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QUANTUM EFFECTS IN PROTON TRANSFER PROCESSES IN POLAR MEDIUM

By

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Abstract

The two main approaches to the theory of proton transfer in polar liquids are discussed. It is shown that when describing proton motion in terms of Morse potentials, classical overbarrier transfer should occur at proton transfer distances (r_0) that exceed 4 A, leading to considerably higher values of activation energy than observed experimentally. Quantum tunnelling from the ground level takes place at $r_0<2.5$ A; at $0.9\,\mathrm{A}<r_0<2.5\,\mathrm{A}$ the process is non-adiabatic, at $0.6\,\mathrm{A}<r_0<0.9$ A partially adiabatic and at $r_0<0.6$ A adiabatic.

Introduction

There are two approaches to the construction of the theory of homogeneous and heterogeneous reactions of proton transfer in polar media. One considers the process of proton transfer as gradual stretching of chemical bond in an AH reagent.[1~9] This approach does not differ essentially from the desciption of proton transfer in gas-phase reactions where the translational energy of reagents is usually also taken into account, i. e., transition is considered on a two-dimensional potential energy surface (depending on the proton coordinate and the distance between reagents).[9] Classical motion of the proton along the potential energy surface is usually postulated from the beginning and the existence of isotope effects is explained by proton tunnelling near the top of the potential barrier.

The other approach provides for the effect of polar medium on the kinetics of reactions involving charge redistribution in the system.[10~11] Unlike the first approach, along with the proton coordinate, normal coordinates that describe the state of polar medium are also taken into account. The second important difference is that the quantum-mechanical theory is consistently applied in the calculation of rate constants of proton transfer and no *a priori* assumptions are made about the character of proton transfer (by classical stretching of the bond or by quantum tunneling through the

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barrier) or about the classical and quantum contributions into the transfer probability.[12~16]

General analysis of the quantum-statistical expression for transfer probability in systems with many degrees of freedom carried out in the harmonic approximation showed[17] that the classical and quantum behaviour of a degree of freedom in a reaction is determined by the ratio between excitation energy of the given degree of freedom, $\hbar\omega$, and thermal energy, kT:

$$\hbar\omega_{\mathrm{cl}} \ll kT, \qquad \hbar\omega_{\mathrm{quant}} \gg kT \tag{1}$$

For anharmonic potentials the criterion of behaviour (classical or quantum) of a degree of freedom takes the form[10]

$$\Delta E_{\mathrm{cl}} \ll kT, \qquad \Delta E_{\mathrm{quant}} \gg kT \tag{2}$$

where ΔE is the characteristic distance between levels in the potential well associated with the given degree of freedom.*) It is assumed here that in the entire energy spectrum ΔE does not vary significantly, otherwise, if in a certain region of the spectrum one of inequalities (2) is true, while in another region the opposite inequality is true, this degree of freedom may behave differently depending on which region of the energy spectrum is significant for the process. It is just this situation that we encounter in the study of the proton subsystem.

A. non-adiabatic process

The full expression for the probability of proton transfer in a unit of time may be written as

$$W = \int e^{-\frac{U(R)}{kT}} W_{\mathrm{if}}(R)\, d\vec{R} \approx e^{-\frac{U(R^*)}{kT}} W_{\mathrm{if}}(R^*)\, \Delta V \tag{3}$$

where W_{if} is the transition probability at a given distance between the reagents and $\exp[-U(R)/kT]$ is the probability of the reagents approaching to distance R. Since the latter probability drops with the decrease of R, while $W_{\mathrm{if}}(R)$ sharply increases, the main contribution into W will be made by the region ΔV corresponding to a certain effective value, R^*. Thus, to calculate the rate constant of proton transfer it is necessary to know the dependence $W_{\mathrm{if}}(R)$ for different distances between the reagents.

*) For a one-dimensional potential energy surface, application of semi-classical wave functions and quantization rule leads to criteria (2), where ΔE is a characteristic scale of the energy spectrum in the potential well, obtained by mirror reflection of the barrier in relation to the coordinate axis.[10]

Let us begin with sufficiently large distances, when interaction leading to transition is weak (more precisely, the matrix element of transition is small) and the quantum-mechanical perturbation theory may be applied. The expression for the probability of transfer obtained within the perturbation theory corresponds to a completely non-adiabatic process :[10,12~14]

$$W_{\mathrm{if}}=\frac{\omega_{\mathrm{eff}}}{2\pi}\frac{|V_{\mathrm{if}}|^2}{\hbar\omega_{\mathrm{eff}}\sqrt{E_s kT/4\pi^3}\,Z_{\mathrm{p}}}\sum_{n,m}\mathrm{e}^{-\frac{E_n}{kT}}|\langle\varphi_n,\varphi_m\rangle|^2 \cdot\exp\left\{-\frac{[E_s+\Delta\mathfrak{F}+E_m-E_n]^2}{4E_s kT}\right\}. \tag{4}$$

Here V_{if} is the electron exchange integral of the interaction leading to transition ; ω_{eff} is the characteristic frequency of dielectric relaxation of the solvent ; $Z_{\mathrm{p}}=\sum_n\exp(-E_n/kT)$ is the proton statistical sum ; n, m and φ_n, φ_m are the quantum numbers and wave functions of the initial and final states of the proton ; E_s is the solvent reorganization energy ; $\Delta\mathfrak{F}$ is the free energy of the reaction which in the normal region of the reaction discussed here is not very great : $|\Delta\mathfrak{F}|<E_s$. Expression (4) includes summation over all quantum numbers (or energies) of the initial and final proton states. To analyze the expressions in the case when W_{if} is described by considerably anharmonic potentials, for instance by Morse potentials, we shall proceed as follows. Since the number of energy levels of the proton when describing its motion in terms of Morse-type potentials, although not infinite, is very great, instead of summation over proton quantum numbers n and m in (4), we shall integrate in respect to the corresponding energies, E_{f} and E_{i}. (The case when the main contribution into the transfer probability is made by several proton levels, *i. e.*, when integration may be inaccurate, we shall consider separately.) The proton transfer probability may then be rewritten as

$$W_{\mathrm{if}}=\frac{|V_{\mathrm{if}}|^2}{2\pi\hbar\sqrt{E_s kT/4\pi^3}\,Z_{\mathrm{p}}}\int \mathrm{d}\Delta j\,\mathrm{e}^{-\frac{[E_s+\Delta\mathfrak{F}+\Delta j]^2}{4E_s kT}}\Gamma(\Delta j), \tag{5}$$

where

$$\Gamma(\Delta j)=\int \mathrm{d}E_{\mathrm{i}}\,\mathrm{e}^{-\frac{E_{\mathrm{i}}}{kT}}|\langle\varphi_{E_{\mathrm{i}}},\varphi_{E_{\mathrm{i}}+\Delta j}\rangle|^2\rho_{\mathrm{i}}\cdot\rho_{\mathrm{f}}\,. \tag{6}$$

Here, $\Delta j=E_{\mathrm{f}}-E_{\mathrm{i}}$, E_{i} and E_{f} are the proton energies in the initial and final states, respectively, ρ_{i} and ρ_{f} are the level densities of the corresponding states, $\varphi_{E_{\mathrm{i}}}$ and $\varphi_{E_{\mathrm{i}}+\Delta j}$ are the wave functions of the initial and final states of the proton, corresponding to motion within U_{i} and U_{f} Morse potentials (Fig. 1).

$$U_i = D_i\left[1-\exp(-\alpha_i r)\right]^2 \qquad (7)$$

$$U_f = D_f\left[1-\exp(\alpha_f r-\alpha_f r_0)\right]^2 \qquad (8)$$

Fig. 1. Potential curves, $U_i(r)$ and $U_f(r)$.

D_i and D_f are the depths of the proton potential wells in the initial and final states, r_0 is the proton transfer distance, *i. e.*, the distance between U_i and U_f minima, α is the parameter characterising the curvature of the potential energy surface that may be related to the proton vibration frequencies at the lower energy levels.

Using the semi-classical approximation for wave functions φ_{E_i} and $\varphi_{E_i+\Delta j}$, integrating according to the Laplace method (6) in respect to the proton coordinate, it is easily seen that $|\langle\varphi_{E_i}, \varphi_{E_i+\Delta j}\rangle|^2$ is proportional to the Gamov factor of tunnelling, *i. e.*,

$$\Gamma(\Delta j)\sim\int_{E_{min}=(|\Delta j|-\Delta j)/2}^{E_{max}=U_i(r^*)} dE_i\,\rho_i\rho_f \exp\left[-\frac{E_i}{kT}\right.$$
$$\left.-\frac{2}{\hbar}\int_{a(E_i)}^{r^*}\sqrt{2m_p(U_i-E_i)}\,dr-\frac{2}{\hbar}\int_{r^*}^{b(E_i+\Delta j)}\sqrt{2m_p(U_f-E_i-\Delta j)}\,dr\right] \qquad (9)$$

Here $a(E_i)$, $b(E_i+\Delta j)$ and r^* are determined by conditions $U_i(a)=E_i$, $U_f(b)=E_i+\Delta j$, $U_i(r^*)=U_f(r^*)-\Delta j$. The expression under the integral in (9) is a function with a sharp maximum. To determine the value of E_i^* that provides the highest contribution to $\Gamma(\Delta j)$ the exponent in (9) should be differentiated:

$$\frac{1}{kT}=\frac{\sqrt{2m_p}}{\hbar}\left[\int_{a(E_i^*)}^{r^*}\frac{dr}{\sqrt{U_i-E_i^*}}+\int_{r^*}^{b(E_i^*+\Delta j)}\frac{dr}{\sqrt{U_f-E_i^*-\Delta j}}\right] \qquad (10)$$

In the case when the potential energy surface is described by Morse potentials (8)-(9), integrals in (10) may be calculated analytically and (10) may be reduced to

$$\frac{\hbar\omega_i}{4kT}=\frac{1}{2}f(t,t_{max})+\frac{1}{2}\frac{\omega_i}{\omega_f}f\left(\frac{D_i}{D_f}(t+\Delta t),\frac{D_i}{D_f}(t_{max}+\Delta t)\right) \equiv F(t,t_{max},\Delta t) \tag{11}$$

where $t=E_i^*/D_i$, $t_{max}=E_{max}/D_i$, $\Delta t=\Delta j/D_i$ and $(|\Delta t|-\Delta t)/2\leqslant t\leqslant t_{max}\leqslant 1$. Function $f(t,t_{max})$ is given by expression

$$f(t,t_{max})=\frac{1}{\sqrt{1-t}}\cdot\ln\frac{(1-\sqrt{t}-\sqrt{1-t})(1-\sqrt{t_{max}}+\sqrt{t_{max}-t}+\sqrt{1-t})}{(1-\sqrt{t}+\sqrt{1-t})(1-\sqrt{t_{max}}+\sqrt{t_{max}-t}-\sqrt{1-t})} \tag{12}$$

A plot of this function for several values of t_{max} is given in Fig. 2. At $t\to 0$, $f(t,t_{max})$ behaves as a logarithmic function and at $t\to t_{max}$, $f(t,t_{max})\to 0$. The right-hand part of (11) is a linear combination of two $f(t,t_{max})$ functions with appropriately displaced and extended arguments. The resultant function, $F(t,t_{max},\Delta t)$, at $t\to t_{max}$ tends to zero and has a logarithmic feature at $t\to 0$ if $\Delta t>0$ or at $t\to|\Delta t|$ if $\Delta t<0$ (Fig. 3). In the simplest case, when $D_i=D_f$, $\omega_i=\omega_f$ and $\Delta t=0$, the right-hand side of (11) coincides with $f(t,t_{max})$. Equation (11) can easily be solved graphically for various values of parameters $D_{i,f}$ and $\omega_{i,f}$ that determine the shape of the surface of proton

Fig. 2. The shape of $f(t,t_{max})$ for certain values of t_{max}.

Fig. 3. The shape of $F(t,t_{max},\Delta t)$; curve (a) $\Delta t>0$, curve (b) $\Delta t<0$.

potential energy in the initial and final states, of parameter t_{max} which implicitly determines the distance r_0 and of parameter Δt which determines the partial dimensionless free energy of the proton transfer reaction when the effect of polar medium is neglected.[4~8]

Certain important conclusions about the solutions of equation (11) depending on the value of $\hbar\omega/4kT$ may be made from the shape of functions $f(t, t_{max})$ and $F(t, t_{max}, \Delta t)$. At $\hbar\omega/4kT \ll 1$ the solution of eq. (11) is determined to a high degree of accuracy by expression $t^* \approx t_{max}$, *i. e.*, $E^* \approx E_{max}$ and proton transition occurs in the classical, nonadiabatic manner. At $\hbar\omega/4kT \gg 1$, $t^* \approx 0$ (if $\Delta t > 0$) or $t^* \approx |\Delta t|$ (if $\Delta t < 0$), *i. e.*, proton transition proceeds by tunnelling, in other words from the lowest possible level. At $\hbar\omega \sim kT$, solution of (11) is in an intermediate region, *i. e.*, transition occurs by preliminary activation to a certain level (E^*) and then by tunnelling. For classical behaviour of the proton subsystem the total activation energy of the process may be determined by integrating (5) in respect to Δj and it corresponds to a saddle point on the intersection of the total potential energy surfaces (including both the proton subsystem and the polar medium) of the initial and final states. In this case the use of a continuous spectrum of E_i and E_f energies in formulae (5)-(6) is justified. In the case of quantum behaviour of the proton subsystem the discreteness of the proton levels should be considered and solution of equation (11) should be interpreted as a transition from a lower proton level in the initial state from which, at a given relative arrangement of U_i and U_f, determined by Δj, transition is possible. Summation in respect to Δj which should be carried out instead of integration in (5) leads at $|\Delta\mathfrak{F}| < E_s$, *i. e.*, in the normal reaction region, to a result corresponding to proton transition from ground initial state to ground final state with activation energy corresponding to $\Delta j = E_f^0 - E_i^0$, or $E_a = [E_s + \Delta\mathfrak{F} + E_f^0 - E_i^0]^2/4E_s$ as obtained in Ref. (10, 12~14) with harmonic potentials. Thus, in the case of quantum, tunnel transition of the proton, the activation energy of the process is determined by the solvent reorganization energy and the pre exponential factor is proportional to the square of the overlap intergral of proton wave functions of the initial and final states.

It is interesting to estimate the effective proton transfer distance from which proton motion is classical. Let us consider the case when $D_i = D_f$, $\omega_i = \omega_f$ and $\Delta j = 0$ and the right-hand side of (11) coincides with $f(t, t_{max})$. For typical proton stretching frequencies ($\omega = 3000 \sim 3200\ \mathrm{cm}^{-1}$) the $\hbar\omega/4kT$ ratio is about 3.5~3.7. As can be seen from Fig. 2, intersection of horizontal line $\hbar\omega/4kT = 3.5$ with the graph of $f(t, t_{max})$ for $t_{max} < 0.4$ corresponds with sufficient accuracy to quantum proton transition from the lowest possible

level. At $D \sim 100$ kcal/mole this corresponds to $r_0^{\mathrm{quant}} \approx 2.5$ A. For a classical transition the distance should be much greater. Thus, for the above-mentioned values, E^* differs by less than 4 kcal/mole from $E_{\max}$ if $r_0 > r_0^{\mathrm{cl}} \approx 4$ A. It should be emphasised that the contribution of just the proton subsystem into the activation energy of the process considerably exceeds the observed activation energies in the case of classical behaviour. Furthermore, the presented analysis shows that the application in certain studies of the classical approach at $r_0 \lesssim 3$ A[4~6] or even at $1\ \mathrm{A} \gtrsim r_0 \gtrsim 0.39$ A[8] is unjustified for these distances.

Partially adiabatic and adiabatic processes

Expression (4) for the proton transfer probability describes a completely non-adiabatic process. During transition the proton cannot adiabatically adjust to the variation of the medium and the electrons cannot adiabatically adjust to the variation of the proton state. If the proton transfer distance is sufficiently small the electron exchange integral may be rather large since the electron subsystem may adiabatically follow the proton subsystem, while the process as a whole remains non-adiabatic, since the proton still cannot adjust to the variation of medium polarization. Criteria determining the possibility of such a partially adiabatic process were obtained in Ref. (18). The boundary between completely non-adiabatic and partially adiabatic processes is given by[18]

$$\frac{2\pi |V_{\mathrm{if}}|^2}{\hbar |v_{\mathrm{p}}| |F_{\mathrm{i}}^{\mathrm{p}} - F_{\mathrm{f}}^{\mathrm{p}}|} \sim 1 . \tag{13}$$

Here, $F_{\mathrm{i}}^{\mathrm{p}}$ and $F_{\mathrm{f}}^{\mathrm{p}}$ are the slopes of electron terms of initial and final states along the proton coordinate in the saddle point on the surface of their intersection and $|v_{\mathrm{p}}|$ is the modulus of the imaginary proton velocity, corresponding to tunnelling under the barrier. Estimations based on the proton potential energy surfaces reported in Ref. (19) at $V_{\mathrm{if}} \sim 1$ eV give $r^{\mathrm{nad}} \approx 0.9$ A.

At even smaller distances the transmission coefficient approaches unity and the process proceeds adiabatically. Estimation of the corresponding value may be obtained from condition[18]

$$\frac{(\Delta E_{\mathrm{ad}}/2)^2}{\hbar \omega_{\mathrm{eff}} \sqrt{kTE_{\mathrm{s}}/4\pi^3}} \sim 1 \tag{14}$$

where ΔE_{ad} is the minimal splitting of electron-proton adiabatic terms, equal to the minimal distance between two lower proton levels in the adiabatic potential having two minima.[18] Estimation on the basis of the adiabatic

surfaces of proton potential energy and its lower levels given in Table 17 and Fig. 116 of Ref. (19) at $E_s \sim 1$ eV and $\omega_{eff} \sim 10^{13} sec^{-1}$ gives $r^{ad} \approx 0.6$ A.

Therefore, we arrive at the following description of proton transfer at different distances between reagents:

1. At $r_0 > r_0^{cl} \approx 4$ A the proton is transfered in the classical over-barrier manner and the activation energy of the process is very great, considerably exceeding the experimentally observed values.
2. At 2.5 A $\approx r_0^{quant} < r_0 < r_0^{cl} \approx 4$ A the proton is transfered by a combination of classical stretching of the bond and subsequent tunnelling. The activation energy associated with the contribution from proton excitation is still considerable; the transmission coefficient is exceedingly small, sharply decreasing when the proton transfer distance is large.
3. In the region, 0.9 A $\approx r_0^{nad} < r_0 < r_0^{quant} \approx 2.5$ A, the process is completely non-adiabatic, the transmission coefficient is determined by proton tunnelling between the ground states of the proton subsystem.*) Activation energy is determined by reorganization of the polar medium.
4. In the region, 0.6 A $\approx r_0^{ad} < r_0 < r_0^{nad} \approx 0.9$ A, the process is partially adiabatic, the transmission coefficient is still less than unity and the activation energy is somewhat reduced in relation to the completely non-adiabatic process.
5. In the region, $r_0 < r_0^{ad} \approx 0.6$ A, the transmission coefficient is equal to unity and is independent of the proton transfer distance. The process is completely adiabatic.

It follows from this analysis that the probability of proton transfer is higher the smaller the distance between reagents. This distance is determined by different factors in different systems. In polar media, where the reagents may draw close to each other the distance is governed by repulsion of electron shells of the reagents and, in the case of complex multiatomic molecules, by steric hindrance as well. In certain cases, for instance, intramolecular proton transfer, the proton transfer distance is solely determined by the geometry of the reacting centres. At considerable distances between reacting centres in such systems proton transfer througn one or several water molecules, according to the bridge mechanism, may be favourable.[21,22] Fixation of proton localisation sites is also important for proton transfer in biological systems.

*) Numerical calculation using Morse potentials[16,20] shows that transitions between a few first excited proton levels may contribute to the probability of completely non-adiabatic transfer.

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