A THEORY OF CONCERTED PROTON-TRANSFER REACTIONS IN A POLAR MEDIUM

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In [1, 2] a theory of electron transfer in a polar medium by an outer-sphere bridge mechanism was developed. In the present article a process of proton transfer by a bridge mechanism is considered, which can serve as a model for catalysis of some chemical proton transfer reactions in a polar medium or for processes on enzymes [3, 4].* The reaction scheme is shown in Fig. 1. In the initial state (i) of the system, a proton performs vibrations in a molecule of the reagent AH^+ about a certain equilibrium value R_{10}^{i}, and the second proton which participates in the reaction vibrates about the equilibrium position R_{20}^{i}. Thereupon, the polarization of the medium performs thermal fluctuations about some equilibrium position which corresponds to the initial charge distribution in the system. In the one-dimensional description of solvent polarization adopted in the present work, using the generalized coordinate q, the solvent potential-energy surface (electron–proton term) at fixed proton quantum states can be depicted in the form of a parabola with an apex corresponding to an equilibrium value of q_0 and an equilibrium energy I_0 (Fig. 2). In the final state, the proton from the AH^+ molecule is on the bridge CH^+ molecule, and the proton which had been previously on the CH^+ molecule goes over to the B molecule. (In particular, the AH^+ and B reagents can belong to a single enzyme macromolecule.)

Transition from the initial to the final state can take place by two parallel mechanisms: a "push–pull" mechanism (k) where the CH^+ molecule initially adds a proton from the AH^+ molecule and then gives up a second proton to a B molecule; or a "pull–push" mechanism (l) in which a bridge CH^+ molecule initially confers a proton to the B molecule and then obtains a proton from the AH^+ molecule. The two corresponding intermediate states of the system are shown in Fig. 1, where the quantum numbers m, n, p, and r characterize excited proton levels. Transition of protons from the initial state to the final one through the intermediate state k or l can be considered as a virtual quantum-mechanical transition whose probability in a unit of time is given by the quantum-mechanical theory formula for second-order perturbations [5]

$$W_{if} = \frac{2\pi}{\hbar} Av_i \sum_f \left| \sum_s \frac{\langle \psi_f V_{fs} \psi_s \rangle \langle \psi_s V_{si} \psi_i \rangle}{E_i - E_s + i\delta} \right|^2 \delta (E_i - E_f). \quad (1)$$

Here Av_i is an average with respect to the initial state of the system, δ is a function which expresses the law of conservation of total energy; ψ_i, ψ_f, and ψ_s are the wave functions of the initial, final, and intermediate states of the system (s = k or l); V_{fs} and V_{si} are interactions which lead to proton transition; E_i, E_f, and E_s are the total energies of the corresponding states; and δ is a positive, infinitely small quantity.

Using an adiabatic approximation to describe the movement of protons and electrons and solvent fluctuations (since the characteristic vibration frequency of protons, $\omega \sim 10^{14}$ sec^{-1}, is much greater than the characteristic frequency of solvent dielectric relaxation, $\omega_0 \sim 10^{11}$ sec^{-1}), one may represent the wave functions of the system in the form of a product of the wave functions of electrons, protons, and solvent [6]

*Proton transfer by a bridge mechanism in electrochemical processes was discussed in [7].

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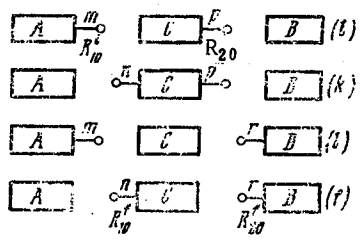

Fig. 1

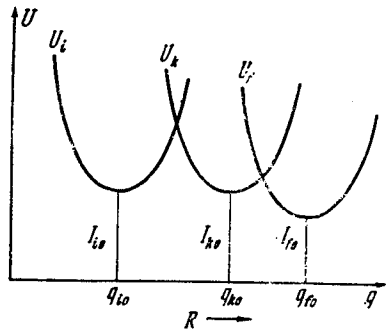

Fig. 2

$$\begin{aligned}
\psi_i &= \chi_i(x)\,\varphi_m(R_1 - R_{10}^i)\,\varphi_p(R_2 - R_{20}^i)\,\psi_{N_i}^{\mathrm{r}}(q - q_{i0}),\\
\psi_k &= \chi_k(x)\,\varphi_n(R_1 - R_{10}^f)\,\varphi_p(R_2 - R_{20}^i)\,\psi_{N_k}(q - q_{k0}),\\
\psi_l &= \chi_l(x)\,\varphi_m(R_1 - R_{10}^i)\,\varphi_r(R_2 - R_{20}^f)\,\psi_{N_l}(q - q_{l0}),\\
\psi_f &= \chi_f(x)\,\varphi_n(R_1 - R_{10}^f)\,\varphi_r(R_2 - R_{20})\,\psi_{N_f}(q - q_{f0}),
\end{aligned} \tag{2}$$

where the N are quantum numbers which describe the state of the solvent and the equilibrium values of the coordinates are denoted by the subscript 0. Assuming for simplicity that the proton frequencies are identical in all states, the total energies of the initial, final, and intermediate states can be written down in the form

$$\begin{aligned}
E_i &= I_{i0} + \hbar\omega_0 N_i + \hbar\omega\,(m+p),\\
E_k &= I_{k0} + \hbar\omega_0 N_k + \hbar\omega\,(n+p);\\
E_l &= I_{l0} + \hbar\omega_0 N_l + \hbar\omega\,(m+r),\\
E_f &= I_{f0} + \hbar\omega_0 N_f + \hbar\omega\,(n+r),
\end{aligned} \tag{3}$$

where $\omega_0 \ll kT/\hbar$ is the characteristic frequency of solvent fluctuations, $\omega \gg kT/\hbar$ is the frequency of proton vibrations, and the equilibrium energies I_{i0}, I_{k0}, I_{l0}, and I_{f0} include the energies of zero proton vibration and zero solvent vibration.

Using Eqs. (2) and (3), the transition probability can be represented in the form (for definiteness, below we have written down the formulas for mechanism k):

$$\begin{aligned}
W_{if} = \frac{2\pi}{\hbar} \sum_{N_i,\,m,\,p} \sum_{N_f,\,n,\,r} & \frac{\exp(-\hbar\omega_0 N_i/kT)}{Q_0} \frac{\exp(-\hbar\omega\,(m+p)/kT)}{Q_1 Q_2}\\
&\times \delta(I_{f0} - I_{i0} + \hbar\omega_0(N_f - N_i) + \hbar\omega\,(n+r-m-p))\\
&\times \left| \sum_{N_k} \frac{\langle\psi_{N_f}\varphi_r V_{fk}\psi_{N_k}\varphi_p\rangle\,\langle\psi_{N_k}\varphi_n V_{ki}\psi_{N_i}\varphi_m\rangle}{I_{i0} - I_{k0} + \hbar\omega_0(N_i - N_k) + \hbar\omega\,(m-n) + i\delta} \right|^2,
\end{aligned} \tag{4}$$

where Q_0 is the statistical sum over the states of the solvent, and the statistical sums with respect to the proton states, $Q_1Q_2 \approx 1$.

Using the Franck–Condon approximation to calculate the matrix elements that enter into (4), it is possible to separate the average and the summation with respect to excited proton states of the system and to calculate the probability of transition at fixed states of a proton subsystem, which is equivalent to calculating the probability of a bridge electron transfer [1, 2]. Then the probability of a transfer W_{if} can be represented in the form

$$W_{if} = \sum_{m,\,p,\,n,\,r} \exp(-\hbar\omega\,(m+p)/kT)\,(\varphi_r, V_{fk}\varphi_p)^2\,(\varphi_n, V_{ki}\varphi_m)^2\,W_{n,r}^{m,p}, \tag{5}$$

where $W_{n,r}^{m,p}$, the probability of transition at fixed proton quantum states, is defined by the expression

$$W_{n,r}^{m,p} = K\exp\{-E_a^{m,p,n,r}/kT\},$$

$$E_a^{m,p,n,r} = \max\begin{cases} E^{ki} = \dfrac{[E_s^{ki} + I_{k0} - I_{i0} + \hbar\omega(n-m)]^2}{4E_s^{ki}} \\ E^{fk} = \dfrac{[E_s^{fk} + I_{f0} - I_{k0} + \hbar\omega(r-p)]^2}{4E_s^{fk}} + I_{k0} - I_{i0} + \hbar\omega(n-m). \end{cases} \quad (6)$$

Here K is a constant which is determined by the mutual position of the terms of the system. The activation energy which enters into (6) has a simple geometrical sense. If one constructs the electron–proton terms of the system (the solvent potential–energy surfaces) for assigned proton quantum states [see, for example, Fig. 2, where for simplicity terms (i), (k), and (f) are shown when m = n = p = r = 0], then the activation energy E can be found as the distance from the minimum in the initial term to the highest of the two points of intersection of the initial term with the intermediate, or the intermediate term with the final one. The parameters E_s^{ki} and E_s^{fk}, called the solvent reorganization energies, are determined by the mutual location of the terms. The terms of excited states of the system can be obtained from terms which correspond to the ground states of protons by addition of excitation energy values $\hbar\omega(m + p)$, $\hbar\omega(n + p)$, or $\hbar\omega(n + r)$ to I_{i0}, I_{k0} or I_{f0}, which leads to a vertical shift of the terms shown in Fig. 2. Here it is necessary to take into account that at some values of (m, p, n, r) the points of intersection of the terms (i) and (k) are located higher, but at other values of (m, p, n, r) the points of intersection of the terms (k) and (f) are higher; therefore different expressions for the partial activation energies (6) correspond to different sets of quantum numbers.

To analyze the contributions of various quantum states of protons to the probability of transition, it is convenient to make use of the results of [6], where a calculation of the quantum-mechanical theory of the proton transfer reaction in a polar medium is carried out. The proton matrix elements which enter into (5) correspond, with an accuracy within factors which do not depend on quantum numbers, with the transmission coefficients $\varkappa_{rp}$ and $\varkappa_{nm}$ for nonadiabatic proton transfer [6]. To calculate the sums in (5), the mutual location of terms when m = n = p = r = 0 is important. If the point of intersection of terms (i) and (k) is higher than the point of intersection of terms (k) and (f), as was shown in Fig. 2, then, as is not hard to see, the factor $\{-[\hbar\omega(m + p) + E^{ki}]/kT\}$ has a maximum value when m = p = n = 0 and does not depend on r. In [1] sums of the type $\sum_{n,n} \varkappa_{nm}\exp\{-(\hbar\omega m + E^{ki})/kT\}$ were analyzed and it was shown that, at a normal relative location of terms (i) and (k), the competition between the factor $\varkappa_{nm}$ which grows with rise in m and n and the factor $\exp\{-(\hbar\omega m + E^{ki})/kT\}$, which rapidly declines leads to the situation that the main contribution to the sum is made by terms with m = 0. Examining the terms of series (5) at a fixed r, one may note that the terms with m = n = p = 0 make the main contribution to the sum. At the same time, in the sum with respect to r there is no exponential declining factor down to the value r*, at which E^{ki} and E^{fk} become equal, but $\varkappa_{r,\,p=0}$ rises with increase in r. When r > r*, the contribution from excited states with respect to r is small because of the rapid rise in E^{fk}. Thus, the main contribution to the probability of transition for the case of the location of terms which is shown in Fig. 2 is made by transitions with m = n = p = 0 and r = r*; since r*, which is determinable from the equation

$$\frac{(E_s^{ki} + I_{k_0} - I_{i0})^2}{4E_s^k} = \frac{(E_s^{fk} + I_{f0} - I_{k0} + \hbar\omega r^*)^2}{4E_s^{fk}} + I_{k0} - I_{i0}. \quad (7)$$

In the case where the point of intersection of terms (k) and (f) is above the point of intersection of terms (i) and (k), a similar analysis shows that states where p = r = n = 0 and m = m* make the main contribution to the probability of transition, where

$$\frac{(E_s^{ki} + I_{k0} - I_{i_0} - \hbar\omega m^*)^2}{4E_s^{ki}} = \frac{(E_s^{fk} + I_{f0} - I_{k_0})^2}{4E_s^{fk}} + I_{k0} - I_{i0}. \quad (8)$$

For the two cases of mutual location of terms examined above, the probability of transition can be represented in the form

$$W_{if} \sim \begin{cases} \varkappa^{fk}_{r^*,0}\,\varkappa^{ki}_{0,0} \exp\left\{-\dfrac{(E^{ki}_s + I_{k0} - I_{i0})^2}{4E^{ki}_s kT}\right\}; \\ \varkappa^{ki}_{m^*,0}\,\varkappa^{fk}_{0,0} \exp\left\{-\dfrac{(E^{fk}_s + I_{f0} - I_{k0})^2}{4E^{fk}_s kT} + \dfrac{I_{i0} - I_{k0}}{kT}\right\}. \end{cases} \tag{9}$$

Thus, proton transfer by the "push–pull" or by the "pull–push" mechanism, in distinction from direct proton transfer, takes place via participation of excited initial or final states of the proton subsystem.

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