1964. Volume 159, No. 1

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 159, No. 1

PHYSICAL CHEMISTRY

E. A. PSHENICHNOV, N. D. SOKOLOV

INTERMOLECULAR PROTON TRANSFERS IN SOLUTIONS

(Presented by Academician V. N. Kondrat' ev on 29 V 1964)

It has long been accepted that proton transfers from one molecule (AH) to another occur under the condition that a hydrogen bond is formed between them ([1–3]). Since, in the formation of the hydrogen bridge AH ... B, a donor-acceptor interaction between the base molecule B and the proton plays a role, it is natural that the hydrogen bond serves as the first stage of proton transfer from A to B. In the gas phase and in nonpolar solutions, the proton transfer $AH \ldots B \rightarrow A^- + (HB)^+$ is practically not realized because of the endothermic character of the process. Under these conditions, the potential well for the proton in the hydrogen bridge, corresponding to localization of H^+ near molecule B (if it is electrically neutral), is probably situated much higher than the first well, which corresponds to the initial configuration AH ... B, and in a number of cases possibly does not exist at all. In polar solvents, owing to orientational polarization of the medium, a second well of sufficient depth can in principle be formed. The following mechanism for the formation of the second well appears most probable. As measurements show, the dipole moments of complexes with a hydrogen bond AH ... B are considerably larger than the sum of the dipole moments of the molecules AH and B, exceeding it by 3–5 D ([4]). At the same time, data on the intensity of deformation vibrations indicate that the effective charge on the H atom upon formation of the hydrogen bridge practically does not change ([5, 6]). This means that the dipole moment of the complex AH ... B is due mainly to the manifestation on A and B of relatively large effective charges $A^{\delta-}$—H ... $B^{\delta+}$. These charges cause equilibrium polarization of the medium, which creates a second potential well near B. The depth of this well may vary depending on the dielectric properties of the medium, as well as on the degree of basicity of B. We shall assume that the well contains at least one vibrational level. In the case when at least one of the reactants is an ion, formation of the second well owing to polarization of the medium proves still easier. Moreover, in this case the presence of a second well may be a property of the ion B.

In a complex with a hydrogen bond, the width Δ of the vibrational levels for

Fig. 1. Double asymmetric potential well for a proton in a complex with a hydrogen bond $A-H\dots B$

Figure 1: Fig. 1. Double asymmetric potential well for a proton in a complex with a hydrogen bond $A-H\dots B$

the proton is, as a rule, much smaller than the spacing ω between them ($\Delta \sim 10^2$ cm^{-1}, $\omega \simeq 3\cdot 10^3$ cm^{-1}). Therefore the calculation of the rate of the multistage process of proton transfer ([7]) from one well to the other can be divided into two independent problems: calculation of the probability of proton transfer between each pair of levels separately, and solution of the system of kinetic equations for the overall process as a whole.

Let us suppose that in the reaction

$$AH + B \to A^- + (HB)^+ \tag{1}$$

the first stage is the formation of a hydrogen bridge with two potential wells, with the first well containing $(n+1)$ vibrational levels $(0, 1, 2, \dots, n)$, while with respect to the second well we shall at first assume-

gate that it contains only one level (with number $(n+1)$, see Fig. 1). At the initial moment of time after formation of the hydrogen bridge this level is unpopulated, and the system begins to relax. Complexes in which the proton is on level $(n+1)$ may be regarded as the ion pair $A^-\dots(HB)^+$, capable of dissociating into two ions. Further, let us assume that all vibrational transitions occur only to a neighboring level, with the exception of transitions near the top of the barrier, where both transitions $(n-1)\to n\to(n+1)$ and $(n-1)\to(n+1)$ may occur (see Fig. 1). In the first case the sequence of stages through which reaction (1) proceeds can be represented in the form

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AH\dots B \underset{p_{10}}{\overset{p_{01}}{\rightleftarrows}} X_1 \underset{p_{21}}{\overset{p_{12}}{\rightleftarrows}} \dots \underset{p_{n,n-1}}{\overset{p_{n-1,n}}{\rightleftarrows}} X_n \underset{p_{n+1,n}}{\overset{p_{n,n+1}}{\rightleftarrows}} A^-\dots(HB)^+ \overset{k_2}{\to} A^- + (HB)^+, \tag{2}$$

where $X_i\,(i=1,2,\dots,n)$ are complexes $AH\dots B$ in vibrationally excited states i, and $p_{i,i+1}$ and $p_{i+1,i}$ are the probabilities of vibrational transitions (per unit time) $i\to i+1$ and $i+1\to i$, respectively. By virtue of the condition of detailed equilibrium,

$$p_{i,i+1} = p_{i+1,i}e^{-E_{i+1,i}/kT}, \quad E_{i+1,i} = E_{i+1} - E_i. \tag{3}$$

Fig. 1. Double asymmetric potential well for a proton in a complex with a hydrogen bond

$$A - H \ldots B$$

If the reaction proceeds along the path $(n-1) \to (n+1)$, then in scheme (2) X_n should be deleted and $p_{n-1,n}$ and $p_{n,n-1}$ replaced by $p_{n-1,n+1}$ and $p_{n+1,n-1}$, respectively.

Solving the system of kinetic equations corresponding to scheme (2) in the quasi-stationary approximation (8) and using relation (3), it is easy to obtain the following expression for the rate constant of the reaction along the path $(n-1) \to n \to (n+1)$:

$$k = k_1 \left[1 + \frac{k_{-1}}{p_{10}} e^{E_{10}/kT} + \ldots + \frac{k_{-1}}{p_{n,n-1}} e^{E_{n,0}/kT} + \frac{k_{-1}}{p_{n,n+1}} e^{E_{n,0}/kT} + \frac{k_{-1}}{k_2} e^{E_{n+1,0}/kT} \right]^{-1}. \tag{4}$$

From the theoretical point of view, the most interesting case is that in which, in reaction (1), the limiting stage is the proton transition from A to B. Then, under the sufficient condition that $k_{-1}/p_{i,i-1} \gg 1$ $(i = 1, 2, \ldots, n)$, $k_{-1}/p_{n,n+1} \gg 1$, and assuming that dissociation of the ion pair occurs rapidly $\left(1/p_{n,n-1} + 1/p_{n,n+1} \gg 1/k_2 e^{(E_n - E_{n+1})/kT}\right)$, from (4) we find

$$k = \frac{k_1}{k_{-1}} \frac{p_{n,n-1} p_{n,n+1}}{p_{n,n-1} + p_{n,n+1}} e^{-E_{n,0}/kT}. \tag{5}$$

The reaction path considered passes over a potential barrier. If the condition $p_{n-1,n+1} \gg p_{n-1,n}$ is fulfilled, the reaction proceeds along the tunneling path $(n-1) \to (n+1)$. Then, analogously to (5), we obtain

$$k = \frac{k_1}{k_{-1}} p_{n+1,n-1} e^{-E_{n+1,0}/kT}. \tag{6}$$

Formulas (5) and (6) are also valid in the case when there is an arbitrary number of levels in the second well, provided that relaxation down these levels occurs sufficiently rapidly and the possibility of parallel proton transitions under the barrier is excluded.

Let us now consider the probabilities of proton transitions between two levels, which occur under the influence of random forces acting on the complex AH ... B from the solvent. With the most–

these transitions will most probably take place as a result of energy exchange between the complex and those molecules (Y) of the medium which have a vibrational frequency Ω close to ω. The resonance defect $|\Omega - \omega|$ can be compensated at the expense of other degrees of freedom of the medium. Let us denote by $H_1(x)$ the Hamiltonian for the motion of the proton in the double well along the

coordinate x, and by $H_2(y)$ the Hamiltonian corresponding to the vibration of the molecule Y with frequency Ω. Then the total Hamiltonian of the system can be written in the form $H = H_1(x) + H_2(y) + V(x, y, t)$, where $V(x, y, t)$ is the energy of interaction of the complex with the molecule Y and with the medium, representing a time-dependent random function. Without loss of generality one may put $\overline{V(x, y, t)} = 0$ and $V(x_0, y_0, t) = 0$, where x_0 and y_0 are the equilibrium values of x and y. Restricting ourselves to the case in which $\Delta x = x - x_0$ and $\Delta y = y - y_0$ are small, we find the corresponding perturbation term:

$$\left(\frac{\partial^2 V}{\partial x\,\partial y}\right)_{00} \Delta x \cdot \Delta y = f(t)\Delta x \cdot \Delta y. \tag{7}$$

For the probability per unit time of the transition $i \to j$ of the proton one may write (see, for example, ([9]))

$$p_{ij} = \frac{2}{\hbar^2}\left|(\Delta x)_{ij}\right|^2 \sum_{a,b} \rho_a \left|(\Delta y)_{ab}\right|^2 \mathrm{Re}\int_0^\infty e^{i(\omega_{ij}+\Omega_{ab})\tau} K(\tau)\, d\tau. \tag{8}$$

Here $(\Delta x)_{ij}$ and $(\Delta y)_{ab}$ are matrix elements, while a and b are the initial and final states of the molecule Y, respectively; $\rho_a = \frac{1}{Q}e^{-E_a/kT}$, where Q is the statistical sum for Y; $K(\tau) = \overline{f(t)f(t+\tau)} = \overline{f^2}e^{-|\tau|/\tau_c}$ is the time correlation function for a stationary Gaussian–Markov process. Carrying out the integration in (8) and retaining only the term with $|\Omega - \omega| \lesssim 1/\tau_c$ and with maximal ρ_a, we obtain

$$p_{i,i-1} = 8\pi^2 \left|(\Delta x)_{i,i-1}\right|^2 \left|(\Delta y)_{01}\right|^2 \frac{\overline{f^2}\tau_c}{1 + \left(\omega_{i,i-1} - \Omega_{10}\right)^2 \tau_c^2} \tag{9}$$

(here it is assumed that the energy is expressed in sec^{-1}).

Let us now estimate the rate constant of reaction (1). In the harmonic-oscillator approximation $(\Delta y)_{01} \simeq 0.2$ Å. For an over-barrier transition $(\Delta x)_{n,n-1} \simeq (\Delta x)_{n,n+1} \simeq 0.3$ Å, and for tunneling (near the top of the barrier) $(\Delta x)_{n-1,n+1} \simeq 0.03$ Å ([10]). Further, $\omega \simeq 3 \cdot 10^{13}$ sec^{-1}, $\tau_c \simeq 10^{-12}$ sec, $k_{-1} \simeq \omega_1 e^{-\varepsilon/kT}$, where ε is the hydrogen-bond energy, $\omega_1 \simeq 6 \cdot 10^{12}$ sec^{-1} is the frequency of longitudinal vibrations (AH) . . . B. An estimate of $\overline{f^2}$ from the averaged energy of dipole-dipole interaction of molecules at a distance $R \simeq 5$ Å and with derivatives of the dipole moments $(\partial\mu_1/\partial x)_0 \simeq 4 \cdot 10^{-10}$, $(\partial\mu_2/\partial y)_0 \simeq 10^{-10}$ CGSE gives $\overline{f^2} \simeq 10^{56}$ cm^{-4} sec^{-2}. Substituting the estimates given above into formulas (5), (6), and (9), we obtain

$$k_{\text{over}} \simeq k_1 \cdot 10^{-1} e^{-(E_{n,0}-\varepsilon)/kT}, \tag{10}$$

$$k_{\text{tunn}} \simeq k_1 \cdot 10^{-3} e^{-(E_{n+1,0}-\varepsilon)/kT}. \qquad (11)$$

For $|\Omega-\omega|\tau_c \gg 1$, formula (9) is inapplicable. In this case it should be assumed that the transfer of energy from the molecule Y occurs simultaneously from two degrees of freedom (y, z); formulas (7)–(9) are correspondingly changed. In particular, instead of formula (7) one should write $(d^3V/dx\,dy\,dz)_{000}\Delta x\cdot\Delta y\cdot\Delta z$. As a result, the rate constants turn out to be two orders of magnitude smaller than those given in (10) and (11).

In a study of the kinetics of bromination of 2-carbethoxycyclopentanone ([11]) and acetone ([12]) in aqueous solutions, it was shown that the slowest

the stage is the transfer of a proton from the protonated form of the reagent to the catalysts CH_2ClCOO^-, F^- ([11]) and Cl^- ([12]), or to water molecules (depending on the experimental conditions). In the temperature interval 10–70° ([11]) and 15–35° ([12]), the corresponding reaction-rate constants were determined. In all the reactions studied, the preexponential factors (A) of the constants fall in the interval 10^4–10^7 $\text{sec}^{-1}\,\text{M}^{-1}$, with the exception of the case with F^- ([11]), where A is of the order of 10^9–10^{10} $\text{sec}^{-1}\,\text{M}^{-1}$. The effective activation energies of the indicated reactions ([11,12]) are 11–17 kcal/mol.

According to Eigen ([13]), in aqueous solutions $k_1 \sim 10^{10}$–10^{11} $\text{sec}^{-1}\,\text{M}^{-1}$. Substituting this value into formulas (10) and (11), we obtain $A_{\text{nadb}} \simeq 10^9$–$10^{10}$, $A_{\text{tunn}} \simeq 10^7$–$10^8$. If several degrees of freedom take part in the transfer of energy, these values decrease; for example, in the case of one additional degree of freedom z, calculation gives $A_{\text{nadb}} \simeq 10^7$–$10^8$, $A_{\text{tunn}} \simeq 10^5$–$10^6$. Taking into account the approximate character of the theoretical calculations, the agreement with the experimental data may be regarded as satisfactory.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
26 V 1964

CITED LITERATURE

1. N. D. Sokolov, DAN, **60**, 825 (1948); UFN, **57**, 205 (1955).

2. N. D. Sokolov, *Elektronentheorie der homöopolaren Bonding*, Tagungsber. chem. Gesellsch. DDR, 1955.

3. H. Zimmermann, Angew. Chem., **76**, 1 (1964).

4. E. N. Guryanova, I. P. Goldshtein, ZhOKh, **32**, 12 (1962); E. N. Guryanova, I. G. Beskina, ZhOKh, **33**, 928 (1963).

5. C. M. Huggins, G. C. Pimentel, J. Chem. Phys., **23**, 896 (1955); J. Phys. Chem., **60**, 1615 (1956).

6. A. V. Iogansen, G. A. Kurkchi, Optics and Spectroscopy, **13**, 480 (1962).

7. E. A. Pshenichnov, N. D. Sokolov, DAN, **137**, 352 (1961).

8. M. I. Temkin, DAN, **152**, 156 (1963).

9. J. Ayant, J. phys. et radium, **16**, 411 (1955).

10. R. L. Somorjai, D. F. Hornig, J. Chem. Phys., **36**, 1980 (1962).

11. R. P. Bell, J. A. Fendley, J. R. Hullet, Proc. Roy. Soc., **235A**, 453 (1956).

12. Yu. L. Khadina, A. I. Tal' vik, V. A. Palm, DAN, **126**, 119 (1959).

13. M. Eigen, Angew. Chem., **75**, 489 (1963).

Note: Figure translations are in progress. See original paper for figures.