni}^{*} \operatorname{th} \frac{\beta\hbar\Omega_{ni}(1-\alpha)}{2} + \sqrt{\frac{\Omega_{nf}}{\Omega_{ni}}} (Q_{nf}^{*} - Q_{n0}) \operatorname{th} \frac{\beta\hbar\Omega_{nf}\alpha}{2} = 0. \tag{7}$$

Finally we report the expression for the preexponential factor A in Eq. (4) (cf. Eq. (3.38) in [5]):

$$A = \frac{\beta L^2}{\hbar} \sqrt{\frac{2\pi}{|H''|}} \prod_{n=A,B} \operatorname{sh} \frac{\beta\hbar\Omega_{ni}}{2} \left\{ \operatorname{sh}^2 \frac{\beta\hbar\Omega_{ni}(1-\alpha)}{2} \operatorname{ch}^2 \frac{\beta\hbar\Omega_{nf}\alpha}{2} + \operatorname{sh}^2 \frac{\beta\hbar\Omega_{nf}\alpha}{2} \operatorname{ch}^2 \frac{\beta\hbar\Omega_{ni}(1-\alpha)}{2} + \frac{\Omega_{ni}^2 + \Omega_{nf}^2}{4\Omega_{ni}\Omega_{nf}} \operatorname{sh} \beta\hbar\Omega_{ni}(1-\alpha) \operatorname{sh} \beta\hbar\Omega_{nf}\alpha \right\} \tag{8}$$

where L is the electron exchange integral and

$$H'' = \frac{d^2}{d\alpha^2} H(Q_n^*(\alpha), \alpha). \tag{9}$$

Solving Eq. (7) for Q_n^* we find Q_n^* as a function of α, and substitute into Eq. (4):

$$H = \beta\alpha\Delta F_0 + \beta\alpha(1-\alpha)E_S + \beta\varphi(\alpha)E_r^A + \beta\varphi(1-\alpha)E_r^B, \tag{10}$$

where

$$\varphi(\alpha) = \left[\frac{\beta\hbar\Omega_0}{2} \operatorname{cth} \frac{\beta\hbar\Omega_R\alpha}{2} + \frac{\beta\hbar\Omega_R}{2} \operatorname{cth} \frac{\beta\hbar\Omega_0(1-\alpha)}{2} \right]^{-1}, \tag{11}$$

$$E_r^A = 3M_L\Omega_0\Omega_R(\Delta R_{0A})^2, \quad E_r^B = 3M_L\Omega_0\Omega_R(\Delta R_{0B})^2. \tag{12}$$

The transfer coefficient α is determined from the condition for the minimum of $H(Q_n^*(\alpha), \alpha)$:

$$\Delta F_0 = (2\alpha-1)E_S - \varphi'(\alpha)E_r^A + \varphi'(1-\alpha)E_r^B. \tag{13}$$

Before proceeding to the quantitative calculation of actual reactions we shall analyze the relations obtained for their physical significance. First we note that the quantity $\frac{1}{\beta}H$ [cf., Eq. (10)] depends on temperature via the functions $\varphi(\alpha)$ and $\varphi(1-\alpha)$ [cf., Eq. (11)], so that it cannot be identified with the energy of activation (more precisely, with part of the energy of activation). The physical reason for this is to be found in the fact that the frequencies of the molecular vibrations of the complexes do not satisfy the condition of "classical" behavior obtained in [1-5]:

$$\alpha\hbar\Omega_0, \ (1-\alpha)\hbar\Omega_0, \ \alpha\hbar\Omega_R, \ (1-\alpha)\hbar\Omega_R \ll 2kT. \tag{14}$$

In fact, $\Omega_0 \simeq 450\ \mathrm{cm}^{-1}$ and $\Omega_R \simeq 360\ \mathrm{cm}^{-1}$, while $2kT/\hbar = 400\ \mathrm{cm}^{-1}$. Providing the vibrations of the ligands were classical in character, i.e., conditions (14) were fulfilled, it would have been possible in Eq. (11) to replace the hyperbolic cotangents by the inverse arguments

$$\varphi_{\mathrm{cl}}(\alpha) \simeq \frac{\alpha(1-\alpha)\Omega_0\Omega_R}{\alpha\Omega_R^2 + (1-\alpha)\Omega_0^2}. \tag{15}$$

In this case $\frac{1}{\beta}H$ is no longer temperature dependent, and assumes the role of an energy of activation, since α does not depend either on temperature, according to Eq. (13). Under conditions opposite to the inequality (14), the hyperbolic cotangents in Eq. (11) could be replaced by unity and

$$\varphi_{\mathrm{cl}}(\alpha) \simeq \frac{2}{\beta\hbar(\Omega_0+\Omega_R)}. \tag{16}$$

In this case Eq. (10) can be rewritten in the form

$$H = \beta\{\alpha\Delta F_0 + \alpha(1-\alpha)E_S\} + \frac{6M_L\Omega_0\Omega_R[(\Delta R_{0A})^2 + (\Delta R_{0B})^2]}{\hbar(\Omega_0+\Omega_R)} = \beta E_a + \sigma, \tag{17}$$

where E_a is an energy of activation wholly caused by classical fluctuations in the polarization of the solvent, while σ is a tunneling factor expressing the fact that ligand rearrangement in the process of the electronic transition involves passage beneath the barrier.

In order to obtain an expression for the specific rate constant of electron transfer one must multiply the transition probability in unit time, $\overline{W}_{if}$, by the probability that the reactants will approach to a distance R, and integrate over all distances:

$$k = \int_0^\infty \overline{W}_{if}(R)e^{-\beta U_c(R)}4\pi R^2\,dR. \tag{18}$$

Here $U_c(R)$ is the potential of mean force acting upon reactants which are at a distance R, i.e., $\exp\{-\beta U_c \cdot (R)\}$ coincides with the pair correlation function $\Phi_{AB}(R)$. In the case of highly dilute solutions, $U_c(R)$ is equated to the coulombic repulsion energy between the reactants, but at somewhat higher concentrations, $U_c(R)$ must be replaced by the Debye–Hückel potential. For highly concentrated solutions a proper theory for the calculation of $\Phi_{AB}(R)$ does not exist at present. To circumvent this difficulty we note that $\Phi_{AB}(R)$ in any case is diminishing sharply as the reactants approach, while $\overline{W}_{if}(R)$ is doing so with increasing R [chiefly because of the exchange integral L(R)]. Therefore the expression under the integral in Eq. (18) must have a sharp maximum at some distance R* between the reactants. Thus, at the distance R* a reaction zone of some thickness δR^* is formed within which the electron jump effectively can take place. Hence Eq. (18) can be rewritten as

$$k = \overline{W}_{if}(R^*)e^{-\beta U_c(R^*)}v^*, \tag{19}$$

$$v_* = 4\pi R^{*2}\delta R^*. \tag{20}$$

It is important to note that, generally speaking, R* does not coincide with the sum of reactant radii: $R^* \geq R_A + R_B$. This is due to the fact that the transmission coefficient $\varkappa$ defining the probability of an actual electron jump in the transition state equals unity (adiabatic transitions) up to certain distances $R \leq R_{cr}$, and only at $R > R_{cr}$ will $\varkappa(R)$ begin to fall off sharply following an exponential law (nonadiabatic transitions). An equation for determining the distance R_{cr} separating adiabatic ($\varkappa \simeq 1$) and nonadiabatic ($\varkappa < 1$) transitions was obtained in [4, 9], and for our case can be written approximately as (cf., e.g., Eq. (4.87) in [4])

$$L(R_{cr}) \simeq \left\{ \frac{\hbar^2 \Omega_0^3 \Omega_R^3}{4\pi^3 \beta} \sum_{n=A,B} \frac{E_r^n}{[\alpha \Omega_{nf}^2 + (1-\alpha)\Omega_{ni}^2]^2} \right\}^{1/4}. \tag{21}$$

The right-hand side of this equation is readily evaluated upon selection of realistic values for the parameters E_r^n (for more details about this cf. below). It is found that $L(R_{cr}) \approx kT = 0.6$ kcal/mole = 0.025 eV. If one knew from quantum chemical calculations the dependence of the exchange integral on R, one could from condition (21) evaluate R_{cr}, i.e., find in effect the distance at which the electron transfer takes place. However, taking into account the low value of $L(R_{cr})$ (≈ 0.025 eV) one can expect R_{cr} to be a little larger than the sum of the ionic radii.

Writing Eq. (19) formally as

$$k = \frac{kT}{h} e^{-\beta \Delta F^{\neq}} \tag{22}$$

one can obtain the following expression for the free energy of activation:

$$\Delta F^{\neq} = U_c^* + \frac{1}{\beta} H - \frac{1}{\beta} \ln 2\pi\hbar\beta v^* A. \tag{23}$$

It can be seen from the above analysis that for a theoretical calculation of the rate constants one must know the following reaction parameters: 1) the parameters $E_r^{(n)}$ defining the energy of intramolecular reorganization of the complexes, and the parameter E_s of reorganization of the polar medium; 2) the energy of coulombic interaction of the reactants, $U_c^* = U_c(R^*)$; 3) the exchange integral $L(R^*)$; 4) the volume v^* of the reaction zone. In principle all these parameters can be found theoretically if the changes in the equilibrium metal–ligand bond lengths are known for all complexes and if from quantum chemical calculations one knows the dependence L(R). However, since at the present time these lengths are not available, we shall try to estimate these parameters by analyzing experimental data on the energies and free energies of activation for symmetrical reactions (A = B) under the assumption that in all these reactions, the distance R^* and $L(R^*)$ are approximately the same.

The most reliable data on the size of ΔR_0 exist for the aquo complex of the iron ion: $\Delta R_0 \simeq 0.16$ Å, from which one can estimate $E_r^{Fe} \cong 15$ kcal/mole. To estimate the remaining E_r^n parameters we shall proceed as follows. We find the energy of activation for the symmetrical reactions ($\alpha = 0.5$):

$$\Delta E_s^{\neq} = \frac{\partial}{\partial\beta} \beta \Delta F_s^{\neq} \cong \frac{E_s}{4} + U_c^* - \frac{3}{2} kT + \beta \frac{\partial U_c^*}{\partial\beta} + E_r \varphi^2(0.5) \frac{\beta^2 \hbar^2 \Omega_0 \Omega_R}{4} \left\{ \frac{1}{\operatorname{sh}^2 \frac{\beta\hbar\Omega_0}{4}} + \frac{1}{\operatorname{sh}^2 \frac{\beta\hbar\Omega_R}{4}} \right\}. \tag{24}$$

Then we establish the difference between the energies of activation for two symmetrical reactions:

$$\delta \Delta E_s^{\neq} = \delta E_r \varphi^2(0.5) \frac{\beta \hbar^2 \Omega_0 \Omega_R}{4} \left\{ \frac{1}{\operatorname{sh}^2 \frac{\beta\hbar\Omega_0}{4}} + \frac{1}{\operatorname{sh}^2 \frac{\beta\hbar\Omega_R}{4}} \right\} \tag{25}$$

From this we find the change in the E_r values for the various ions. These estimates lead to the following E_r values for different ions, provided that we use the value $E_r^{Fe} = 15$ kcal/mole:

$$E_r^{Co} \simeq 13;\quad E_r^{Cr} \simeq 30;\quad E_r^{V} \simeq 26;\quad E_r^{Mn} \simeq 22 \text{ kcal/mole.}$$

We estimated the analogous difference between the free energies of activation for two symmetrical reactions:

$$\delta \Delta F_s^{\neq} \simeq 2\varphi(0.5)\delta E_r - 2.3\, kT \delta \ln L^2. \tag{26}$$

Using the E_r thus found and the experimental $\Delta F_S^{\neq}$ data one can readily see that the exchange integrals for all symmetrical reactions are approximately equal to within one order of magnitude. Under the assump-

TABLE 1. Kinetic Parameters of Electron Transfer Reactions

Reactions	α	$\Delta F^{\neq}_{\text{theor}}$	$\Delta F^{\neq}_{e}$	ΔF_0	Literature
$Co[H_2O]_6^{3+}+Mn[H_2O]_6^{2+}$	0,43	16,6	14,6	−7.124	[10]
$Co[H_2O]_6^{3+}+Fe[H_2O]_6^{2+}$	0,29	11	14,2	−25.208	[10]
$Co[H_2O]_6^{3+}+Cr[H_2O]_6^{2+}$	0,16	8,2	11,9	−51,65	[11]
$Co[H_2O]_6^{3+}+V[H_2O]_6^{2+}$	0,164	8	9,4	−48,22	[11]
$Co[H_2O]_6^{3+}+Co[H_2O]_6^{2+}$	0,5	18,45	17		[12]
$Fe[H_2O]_6^{3+}+Fe[H_2O]_6^{2+}$	0,5	19.4	16,8		[13]
$Cr[H_2O]_6^{3+}+Cr[H_2O]_6^{2+}$	0,5	26,3	24,1		[14]
$V[H_2O]_6^{3+}+V[H_2O]_6^{2+}$	0,5	24.48	22,2		[15]
$Mn[H_2O]_6^{3+}+Mn[H_2O]_6^{2+}$	0,5	22,6	22,2		[16]

tion that the transmission coefficient approaches unity ($\varkappa = 1$) one can use Eq. (21) to estimate L, which was found to be about 0.5 kcal/mole, i.e., very close to kT.

Knowing $E_r^{(n)}$ and L^2 one can estimate the quantity $\left(\frac{E_s}{4}+U_c^*\right)$, if one adopts the reasonable value $v^* \approx 1$ liter/mole. We obtain $\left(\frac{E_s}{4}+U_c^*\right) \simeq 15$ kcal/mole. The values of E_s and U_c^* can be found separately from Eq. (24) if we assume that U_c^* depends on temperature only via the static dielectric constant $\varepsilon_s(T)$. As a result we find $E_s \simeq 36$ kcal/mole and $U_c^* = 6$ kcal/mole.

If for U_c^* we take the energy of coulombic interaction $U_c^* = \frac{z_1 z_2 e^2}{\varepsilon_s R^*}$ we obtain about 7 Å for R^* which is somewhat larger than the sum of the ionic radii ($R_A + R_B = 6.5$ Å).

With the aid of above values for the parameters we have calculated the free energies of activation by Eq. (23) (Table 1). Considering the crudeness of the assumptions adopted by us one must admit that the agreement between the theoretical and experimental $\Delta F^{\neq}$ values is satisfactory.

It is of interest to compare the results obtained with a calculation of $\Delta F^{\neq}$ that was carried out under the assumption that the condition of classical behavior (14) is fulfilled. To this end the $\Delta F^{\neq}$ were calculated in the classical approximation. It was found that the deviation of the $\Delta F^{\neq}_{cl}$ from the $\Delta F^{\neq}$ is about 1-2 kcal/mole.

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