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THEORY OF HOMOGENEOUS REACTIONS INVOLVING PROTON TRANSFER*

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Abstract—A quantum-mechanical theory for proton transfer processes in solutions is given. The Brønsted rule and isotope effect for these processes are also discussed.

Résumé—Theorie quanto-mechanique du processus du transfert du proton dans la solution. Discussion de la règle de Brønsted et du effet isotopique, propre aux processus.

Zusammenfassung—Eine quantenmechanische Theorie der Protonenübergangreaktionen in die Losungen ist entwickelt. Die Brønstedsche Regel und der Isotopeneffekt für diese Vorgänge sind diskutiert.

WE HAVE treated[1] theoretically chemical reactions in solutions involving charge transfer, considerable attention being given to the simplest possible type of these reactions—redox reactions occurring without breaking or deformation of chemical bonds.

Good agreement between theory and experiment can be considered as confirmation both of the main assumptions of the theory—the assumption of the existence of a strong interaction between ion and polar solvent model used. This enabled us to pass to the consideration of the general case of a charge-transfer reaction in polar solvents involving breaking of chemical bonds. The general theory has been given,[2,3] and also the theory of reactions involving proton transfer under the conditions of an electrode process (theory of hydrogen overvoltage).[4,5]

In this paper we shall discuss in detail the results of a quantum-mechanical calculation of the rate constant of homogeneous proton transfer reactions†

$$AH + B^- \rightarrow A^- + BH. \qquad (1)$$

In our calculations we use the model described in detail in the treatment of the hydrogen-ion discharge on metals.[4,5] In particular, in describing the solvent we use as before a dielectric continuum approximation. In describing the proton state in AH and BH compounds, we take into consideration the fact that proton forms strong enough chemical bonds. Characteristic proton vibration frequencies, ω, along the valence bonds lie within the range *ca* 2600–3600 cm^{-1}. In all known cases at room temperature $\hbar\omega_i$ is much larger than kT, whence it follows that there is large probability that in the initial and final states the proton is localized at ground vibrational levels. In this study, however, account was taken of excited vibrational levels of the proton in the initial and final states.

In a quantum-mechanical calculation of the reaction rate constant, the proton

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† For convenience, we shall consider, without loss of generality, AH, BH to be neutral molecules, and A$^-$ and B$^-$ their respective ions.

state in the AH molecule was taken as the initial state. Proton interaction with ion B^- appeared as a perturbation leading to proton transfer from the initial to final state in the BH molecule. As was shown,[5] the reaction path can be conveniently interpreted, using, instead of usual electron terms, the electron–proton terms, where the generalized co-ordinate of the only classical sub-system—the solvent—appears as the reaction co-ordinate. According to the condition $h\omega_i \gg kT$, the proton motion, just as the electron motion, is of an essentially quantum nature.

The Hamlitonian of the system in which a proton exchange between two particles occurs can be conveniently written as

$$\begin{aligned}\mathscr{H}(x_A, x_B, R, q) &= \mathscr{H}_i^{\circ}(x_A, x_B, R, q) + V_{pB}(x_B, R)\\ &= \mathscr{H}_f^{\circ}(x_A, x_B, R, q) + V_{pA}(x_A, R).\end{aligned} \tag{2}$$

where x_A, x_B are electron co-ordinates of ion A^- and in ion B^-, respectively, R is the proton co-ordinate, q a set of normal co-ordinates of the solvent, $\mathscr{H}_i^{\circ}$ and $\mathscr{H}_f^{\circ}$ are the unperturbed Hamiltonians of the system in initial and final states, respectively and V_{pA} and V_{pB} the energies of proton interaction with ion A^- and B^- respectively.

Operator $\mathscr{H}_i^{\circ}$ includes the energy of the ion B^- in the solvent, the energy of the AH molecule in the solvent, and the Hamiltonian of the solvent proper (2). Operator $\mathscr{H}_f^{\circ}$ has a similar sense and differs from $\mathscr{H}_i^{\circ}$ only in that proton is bound with ion B^- and ion A^- is free. In this case the interaction of proton bound in AH molecule, with ion B^- which is described by the term $V_{pB}(x_B, R)$ isolated in Hamiltonian (2), leads to the proton jump from AH to B^-. Accordingly, the term $V_{pA}(x_A, R)$ leads to the proton jump from BH to A^-.

ADIABATIC APPROXIMATION

The system under consideration is characterized by the presence of three basic types of frequencies: frequencies of orientational (librational) vibrations of the medium dipoles (ω_0), frequencies of vibrations of bound proton in initial and final states (ω_p) and frequencies of electron motion in reacting ions (ω_e). The value of ω_0 can be found from measurements of the orientational relaxation times. In particular, for water $\omega_0 \approx 10^{11}\ s^{-1}$. These three types of frequencies differ significantly in their orders of magnitude: $\omega_0 \approx 10^{11}\ s^{-1} \ll \omega_p \approx 10^{14}\ s^{-1} \ll \omega_e \approx 10^{15}\ s^{-1}$. In accordance with this frequencies ratio, it is possible to divide the system consideration into sub-systems by the following methods:

(1) the fast sub-system—electron, the slow sub-system—proton and solvent (adiabatic approximation);

(2) the fastest sub-system—electron, a slower sub-system—proton, the slowest sub-system—solvent (double adiabatic approximation).

As known from quantum mechanics, such division of the system into slow and fast sub-systems permits us to use adiabatic perturbation theory. Two methods of solution of the problem are possible, corresponding to the two methods of division of the system. Below we shall consider these two methods and show that both the adiabatic approximation and the double adiabatic approximation lead to practically the same results.

(*a*) *Adiabatic perturbation theory*

The physical significance of this approximation is that in determining the wave function of the electron sub-system it is possible to ignore the kinetic energy of the slow sub-system, proton and solvent, owing to the slowness of their motion. In other words, the electron state can be accurately enough determined considering proton and solvent to be nearly stationary. The adiabatic approximation for the slow sub-system involves interaction of proton and solvent with the diffuse cloud of a fast moving electron, rather than with the "point" electron. This corresponds to the concept of the wave function of initial and final states as

$$\Psi_i^\circ(x_A, x_B, R, q) = \psi_B(x_B, q)\psi_A(x_A, R, q)\chi_A(R, q), \tag{3a}$$

$$\Psi_f^\circ(x_A, x_B, R, q) = \psi_B(x_B, R, q)\psi_A(x_A, q)\chi_B(R, q), \tag{3b}$$

where $\psi_A(x_A, R, q)\psi_B(x_B, q)$ are the electron wave-functions of the initial state, $\psi_A(x_A, q)\psi_B(x_B, R, q)$ the electron wave-functions of the final state and $\chi_A(R, q)$, $\chi_B(R, q)$ wave functions of the slow sub-system in the initial and final state, respectively.

It can be easily shown that the potential energies of the slow sub-system in the initial and final states are determined by the expressions

$$U_i^e(R, q) = \epsilon_A(R, q) + \tfrac{1}{2}\hbar\omega_0 \sum_K q_K^2 + \epsilon_B(q), \tag{4a}$$

$$U_f^e(R, q) = \epsilon_A(q) + \tfrac{1}{2}\hbar\omega_0 \sum_K q_K^2 + \epsilon_B(R, q), \tag{4b}$$

where $\epsilon_A(R, q)$, $\varepsilon_B(R, q)$ are the energies of molecules AH and BH present in the solvent with fixed co-ordinates of proton and solvent, and $\epsilon_A(q)$, $\epsilon_B(q)$ the energies of ions A^- and B^- with fixed co-ordinates of solvent. The functions $U_i^e(R, q)$ and $U_f^e(R, q)$ are usually called potential energy surfaces or electron terms of the system. For simplification, in this section we shall assume proton to perform in AH and BH molecules harmonic motion with the same frequencies $\omega_i = \omega_f = \omega_p$. Then, passing to new generalized co-ordinates, we obtain the following expressions for the terms

$$U_{ie} = J_{Ae} + \tfrac{1}{2}\hbar\omega_0(\eta - \eta_0)^2 + \tfrac{1}{2}\hbar\omega_p\xi^2, \tag{5a}$$

$$U_{fe} = J_{Be} + \tfrac{1}{2}\hbar\omega_0\eta^2 + \tfrac{1}{2}\hbar\omega_p(\xi - \xi_0)^2, \tag{5b}$$

where

$$\xi_0 = (R_{OB} - R_{OB})\sqrt{\frac{M\omega_p}{\hbar}}; \; |R_{OA} - R_{OB}| = \Delta R, \tag{6}$$

$$\eta_0^2 = \sum_K (q_{KOA} - q_{KOB})^2. \tag{7}$$

In formulae (6) and (7) q_{KOA}, q_{KOB} and R_{OA}, R_{OB} are equilibrium co-ordinates of solvent and proton in AH and BH molecules, respectively, and M is the proton mass. The terms J_A^e, J_B^e are of the form

$$J_A^e = \epsilon_A(R_{OA}, q_{OA}) + \epsilon_B(q_{OA}) + \tfrac{1}{2}\hbar\omega_0 \sum q_{KOA}^2, \tag{8a}$$

$$J_B^e = \epsilon_B(R_{OB}, q_{OB}) + \epsilon_A(q_{OB}) + \tfrac{1}{2}\hbar\omega_0 \sum q_{KOB}^2. \tag{8b}$$

Let us note that we have written the terms U_i^e and U_f^e as two-dimensional terms and we have discarded the terms (Fig. 1) which do not change upon proton transfer from the initial to the final state. From the assumption made here of the absence of the solvent frequency dispersion, it is possible to interpret clearly the reaction path

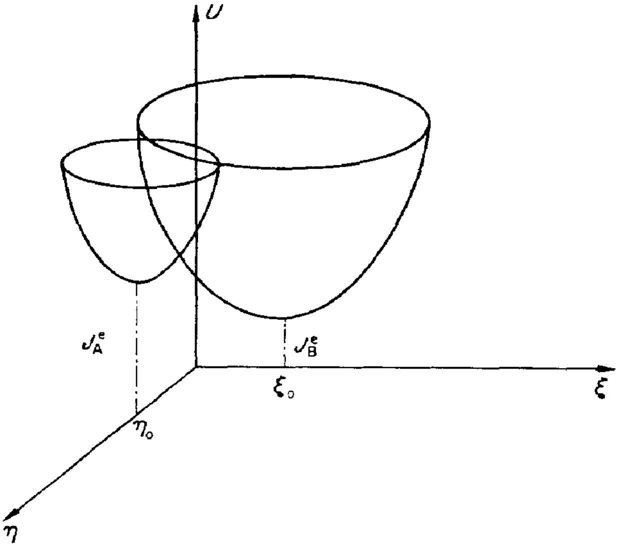

FIG. 1.

on the potential energy surface. As shown by calculation, the result given in this paper is valid also under the assumption of a small frequency dispersion.[3,4]

The assumption that proton performs harmonic vibrations permits us to consider the motion of proton and solvent independently and to express the function $\chi_{A,B}(\eta, \xi)$ in terms of the product of oscillatory functions of proton and solvent,

$$\chi_{A,B}(\eta, \xi) = \Phi_{A,B}(\xi)\varphi_{A,B}(\eta). \tag{9}$$

(b) Double adiabatic perturbation theory

In a double adiabatic approximation the wave functions of the initial and final states can be written as the product of the wave functions of the three sub-systems,

$$\Psi_i^{\circ} = \psi_A(x_A, R, q)\psi_B(x_B, q)\Phi_A(R, q)\varphi_A(q), \tag{10a}$$

$$\Psi_f^{\circ} = \psi_A(x_A, q)\psi_{B},\, (x_B, R, q)\Phi_B(R, q)\; \varphi_B(q), \tag{10b}$$

where $\Phi_{A,B}(R, q)$ are oscillatory wave functions describing the bound proton state in AH and BH molecules, and $\varphi_{A,B}(q)$ the corresponding wave functions of solvent. In the approximation under consideration for the potential energies of the initial and final states of the slowest sub-system—solvent—we have the functions[4]

$$U_{im}^{ep} = J_{Am} + \tfrac{1}{2}\hbar\omega_0(\eta - \eta_0)^2, \tag{11}$$

$$U_{fm'}^{ep} = J_{Bm'} + \tfrac{1}{2}\hbar\omega_0\eta^2, \tag{11b}$$

where

$$J_{Am} = \epsilon_A(R_0, q_{0A}) + \epsilon_B(q_{0A}) + \mathscr{E}_{mi}^{p} + \tfrac{1}{2}\hbar\omega_0 \sum_K q_{K0A}^2, \tag{12a}$$

$$J_{Bm'} = \epsilon_A(q_{0B}) + \epsilon_B(R_0 q_{0B}) + \mathscr{E}_{m'f}^{p} + \tfrac{1}{2}\hbar\omega_0 \sum_K q_{K0B}^2. \tag{12}$$

In expressions (12a) and (12b) the quantities $\mathscr{E}_{mi}^{p}$ and $\mathscr{E}_{m'f}^{p}$ are proton vibration energies in the initial and final states, respectively. Assuming that proton performs harmonic vibrations along the chemical bond, $\mathscr{E}_{mi}^{p} = \hbar\omega_i(m + \frac{1}{2})$ and $\mathscr{E}_{m'f}^{p} = \hbar\omega_f(m' + \frac{1}{2})$. By analogy with the electron term, we shall call the functions U_i^{ep} and U_f^{ep} the electron–proton terms of the system. By expressing U_i^{ep} and U_f^{ep} in terms of (11a) and (11b) we can consider the terms as being one-dimensional (Fig. 2).

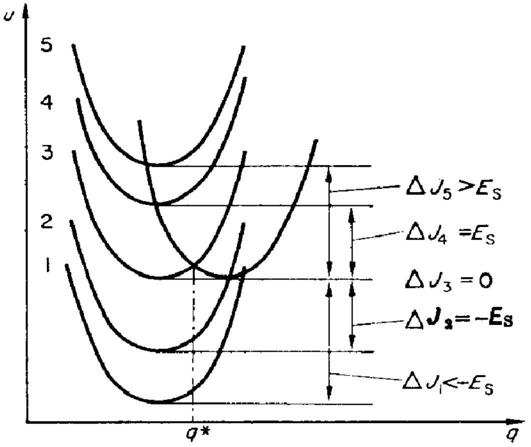

FIG. 2.

CALCULATION OF TRANSFER PROBABILITY

(a) *Calculation to a harmonic approximation*

Now let us calculate the proton-transfer probability from molecule AH to ion B^-. Let us use the general formula of the perturbation theory for the transfer probability,

$$W_{if} = \frac{2\pi}{\hbar} |\langle \Psi_f^\circ | V_{pB} | \Psi_i^\circ \rangle|^2 \rho_f. \tag{13}$$

The wave functions of the final and initial states of the system contained in the expression for the matrix element are solutions of Schrödinger's equation for the unperturbed Hamiltonians $\mathscr{H}_i^\circ$ and $\mathscr{H}_f^\circ$, and the potential V_{pB} contained in (13) describes the interaction of proton, bound in molecule AH, with ion B^-, which leads to the proton jump. The quantity ρ_f in formula (13) is the level density of the final state of the system equal to $1/\hbar\omega_0$. Functions Ψ_f° and Ψ_i° belong to the states with equal values of total energies of the system before and after proton transfer,

$$\begin{aligned} E_i &= J_A^e + (m + 1/2)\hbar\omega_p + (n + 1/2)\hbar\omega_0 \\ &= E_f = J_B^e + (m' + 1/2)\hbar\omega_p + (n' + 1/2)\hbar\omega_0. \end{aligned} \tag{14}$$

In calculating the matrix element, we shall use Condon's approximation, according to which the wave functions of the fast sub-system depend slightly on the co-ordinates of the slow sub-system R, q and therefore can be taken at point corresponding to the maximal contribution of the overlapping integral of the heavy sub-system,

$$\begin{aligned} &|\langle \psi_B(x_B, R, q)\psi_A(x_A, q)\chi_B(R, q)|\ V_{pB}|\psi_B(x_B, q)\psi_A(x_A, R, q)\chi_A(R, q)\rangle|^2 \\ &\qquad = |L_e|^2\ |\langle \chi_B(R, q)\chi_A(R, q)\rangle|^2, \end{aligned} \tag{15}$$

where L_e is exchange integral with electron wave-functions. To a harmonic approximation, the wave function of the slow sub-system can be written as the product (9). To calculate the total probablity of proton transfer in unit time, it is necessary to carry out a statistical averaging over all possible initial states of the system and summation over final states. In this case we have

$$\bar{w} = \frac{2\pi\,|L_e|^2}{\hbar\,.\,\hbar\omega_0 Q_1 Q_2}\sum_{\substack{mm'\\nn'}}\exp\left[-\frac{(m+\frac{1}{2})\hbar\omega_p}{kT}\right]\exp\left[-\frac{(n+\frac{1}{2})\hbar\omega_0}{kT}\right]\times$$

$$\times\,|\langle\Phi_{m'}(\xi-\xi_0)\Phi_m(\xi)\rangle|^2\,|\langle\varphi_{n'}(\eta)\varphi_n(\eta-\eta_0)\rangle|^2\,\delta_{[\Delta J/\hbar\omega_0-\omega_p/\omega_0(m-m')-(n-n')]0}, \quad (16)$$

where Q_1 and Q_2 are corresponding statistical sums, δ is the Kronecker symbol and expresses the conservation of energy law (14), and $\Delta J = J_B{}^e - J_A{}^e$. Calculating the matrix elements and carrying out necessary summations, as well as making use of the fact that $\hbar\omega_0 \ll kT$ and $\hbar\omega_p > kT$, we obtain for the mean probability $\bar{w}$

$$\bar{w} = \frac{\omega_0}{2\pi}\frac{|L_e|^2}{L_c{}^2}\exp\left[-\frac{E_p}{\hbar\omega_p}\right]\sum_{l=-\infty}^{\infty}\left(\frac{E_p}{\hbar\omega_p}\right)^l\frac{\exp\left[-\frac{\hbar\omega_p}{2kT}(|l|+l)\right]}{|l|!}\,x$$

$$\times\exp\left[-\frac{(E_s+\Delta J-l\hbar\omega_p)^2}{4E_s kT}\right], \quad (17)$$

where $L_c{}^2 = \frac{\hbar\omega_0}{2}\sqrt{\frac{E_s kT}{\pi^3}}$, $E_s = \hbar\omega_0\frac{\eta_0{}^2}{2}$—repolarization energy of solvent upon proton transfer—and $E_p = \hbar\omega_p\frac{\xi_0{}^2}{2}$.

It should be noted in calculating the sum contained in (17) at different values of ΔJ that the main contribution to the sum is usually made by one term corresponding to a certain $l = l^*$, which can be determined from the exponential factor in (17). The factor $\frac{(E_p/\hbar\omega_p)^{|l|}}{|l|!}$ changes less fast then the exponential factor and can be shown not to affect significantly the values of l^*. We have

$$l^* = \begin{cases}\dfrac{\Delta J - E_s}{\hbar\omega_p}, & E_s \leqslant \Delta J,\\[2mm] 0\;, & -E_s < \Delta J < E_s,\\[2mm] \dfrac{\Delta J + E_s}{\hbar\omega_p}, & \Delta J \leqslant -E_s.\end{cases} \quad (18)$$

Thus restricting ourselves to one term in the sum, we obtain

$$\bar{w} = \frac{\omega_0}{2\pi}\frac{|L_e|^2}{L_c{}^2}\exp\left(-\frac{E_p}{\hbar\omega_p}\right)\left(\frac{E_p}{\hbar\omega_p}\right)^{|l^*|}\exp\left[-\frac{\hbar\omega_p}{2kT}(|l^*|+l^*)\right]$$

$$\times\exp\left[-\frac{(E_s+\Delta J-l^*\hbar\omega_p)^2}{4kTE_s}\right]. \quad (19)$$

Expression (19) for the transfer probability has an Arrhenius form with the activation energy equal to

$$E_a = \frac{(E_s+\Delta J-l^*\hbar\omega_p)^2}{4E_s} + \frac{\hbar\omega_p}{2}(|l^*|+l^*). \quad (20)$$

Using (18) we can rewrite (20) as

$$E_a = \begin{cases} \Delta J, & E_s \leqslant \Delta J, \\ \dfrac{(E_s + \Delta J)^2}{4E_s}, & -E_s < \Delta J < E_s, \\ 0, & \Delta J \leqslant -E_s. \end{cases} \tag{21}$$

Parameter E_s contained in the expression for E_a is an important parameter of the theory, characterizing the effect of the solvent on the kinetics of a chemical reaction. A significant result of the present treatment is the fact that the activation energy in the proton-transfer reaction is characterized not by the shape of the potential wells determining proton vibrations in AH and BH, as was assumed in Horiuti and Polanyi theory[11] but by vibrational electron–proton terms of the solvent, this dependence being determined by a single parameter E_s the repolarization energy of the solvent. The value of E_s can be estimated theoretically[3] and is a quantity of the order of 1–2 eV. At the same time, as will be shown below, the repolarization energy of the solvent can be determined from experimental data on the dependence of the reaction rate constant on the reaction heat.

Introducing the notion

$$\kappa^* = \frac{|L_e|^2 \exp\left(-\dfrac{E_p}{\hbar\omega_p}\right)\left(\dfrac{E_p}{\hbar\omega_p}\right)^{|l^*|}}{L_0^2\,|l^*|!} \tag{22}$$

we can finally rewrite (19) for the transfer probability $\bar{w}$

$$\bar{w} = \kappa^* \frac{\omega_0}{2\pi} e^{-E_a/kT}. \tag{23}$$

The coefficient κ^* is usually called the transmission coefficient. It follows from the calculation carried out that κ^* characterizes the probability of a transition of the system from one term to the other when passing through an activated state. Generally speaking, it should be noted that each value of κ_l corresponds to a particular term of the sum in (17). Therefore, the symbol κ^* corresponds to the term (17) which makes the main contribution to the transition probability.

(b) *Double adiabatic approximation*

For a double adiabatic approximation the transfer probability is determined by the matrix element of transfer equal to

$$\begin{aligned} &\langle \Psi_f^\circ\,|V_{pB}|\,\Psi_i^\circ\rangle \\ &= \int \psi_A(x_A)\psi_A(x_A,\ R)\,dx_A \,.\, \Phi_A(R_A)\Phi_B(R_B)\left[\int \psi_B(x_B, R)V_{pB}(x_B, R)\psi_B(x_B)\,dx_B\right] \\ &\qquad \times dR \,.\int \varphi_B(q)\varphi_A(q)\,dq. \end{aligned} \tag{24}$$

The functions $\psi_B(x_B)$ and $\psi_B(x_B, R)$, which describe the state of the electrons of ion B^- in initial and of molecule BH in final states, are respectively solutions of Schrödinger equations

$$\mathscr{H}_e(x_B)\psi_B(x_B) = \epsilon_{0B}\psi_B(x_B), \tag{25}$$

$$[\mathscr{H}_e(x_B) + V_{pB}(x_B R)]\psi(x_B, R) = \epsilon_B(R)\psi_B(x_B, R). \tag{26}$$

On the basis of (25) and (26) let us rewrite (24) as

$$\langle\Psi_f^\circ|V_{pB}|\Psi_0^\circ\rangle = \int \psi_A(x_A)\psi_A(x_A, R)\,dx_A\,, \int \psi_B(x_B, R)\psi_B(x_B)\,dx_B\,.\,(\epsilon_B(R) - \epsilon_{OB})\Phi_B(R_B)\Phi_A(R_A) \times dR\,.\int \varphi_A(q)\varphi_B(q)\,dq. \quad (27)$$

The expression $V_M(R) = \epsilon_B(R) - \epsilon_{OB}$ is the potential of interaction of proton with ion B^-, which is usually approximated by the Morse potential. Unlike redox reactions, in this case the overlapping integrals of electron wave-functions give a factor of the order of unity, which we shall discard. This corresponds to a slight distortion of electron functions when proton leaves the ion. Thus, the total transfer probability in unit time can be written to a double adiabatic approximation

$$\bar{w} = \frac{2\pi}{\hbar}\cdot\frac{1}{\hbar\omega_0}\sum_{\substack{mm'\\nn}}\frac{\exp[\mathscr{E}_{im}{}^p/kT]}{Q_1}\cdot\frac{\exp[-\hbar\omega_0(n+\frac{1}{2})/kT]}{Q_2} \times |\langle\Phi_{m'B}(R-R_0)\,V_{BH}(R)|\,\Phi_{mA}(R)\rangle|^2 \times |\langle\varphi_{n'}(q-q_0)|\,\varphi_n(q)\rangle|^2\,.\,\delta_{\Delta J/\hbar\omega_0-(\mathscr{E}_{im}{}^p-\mathscr{E}_{fm}{}'^p/\hbar\omega_0)-(n-n'),0}, \quad (28)$$

where Q_1 and Q_2 are corresponding statistical sums.

On the basis of the results obtained earlier, this probability can be written

$$\bar{w} = \sum_{mm'}\frac{1}{Q_1}\exp[-\mathscr{E}_{im}{}^p(kT]W_{m'm};$$
$$W_{m'm} = \kappa_{m'm}\frac{\omega_0}{2\pi}\exp\left\{-\frac{(E_s+\Delta J+\mathscr{E}^p_{m'i}-\mathscr{E}_{mf}{}^p)^2}{4E_s\,kT}\right\}. \quad (29)$$

Expression (29) has the same form as the corresponding formula for the electron-transfer probability obtained for redox reactions. But there is the following essential difference between them. The exponential in (29) contains the energy of proton vibrations. The transmission coefficient $\kappa_{m'm}$ depends on the overlapping of electron and proton wave-functions. Then

$$\kappa_{m'm} = \frac{|L_{m'm}|^2}{L_c^2} < 1 \quad \text{(for non-adiabatic reactions)}, \quad (30)$$

$$\kappa_{m'm} = 1 \quad \text{(for adiabatic reactions)}, \quad (31)$$

where

$$L_{m'm} = \int \Phi^M_{m'B}V_M\Phi_{mA}{}^M\,dR.$$

Moreover, in the theory of redox systems in the case of nonadiabatic reactions, the smallness of the coefficient $\kappa_{m'm}$ is due to slight overlapping of electron wave-functions. In the systems under consideration, when proton transfer occurs by a non-adiabatic mechanism, the smallness of $\kappa_{m'm}$ is due to slight overlapping of proton wave-functions, and the overlapping integral of electron wave functions is of the order of unity. In the theory of redox reactions the solvent transition from the initial to the final state was shown to follow the classical path through the intersection point of electron terms. In the case of proton transfer reactions in solution, the solvent transition by the classical path occurs on electron–proton terms.

The proton-transfer probability calculated above permits us to interpret the reaction path by means of two-dimensional electron terms as well. In that case the corresponding diagrams are of a more complex form. Thus, activation of the solvent first occurs, with a fixed proton state. Then at point q^*, with fixed co-ordinate of the solvent, the quantum transition of proton occurs, followed by the relaxation of solvent into a new equilibrium state.

Knowing the proton-transfer probability in unit time, $\bar{w}$, it is easy to write an expression for the rate constant of reaction (1) as[1]

$$k = \int \bar{w}(R) f_{\mathrm{AH.B}}(R)\,\mathrm{d}V \approx \bar{w}(R^*)v^*, \tag{32}$$

where $f_{\mathrm{AH.B}}(R)$ is the probability of approach of molecules to the distance R, and v^* the effective reaction volume.

It is clear from (28) that if harmonic oscillator functions are used as proton wavefunctions and use is made of the Condon approximation, (28) changes exactly into (16), obtained for a haromonic approximation. The advantage of the first approach consists in the generality of analytical treatment, which permits us to elucidate some general physical regularities. But in order to obtain quantitative results for particular reactions, it is more convenient to use the double adiabatic approximation.

THE BRÖNSTED RELATION

On the basis of general theoretical results obtained in the investigation of the reaction of proton transfer from one molecule to another, we shall consider one of the most important relations in the kinetics of chemical reactions—the Brönsted relation.

In an experimental investigation of acid–base catalysis involving proton transfer from or to catalyst molecule, Brönsted established a relationship between the rate constant k of catalytic reactions and dissociation constants K of acids (bases),[6]

$$\log k = \text{const} + \alpha \log K \tag{33}$$

Later it was shown that for a certain class of reactions the Brönsted equation expresses the relation between activation energy and reaction heat,

$$-\Delta E_{\mathrm{a}} = \alpha\,\Delta Q. \tag{34}$$

In a more general case (34) can be written as

$$\alpha = -\frac{\mathrm{d}E_{\mathrm{a}}}{\mathrm{d}Q}, \tag{35}$$

where α is usually called the Brönsted coefficient. In most studies concerned with the investigation of the Brönsted relation, it was usually interpreted as a principle of linear relationship between activation energy and reaction heat. Actually, as was pointed out by Brönsted, α is not a constant, but can vary from one compound to another in the series being studied. The experimentally observed linear relationship, corresponding to a constant value of α, is an approximate one, valid only with reaction heat changing within relatively narrow limits. Experiments on proton transfer carried out recently for a large number of compounds corresponding to reaction heat varying within wide limits showed[7] the coefficient to range widely between zero and unity. As is shown by a calculation carried out under the assumption that proton vibrations in AH and BH are of a harmonic nature, the Brönsted relation for the reaction in question is of the form

$$\alpha = \frac{dE_a}{d\Delta J} = \begin{cases} 1 & E_s < \Delta J \\ (\Delta J + E_s)/2 & -E_s < \Delta J < E_s, \\ 0 & -E_s > \Delta J \end{cases} \tag{36}$$

where the quantity $-\Delta J$ equal to the difference of energies at the minima of initial and final electron–proton terms appears as the reaction heat (see Fig. 2). E_s is the reorganization energy of the solvent upon transition and is basic parameter of the theory. It follows from (36) that α ranges from 0 to 1 with the reaction heat varying from $-E_s$ to E_s.

The behaviour of α as the function of the reaction heat can be conveniently illustrated by plots of electron–proton terms. For this purpose, let us consider the electron–proton terms of the initial and final states corresponding to basic vibrational states of proton in AH and BH molecules. Figure 2 shows five different cases of mutual arrangement of initial and final terms. It follows from the results of calculations that the system transition from initial to final state occurs through the intersection point of the electron proton terms (*ie* it corresponds to the classical path). Therefore, the activation energy of proton transfer between the ground vibrational levels is equal to the distance from the initial term minimum to the intersection point of the terms (see Fig. 2), *viz*, $E_a^{00} = (\Delta J + E_s)/4E_s$. Hence it follows that the Brönsted coefficient α^{00}, corresponding to proton transfer from unexcited initial to unexcited final state, is equal to

$$\alpha^{00} = \frac{\Delta J + E_s}{2E_s}. \tag{37}$$

It is clear from (37) that if ΔJ varies within the range $-E_s < \Delta J < E_s$, *ie* if the term of final state (term 3) is located between curves (2) and (4), the coefficient α^{00} is in the range from 0 to 1. The proton transfer corresponding to this arrangement of the terms we shall call normal. In the range of ΔJ change between $-E_s$ and E_s, transfer occurs mainly between ground proton states. This corresponds to increasing from 0 to 1 on the plot $\alpha(\Delta J)$ (Fig. 3).

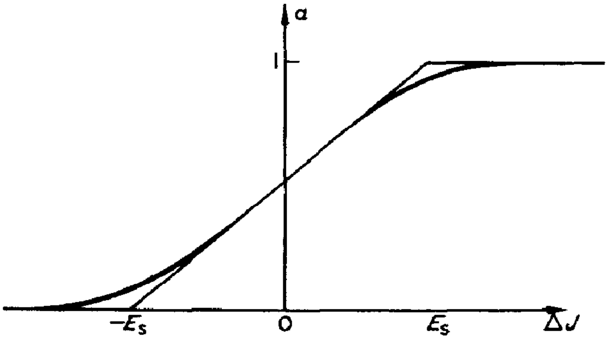

FIG. 3.

The transfers corresponding to terms (2) and (4) we shall call activationless and barrierless ones, respectively. In fact, in the case of term (2), $\Delta J = -E_s$ and the activation energy is 0. For term (4) $\Delta J = E_s$ and the activation energy value coincides with that of reaction heat (no barrier). These transfers correspond to the $\alpha^{00} = 0$ and $\alpha^{00} = 1$ respectively. Let us consider now term (1). It is clear from (37) that the Brönsted coefficient for this term is negative, *ie* the activation energy increases with the reaction heat. The calculation shows, however, that it is in this region that the transfers to final excited proton states are of essential importance. As a result, the effective Brönsted coefficient for the reaction as a whole cannot be negative. Similarly, it proves that in spite of the coefficient α^{00} for term (5) being larger than unity, the effective Brönsted coefficient remains less than unity, since in the barrierless region transfers from excited initial proton states are of essential importance.

It should be noted that since in the activationless region $E_a = 0$, the corresponding reaction rate constants are large. This makes the investigation of these reactions difficult. It should be borne in mind that in our case the reaction rate constants are not too large, being such that $\tau_{\mathrm{react}} \gg \tau_{\mathrm{dif}}$ where τ_{react} is the mean time necessary for one act of proton transfer and τ_{dif} the mean time of the diffusional jump of ions, *ie* the mean time of residence of reagents in the reaction zone. Since τ_{react} is the reciprocal of the reaction rate constant, which increases with decreasing activation energy, it is possible that in some cases the relation $\tau_{\mathrm{react}} \gg \tau_{\mathrm{dif}}$ becomes not valid for the final value of activation energy. This means that in corresponding systems there will be no activationless region, since the diffusion effects will begin to come into play. An experimental observation of the activationless region of reaction seems to be possible in the case of a strongly non-adiabatic reaction ($\kappa \ll 1$), when in spite of the smallness of the activation energy, the reaction rate constant is still relatively not large ($k \ll 1/\tau_{\mathrm{dif}}$). An experimental investigation of barrierless transfers also presents certain difficulties, since the activation energies in this region are maximal and the corresponding rate constants small. Recently, however, barrierless transfers were detected and investigated in detail in electrochemical reactions of hydrogen-ion discharge.[8] In a quantum-mechanical calculation all proton levels, both the ground level and excited levels, were formally taken into account. The final result for the transfer probability is of the form

$$\bar{w} = \frac{\omega_0}{2\pi} \sum_{mm'} \kappa_{m'm} \exp - \left(\frac{\mathscr{E}_{m\mathrm{i}}{}^{\mathrm{p}}}{kT}\right) \exp - \left(\frac{E_{\mathrm{a}}^{m'm}}{kT}\right). \tag{38}$$

Here ω_0 is frequency of polarization fluctuations of the solvent, $\kappa_{m'm}$ the transmission coefficient, $\mathscr{E}_{m\mathrm{i}}{}^{\mathrm{p}}$ the proton excitation energy, $E_{\mathrm{a}}^{m'm}$ the activation energy. Indices m and m' indicate that proton passes from initial level $\mathscr{E}_{m\mathrm{i}}{}^{\mathrm{p}}$ to final level $\mathscr{E}^{\mathrm{p}}_{m'\mathrm{f}}$.

The analysis of formula (38) shows that generally the main contribution to the transfer probability is made only by some terms in the sum, corresponding to proton transfer between states m and m'. These states depend on the value of ΔJ and hence on the region in which the corresponding value of α is to be found. In the normal region, where $\Delta J \approx 0$, $\alpha \approx \frac{1}{2}$, the exponent in (38) can be written

$$-\frac{E_{\mathrm{s}}}{4kT} - \frac{\mathscr{E}_{m\mathrm{i}}{}^{\mathrm{p}} - \mathscr{E}^{\mathrm{p}}_{m'\mathrm{f}}}{2kT} - \frac{(\mathscr{E}^{\mathrm{p}}_{m'\mathrm{f}} - \mathscr{E}_{m\mathrm{i}}{}^{\mathrm{p}})^2}{4E_{\mathrm{s}}kT}. \tag{39}$$

It follows from (39) that the main contribution to the transfer probability in the normal region is made by the transfer between unexcited states. In the barrierless region, where $\Delta J \approx E_s$, $\alpha \approx 1$, the index of the exponential in (38) is

$$-\frac{E_s}{kT'} - \frac{\mathcal{E}^{\mathrm{p}}_{m'\mathrm{f}}}{kT} - \frac{(\mathcal{E}^{\mathrm{p}}_{m'\mathrm{f}} - \mathcal{E}_{m\mathrm{i}}{}^{\mathrm{p}})^2}{4E_s\, kT}. \tag{40}$$

It follows from this expression that in the barrierless region, the transfer can occur from a small number of excited initial states to the ground final state.

Similarly, in the activationless region, where $\alpha \approx 0$, the transfer can be shown to occur from the ground initial state to a small number of excited final states.

So far, examining the contribution of excited states to the transfer probability, we have not taken into consideration the transmission coefficient, the value of which depends essentially on the states between which the transfer occurs.

The transmission coefficient $\kappa_{m'm}$, corresponding to the transfer between proton excited vibrational levels, increases with increasing excitation energy of initial and final states owing to a greater overlapping of corresponding wave fuctions.

Therefore, the total value of proton-transfer probability is determined by the competition between $\kappa_{m'm}$ and the value of the exponential, diminishing with increasing excitation energy over the whole range of α. Numerical calculations have shown, however, that with an allowance made for the transmission coefficient as well, excited states are of most importance only in the regions where $\alpha \approx 0$ and $\alpha \approx 1$.

Now we can compare the theoretical results obtained with some experimental data. We shall show, by way of illustration, for the case of a certain class of reactions that the theory expresses not only qualitatively, but also quantitatively, the relationship between the reaction rate constant and the reaction heat for a large series of reactants.

In order to calculate the absolute value of the reaction rate constant, it is necessary to know the transmission coefficient and the activation energy. It is possible to calculate the transmission coefficient if we choose some reasonable form of proton potential energy in AH and BH molecules and pre-set the distance ΔR over which proton is transferred (see Fig. 4). In the present study the Morse potential was made use of for concrete calculations. The Morse potential is determined by two parameters by the potential well depth D characterizing the energy of proton affinity for ions A^- and B^- in solution and by the characteristic vibration frequency ω_p.

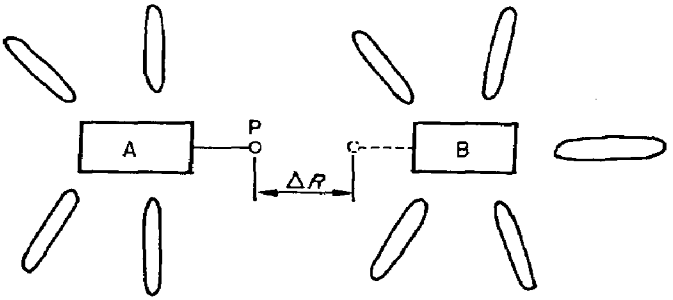

FIG. 4.

In the determination of the activation energy, the basic parameter is the solvent repolarization energy E_s.

The value of E_s can be estimated theoretically. But such an estimate is only a very rough approximation. Therefore, in the present paper the value of E_s is taken from an analysis of experimental data. The calculation carried out above showed the change of α from zero to unity as the function of ΔJ to be almost linear in the range $\Delta J = 2E_s$. Thus, it is possible from the slope of the curves $\alpha = \alpha(\Delta J)$ in the normal region to determine E_s.

In the present study theoretical results were compared with experimental data obtained by Eigen,[7] who investigated the proton–transfer reactions between acetylacetone $CH_3COOCH_2COCH_3$ and various acceptors (the reaction under consideration is one of the steps of an acid–base catalysis). In our calculations we took the proton vibration frequency in the initial state (AH) to be equal to the frequency of the valence bond C–H in $>C–H_2$ (*ca* 2900 cm^{-1}). The frequency of proton valency vibrations in the final state (BH) is taken to be equal to the frequency of stretching vibrations of the O–H bond. The range of variation of D for the compounds under consideration is 7–8 eV. In our calculations we took the value of D to be 8 eV for all compounds.

The values of ω and D for acceptors were chosen the same for the sake of simplicity, but it should be noted that in the case of an adiabatic reaction, the rate constant is not susceptible to changes of ω and D. ΔR was taken to be 0·75Å. It was found from the slope of the experimental curve $\alpha(\Delta J)$ that $E_s = 1$ eV. This value conforms reasonably well with the value of $E_s = 2$ eV, obtained in homogeneous electron-transfer reactions and in electrode reactions involving proton transfer. In electron-transfer reactions the repolarization energy is greater since electron is transferred through a larger distance. In the case of H_3O^+-ion discharge at the electrode, the larger E_s is due to the disappearance of solvent polarization caused by the hydroxonium ion.

At the parameter values chosen, the theoretical log $k/\Delta J$ curve calculated by means of an electronic computer proved to agree well with experimental data, Fig. 5.

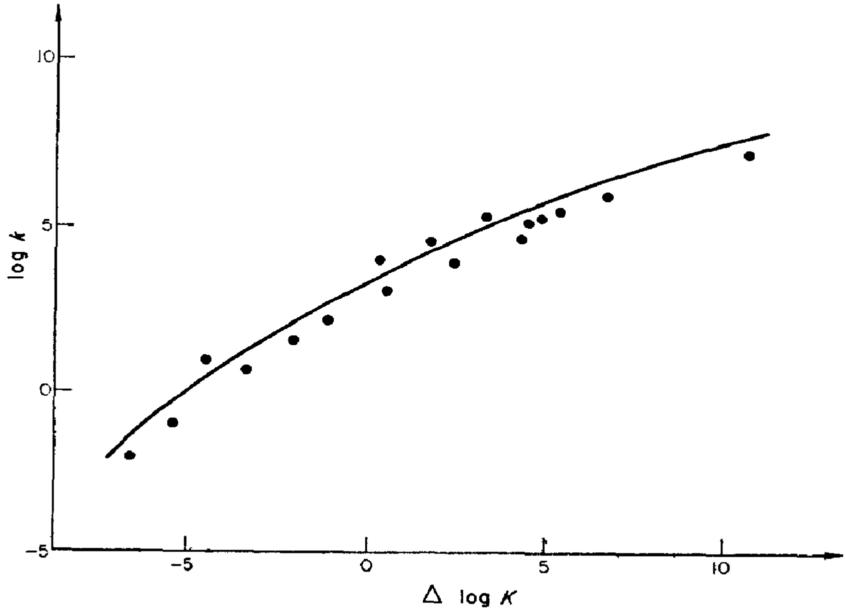

FIG. 5.

To study the dependence of the results on the kind of proton potential energy in reagents, a similar calculation was carried out assuming harmonic vibrations in AH and BH molecules. The curve thus obtained proved to coincide practically with the curve calculated for the Morse potential, with the value of ΔR differing but little from that indicated above.

In the previous section we showed that the present theory permits us to calculate both the pre-exponential and the activation energy, and thus to estimate the absolute value of the rate constant of the proton-transfer reaction. On this basis it is possible to elucidate the question how the rate of the reaction of type (1) will change if proton is substituted by one of its isotopes. The ratio of the rate constants of proton and its isotope transfer reactions $K_H/K_{D(T)}$ characterizing the isotope effect contains very important information and therefore its calculation is of great interest for the study of the mechanism of chemical reactions.

A proton exchange for one of hydrogen isotopes leads to a change in the positions of vibrational levels of hydrogen isotopes in the molecules AD, AT, BD, BT and hence to a change in the values of transmission coefficients and activation energies. In the theory of absolute reaction rates, a formula is generally used for the estimation of the magnitude of the isotope effect which takes account of zero energies of initial states when proton is exchanged for hydrogen isotopes,

$$k_H/k_D = \exp\left\{\frac{E_H{}^0 - E_D{}^0}{kT}\right\}. \tag{41}$$

It should be noted in using (41) that the vibration frequencies in the activated complex are assumed to be the same for proton and deuteron. Formula (41) imposes rather rigorous conditions on possible values of isotope effects for individual types of bonds and cannot account for the great variety of the isotope-effect values. In these cases other reasons are sometimes thought of, such as change of the vibration frequency of hydrogen isotopes in the activated state. However, according to the theory of absolute reaction rate, an activated complex is a "loose" system with small variations of vibration frequency, and what is more, our knowledge of these frequencies is rather uncertain.

Also, as shown by Krishtalik,[9] it is impossible in principle by means of the equation of the absolute reaction rates theory to explain the values of the isotope separation factors in electrochemical reactions and their dependence on the electrode potential.

On the basis of the theory developed in the present paper, it is possible to obtain a formula for the ratio of the proton-transfer rate constants, which in the normal region is

$$k_H/k_D = \frac{\kappa_{00}{}^H}{\kappa_{00}{}^D} \exp\left\{\frac{\alpha[(E_A{}^{DH} - E_B{}^{OH}) - (E_A{}^{OD} - E_B{}^{OD})]}{kT}\right\}. \tag{42}$$

Simple estimates in which account is taken of the fact that the zero energy values of proton and deuteron initial and final states are related approximately as the square root of the isotope mass ratio, show that the exponential factor in (42) gives no contribution to the isotope effect. Thus, the isotope effect is determined by the ratio of the transmission coefficients of transfer from ground initial to ground final state for proton and deuteron. The transmission coefficients, in their turn, are determined by overlapping integrals of the proton and deuteron wave-functions of the initial and final states and depend on the distance ΔR, over which the proton jumps. The comparison of experimental data on the isotope effect of proton transfer reaction from ethyl-α-methylacetonate to ions of chloro-substituted compounds of acetic acid[10] and theory made it possible to determine the value of ΔR for the above reactions, 0·65 Å. In this case the calculations show that the proton transfer follows an adiabatic path, whereas the deuteron transfer follows a nonadiabatic one.

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