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2 *The kinetics of exchange and proton transfer processes in hydrogen-bonded systems in inert media*

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2.1 Introduction

The traditional approach to the investigation of hydrogen bonding is the study of static characteristics of complexes. The general tendencies in the development of this approach are connected with the study of optical and NMR spectra which makes it possible to determine geometry, electrooptical and thermodynamic characteristics of complexes, and to obtain information on parameters of the potential surface of proton donor and proton acceptor interaction (Schuster *et al.*, 1976). Among the conventional problems, that of correlation between electronic structure of partner molecules, on the one hand, and thermodynamic and spectral properties of hydrogen-bonded systems, on the other, is of significance.

In treating some static characteristics of complexes the question of dynamic properties of hydrogen-bonding already arises, the possible influence of fast exchange processes upon the shape of bands in optical and NMR spectra being of interest. The study of the dynamics of systems with hydrogen bonding is interesting in itself, since hydrogen bonding plays a decisive role in the kinetics of a number of processes, in particular, the processes of proton transfer and proton exchange. By investigation of the kinetics of these processes we may gain information on the values of the barriers separating the minima on the potential energy surface, and give answers to some fundamental questions concerning the nature and spectral properties of hydrogen bonding. Because of high speed of the reactions at room temperature, most of the problems referring to the kinetics of hydrogen bonded systems depend, to a large extent, on the development of special techniques for the study of fast reactions (Hammes, 1974).

Although the interest in hydrogen bond dynamics has increased considerably in recent years (a number of papers on measurements of the lifetime of complexes in a condensed phase testify to that: Rassing, 1975; Tabuchi, 1976; Hopmann, 1976; Denisov and Golubev, 1978) yet it is still not clear, how to approach these problems. Besides, most results have been obtained by studying concentrated solutions and pure liquids, in cases when the interaction with the surrounding medium, which influence the mechanism of the process qualitatively, not only cannot be excluded but becomes decisive.

This fact makes investigation of the dynamics of hydrogen-bonded systems expedient under conditions of minimum interaction with the surroundings, i.e. in the gas phase, or at a low concentration in inert solvents whose energy of interaction with the molecules under investigation is apparently lower than the energy of interaction between the partner molecules. The kinetic study of processes in solvents, whose molecules do not stimulate electrolytic dissociation, allows one to neglect consideration of acid–base catalysis and is of greatest interest for finding the mechanism of the initial interaction between the molecules concerned. However, it is not improbable that even a neutral solvent may play a vital role in the kinetics of processes involving hydrogen bonding. Therefore, it would be desirable to carry out experiments under conditions where it is possible to separate the influence of the surrounding medium from that of the partner molecules, on the dynamics of hydrogen bonding. Interesting conclusions may be drawn by comparing the results of experiments in solution, where the energy exchange between the molecules of a solvent and complexes is almost uninterrupted, with the data obtained in the gaseous phase.

The kinetic characteristics of hydrogen bonding, a well as the rates of conventional chemical reactions, depend largely on the kind of potential surface of interaction between a proton donor and a proton acceptor. As a generalization, one can consider three types of processes occurring in hydrogen-bonded systems.

2.1.1 *Formation and breaking of hydrogen bonds*

The process of complex formation in the gaseous phase requires no activation energy and, apparently, proceeds with the participation of a third particle:

$$AH + B + M \underset{k_{diss.}}{\overset{k_{ass.}}{\rightleftarrows}} AH \cdots B + M$$

The particle M removes the excess energy, consisting of the energy of the hydrogen bond ΔH_0 and part of the kinetic energy of the colliding partners AH and B; the probability of transfer of this energy onto the vibrational degrees of freedom of the AH · · · B complex is very small, as in the processes

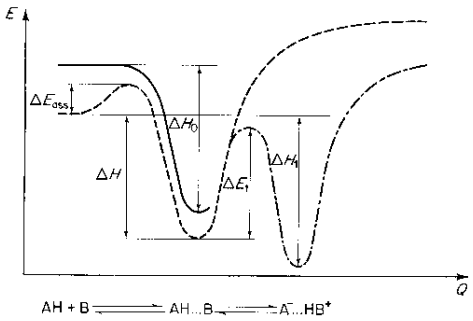


Figure 2.1 Reaction path profiles for the formation of a complex containing a hydrogen bond: in the gaseous phase (——); in solution (– – –). Reaction path profile for proton transfer (–·–·–·–)

of recombination of free radicals and atoms. Interaction with a solvent affects the thermodynamic characteristics of a complex ($\Delta H_0 \neq \Delta H$, Figure 2.1), as well as the lifetime of an individual hydrogen bond, the lifetime in solution being decreased apparently due to a more effective energy transfer in the condensed phase. In this case complex formation does require some activation energy ΔE_{ass}, which is obtained by the interaction of donor and acceptor molecules with those of the solvent. Directly connected with these processes is the process of molecular exchange between hydrogen-bonded complexes:

$$AH \cdots B + A'H \cdots B' \rightleftarrows AH \cdots B' + A'H \cdots B,$$

AH and A'H, B and B' being either the same, or different molecules.

2.1.2 *Reversible proton transfer inside a complex, or 'molecular–ionic tautomerism'*

Reversible transfer of a proton inside a hydrogen-bonded complex, $AH \cdots B \rightleftarrows A^- \cdots HB^+$, occurs in systems having two minima on the potential surface of proton donor–proton acceptor interaction, separated by a barrier ΔE_1 and corresponding to two kinds of a complex, ionic and molecular, which are in equilibrium with free molecules. Such states exist for only a limited number of systems. In the case of one-minimum potential surface, it is possible to observe the process of setting up of an equilibrium either between free molecules and an ionic pair, $AH + B \rightleftarrows A^- \cdots HB^+$

(here, there is no molecular complex), or between free molecules and a molecular complex, $AH+B \rightleftarrows AH \cdots B$. In some cases a complex has an intermediate composition. Investigation of the structure of complexes and the types of equilibria in systems with different values of proton donor and proton acceptor ability under static conditions makes it possible to obtain an idea of the shape of the potential surface and to determine the depth of the minima, ΔH and ΔH_1. The value of the potential barrier, ΔE_1, determining the rate of transfer from one state to the other, may be obtained from kinetic measurements only. It must be emphasized that up to the present day no one has succeeded in recording the equilibria between a molecular complex and an ionic pair in the gaseous phase. Therefore, in this respect, the question of the influence of a medium on the parameters of the surface and the kinetics of the process acquires special importance.

2.1.3 *Proton exchange between molecules or complexes*

The decisive role of hydrogen bonding in proton exchange kinetics $AH+BH^* \rightleftarrows AH^*+BH$, between molecules capable of acting both as proton donor and as proton acceptor, has been indicated in a number of papers (Brodsky, 1964, Denisov and Tokhadze, 1973; Bureiko *et al.*, 1976, 1977b). A study of the kinetics of this process provides some information on proton transfer in systems having one minimum on the potential surface, belonging to a molecular complex, $AH \cdots B$. As a rule, proton exchange is a complicated process involving several stages, in particular, the process of complex formation. In the gaseous phase and in dilute solution in inert solvents, proton exchange between individual molecules occurs in hydrogen-bonded complexes. In (see section 2.4) the simplest case, the first step of exchange is cooperative proton transfer in a cyclic hydrogen-bonded complex. The existence of a minimum on the potential surface of interaction between AH and BH, referring to a cyclic complex with two hydrogen bonds, $AH \cdots B$ and $BH \cdots A$ (A and B may be the same), indicates the existence of another minimum, which results from the symmetry (Figure 2.2). These two minima refer to two physically indistinguishable states of a complex, and the transfer of a proton from one state to the other requires some activation energy, $\Delta E^{\neq}$ (Denisov and Tokhadze, 1973).

The present chapter discusses the results of experimental investigations of the kinetics of these processes in inert solvents and in the gaseous phase. Results have been obtained mainly by means of NMR and kinetic IR spectroscopy. As to the theoretical aspects of the problem, they have not been adequately developed so far. The few papers referring to these problems are concerned with the simplest model processes. Here, special attention is devoted to the influence of the electronic structure of the interacting molecules on the rate of the process; and comparison is made of static and dynamic characteristics of hydrogen bonding.

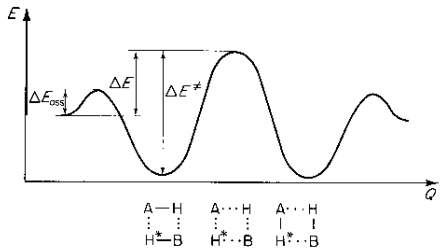


Figure 2.2 Reaction path profile for proton exchange (the case of cooperative proton transfer)

2.2 Lifetimes of Hydrogen-Bonded Complexes

Experimental study of the kinetic characteristics of hydrogen-bonded complexes is of great importance for understanding some fundamental questions connected with the nature of hydrogen bonding and its spectral manifestations. The main kinetic characteristic of a complex is its lifetime. The lifetime of an individual complex can be determined by various processes of molecular exchange between complexes. Such processes may be, for example, the exchange of proton acceptor molecules:

$$AH \cdots B' + B'' \rightleftarrows AH \cdots B'' + B'; \tag{2.1}$$

or proton donor molecules:

$$AH' \cdots B + AH'' \rightleftarrows AH'' \cdots B + AH'; \tag{2.2}$$

B′ and B″, AH′ and AH″ being either different, or identical molecules. Some exchange processes occur with the help of self-associates, e.g.:

$$(AH)_2 + 2B \rightleftarrows 2AH \cdots B, \tag{2.3}$$

or

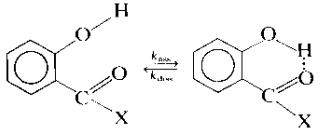
$$2AH \rightleftarrows (AH)_2 \overset{AH}{\rightleftarrows} (AH)_3 \rightleftarrows \cdots \rightleftarrows (AH)_n \tag{2.4}$$

The lifetimes of complexes, determined by these equilibria, have a complicated dependence on the concentrations of species. Of particular importance is the lifetime, determined by the monomolecular dissociation process:

$$AH \cdots B \rightleftarrows AH + B, \tag{2.5}$$

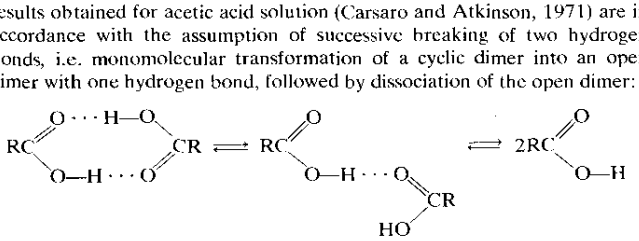
which is a characteristic of the kinetic stability of the AH · · · B complex. This value could be found by studying more complicated processes such as (2.1) or (2.2), provided the simple process (2.5) was one of the stages.

The lifetimes of hydrogen-bonded complexes have been measured by various techniques—ultrasonic relaxation and dynamic NMR being most effective. Investigation of hydrogen-bonded systems by ultrasonic methods shows that in most cases, at room temperature, the rate of hydrogen bond formation is close to the rate of molecular collisions in liquids and is limited by diffusion. As a rule, the bimolecular rate constants, k_{ass}, are within the range 10^8–10^{11} l mol^{-1} s^{-1}. The fact that they are less than the diffusion limit may be accounted for by the entropy factor, since this process requires the collision of definitely orientated molecules. Such rates were observed for the dimerization of benzoic acid (Maier, 1960), caprolactam (Bergman *et al.*, 1963), pyridone (Hammes and Lillford, 1970), and other compounds. The activation energy in all these systems does not exceed $\Delta E_{ass} \sim 1$–3 kcal mol^{-1}, and coincides with the activation energy of diffusion. To a first approximation, the rate of dissociation of complexes is determined by the energy of hydrogen bonding, and generally decreases as the energy increases, with the lifetime of the complex getting longer. For example k_{diss} of the NH $\cdots$ O bond in 2-pyridone is less than that of the NH $\cdots$ S bond in 2-thiopyridone (2.2×10^7 and 4.4×10^7 s^{-1}) due to the greater strength of the former complex. The difference in the activation energies for dissociation and association coincides, as a rule, with the energy of the complex measured under static conditons. For intramolecular hydrogen bonds, like OH $\cdots$ O=C in salicylates and in salicylic aldehyde, the process



is monomolecular, and for X = H, OCH_3 $k_{ass} = 2.2 \times 10^7$, 2.6×10^7, and $k_{diss} = 3 \times 10^5$, 9.5×10^5 s^{-1}, respectively (Yasunaga *et al.*, 1969).

In some cases, ultrasonic methods can be used for a more detailed investigation of the mechanism of the monomer–dimer relaxation. The results obtained for acetic acid solution (Carsaro and Atkinson, 1971) are in accordance with the assumption of successive breaking of two hydrogen bonds, i.e. monomolecular transformation of a cyclic dimer into an open dimer with one hydrogen bond, followed by dissociation of the open dimer:



Carsaro and Atkinson (1971) suggested that the rate of cyclic complex formation, $k_{ass} = 3.4 \times 10^6\ s^{-1}$, is determined by the internal rotation around the hydrogen bond, and depends upon viscosity. Analysis of the ultrasonic absorption in the range 300–1500 MHz has shown that the lifetime of the open dimer is $\tau = 2 \times 10^{-10}$ s (Bader and Plass, 1971). The step-by-step mechanism of dissociation has been found also for propionic acid in cyclohexane solution at concentrations of 0.3–1 mol l^{-1}, the rate constants being $k_{diss} \sim 10^4\ s^{-1}$ and $k_{ass} \sim 10^7\ s^{-1}$ (Tatsumoto *et al.*, 1972).

A study of the kinetics of hydrogen bonding in various solvents has led to some interesting conclusions. In a more active solvent, the activation energy of dissociation of the complex, ΔE_{diss}, decreases, the value of ΔE_{ass} remaining unchanged. The decrease of ΔE_{diss} results in an increase in the dissociation rate constant. Thus for caprolactam at 22 °C in CCl_4 $k_{diss} = 4.6 \times 10^7\ s^{-1}$, and in, C_6H_6, $k_{diss} = 26 \times 10^7\ s^{-1}$ (Bergman *et al.*, 1963; Maeyer *et al.*, 1968). Consequently, a decrease of the equilibrium constant takes place, as is well known from static measurements. This statement may be illustrated by the results for benzoic acid in various solvents: C_6H_{12}, CCl_4, C_6H_5Cl, $C_6H_5CH_3$ (Borucki, 1967). For these solvents k_{diss} increases from 0.22×10^6 to $3.3 \times 10^6\ s^{-1}$, and ΔH_{diss} decreases from 13.9 to 9.9 kcal mol^{-1}. In this series the solvent activity rises according to the rise of its proton acceptor ability. The energy of a hydrogen bond measured under static conditions is equal to the difference in energies of the initial and final states: $\Delta H = (\Delta H_0 + E^S_{AH\cdots B}) - (E^S_{AH} + E^S_B)$, where $\Delta H_0 + E^S_{AH\cdots B}$ is the total energy of the complex in a solvent, $(E^S_{AH} + E^S_B)$ is the energy of the initial state, corresponding to the free molecules of donor and acceptor in solution, ΔH_0 is the energy of the hydrogen bond in the gaseous phase, $E^S_{AH\cdots B}$, E^S_{AH}, and E^S_B are the interaction energies of the complex, free donor, and acceptor molecules with a solvent (Figure 2.3). Since the active centres of the complex are blocked ($E^S_{AH\cdots B}$ in different solvents are very close), the total

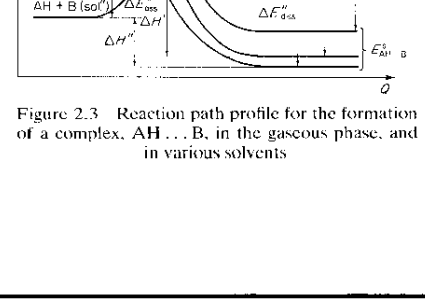


Figure 2.3 Reaction path profile for the formation of a complex, AH ... B, in the gaseous phase, and in various solvents

energy of a complex remains almost unchanged, on its transfer from gaseous to liquid phase, or in different solvents. The interaction energy of free molecules grows with the growth of the solvent's activity, which results in $\Delta H'' < \Delta H' < \Delta H_0$. The value, ΔE_{ass}, is almost unaffected by the medium, which means that interaction with the medium has existed in the transitional state.

It is necessary to emphasize that, in ultrasonic experiments, there is some degree of uncertainty in establishing correspondence between the absorption observed and the process under investigation. The registered dependence of the absorption coefficient on the frequency permits determination of the relaxation time only in those cases where one process is going on. However, most results are available for concentrated solutions and pure liquids, where more complicated processes are possible.

In the liquid phase, due to the high rate of energy transfer, the mechanism of the processes discussed above cannot be studied in detail. In particular, a study of the role of triple collisions and of intramolecular energy redistribution during the formation of hydrogen-bonds is possible only in the gaseous phase. For this reason measurement of the lifetime of complexes in the gaseous phase is of special interest. An effort has been made to study monomer–dimer relaxation in a gas by means of the shockwave technique using IR monitoring (Tokhadze, 1975; Gerasimov *et al.*, 1981). This technique studies relaxation processes taking $\sim 10^{-6}$ s, at concentrations $\sim 10^{-5}$ mol l.$^{-1}$, by measuring the changes in intensity of IR absorption bands. Strongly hydrogen-bonded complexes have been used: cyclic dimers of trifluoroacetic and acetic acids ($\Delta H \sim 12$–14 kcal mol^{-1}) and mixed complexes $CF_3COOH \cdots O(C_2H_5)_2$ ($\Delta H = 8.4$ kcal mol^{-1}) and $CF_3CF_2CH_2OH \cdots N(CH_3)_3$ ($\Delta H = 8.8$ kcal mol^{-1}). Unfortunately, in all the systems within the temperature range 40–100 °C, the decay of the complexes comes to an end at the front of the shock wave, and an estimate of the upper limit of the lifetimes, $\tau < (1$–$2) \times 10^{-6}$ s, only, is possible. However, even such estimates suggest a possible mechanism for the process in the gas phase. Thus in the case of cyclic dimers, the rate of dissociation observed can be explained only on the supposition that the two hydrogen bonds do not break simultaneously. This is in accordance with the ultrasonic absorption data, where two relaxation processes are observed, corresponding to the conversion of the cyclic dimer to an open dimer, and of the open dimer to the monomer. The high rate of dissociation of a single hydrogen bond ($\Delta H \sim 9$ kcal mol^{-1}) may be explained in terms of the model, taking into account the consequent exitation of the energy levels of the complex, corresponding to low-frequency vibrations of the hydrogen bond, $\Delta\nu \sim 20$–100 cm^{-1}, the probabilities of the vibrational translational energy transfer for the low-frequency vibrations of polyatomic molecules being used in the model.

Dynamic nuclear magnetic resonance (DNMR) is one of the most convenient and reliable experimental methods for studying the kinetics of fast exchange processes (see, for example, Jackman and Cotton, 1975). This method can be used to investigate reactions within a large time range ($1–10^{-8}$ s, if pulse techniques are used), and is of considerably higher sensitivity compared to the ultrasonic method. Indeed, at present, the Fourier-transform ^{1}H NMR spectra suitable for carrying out the lineshape analysis can be obtained easily at concentrations of about 10^{-4} mol l^{-1}. One of the benefits of DNMR is that the composition of an equilibrium mixture and the structure of the molecular forms involved can be ascertained simultaneously. This makes it considerably easier to attribute the rate measured to a certain process. Proton chemical shifts are very susceptible to the formation of even weak hydrogen bonds. Strong hydrogen bonding is apt to shift the signal of the proton involved by up to 20 p.p.m., which exceeds the interval of proton chemical shifts (for molecules with no hydrogen bonding). Therefore, it would be natural to assume that the application of DNMR to a study of the kinetics of hydrogen bonding could be rather fruitful. However, attempts to determine the lifetimes of hydrogen-bonded complexes by DNMR in a direct way have not been successful until recently. Among the earlier works it is worth mentioning a number of papers by Grunwald and coworkers (see Grunwald and Ralf, 1971), where information on the kinetics of dissociation of a complex was obtained indirectly, through a study of proton exchange kinetics. Having assumed a certain mechanism, the authors evaluated the lifetimes of the complexes of ammonia and mono- and trimethylamine with water at ~300 K as 10^{-12}, 10^{-11}, and 10^{-10} s, respectively. This order of values is in accordance with the increase of bond strength in this series, although such a large effect is unexpected and can hardly be accounted for by the difference in hydrogen bond energy only. Since the lifetimes mentioned above are of the same order as the characteristic diffusion times in liquids, diffusion must play an important part in the kinetics of breaking and re-forming of these bonds. Fraticllo *et al.* (1973) found that at temperatures below −100 °C the rate of exchange processes in systems with strong hydrogen bonding may be so retarded that separate signals belonging to different complexes are observed. Thus velocities of molecular exchange processes, under conditions where they are not limited by diffusion (i.e. the lifetime of the complexes being $10^{-6}–10^{-2}$ s), may be estimated.

The lifetimes of complexes determined by different kinds of equilibria were obtained recently by a study of separated signals. As mentioned above, the simplest equilibrium (2.5) is between a binary complex, AH · · · B, and molecules with no bonding. Unfortunately, study of such a simple process is possible only rarely, for most proton donor molecules are capable of self-association. At low temperature this leads to the formation of various

complexes involving more than two molecules. Moreover, between molecules containing hydroxyl groups intensive proton exchange would occur which, as well as the process under investigation, could result in the averaging of signals. (In section 2.4 these phenomena will be shown to accompany each other, because both self-association and proton exchange are affected by the ability of an AH molecule to form hydrogen bonds as a proton donor and as a proton acceptor, simultaneously.) Therefore, it would be worth choosing a proton donor which had very little acceptor ability. Equilibrium (2.5) involving a complex of CHF_3 with triethylamine in liquid argon was described by Golubev *et al.* (1977b). In the ^1H NMR spectra, at 90 K, broadening of the resonance CHF_3 signal was seen, which was at a maximum when the binary complex and free CHF_3 molecule concentrations were comparable. This broadening was not observed in the absence of the acceptor, or if it were great excess. In the latter case equilibrium (2.5) was completely shifted to the left. Thus it was concluded that the linewidth was determined by the process of hydrogen bond breaking and re-forming. Estimation of the lifetime of the complex at 90 K gave the value $\tau = 7 \times 10^{-4}$ s, which is much greater than the characteristic diffusion time in liquid argon.

The complex of $(CF_3)_3COH$ with hexamethylphosphoroustriamide (HMPT) is another example (Golubev and Denisov, 1981). Since the acceptor ability of this alcohol is greatly lowered, at concentrations less than 10^{-2} mol l^{-1} no self-associates or complicated complexes have been revealed even at 110 K. Figure 2.4 shows the ^1H NMR spectra of a solution containing HMPT and $(CF_3)_3COH$ (the latter in excess) in CDF_2Cl. At 110 K, two signals are seen,

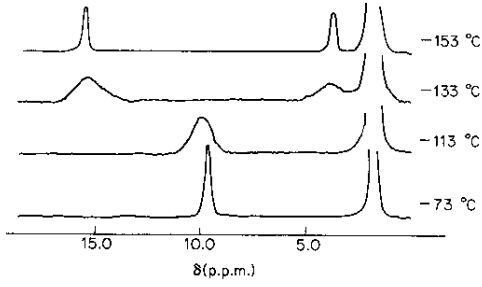


Figure 2.4 ^1H NMR spectra of a solution containing $(CF_3)_3COH$ (0.01 mol^{-1}) and $[(CH_3)_2N]_3PO$ (0.005 mol $^{-1}$) in CDF_2Cl

the high-field signal belonging to the free hydroxyl groups, and the low-field one attributed to a binary complex with HMPT. As relative concentrations are varied, so are their relative intensities, but not their chemical shifts. As the temperature rises, the signals broaden, overlap, and collapse. The averaging of the free molecule and complex signals could be caused either by the breaking and re-forming process (2.5), or by the bimolecular exchange (2.2), where AH′ and AH″ are identical molecules, or by proton exchange between these forms. However, the lineshapes have been shown to be unaffected by dilution of a solution with a given $[AH]_0/[BH]_0$ concentration ratio. The authors consider this fact to be an argument in favour of the monomolecular process (2.5). Indeed, in this case,

$$\tau_{AH\cdots B} = k_{diss}^{1}$$

$$\tau_{AH} = k_{ass}^{-1}[B]^{-1} = Kk_{ass}^{1}\frac{[AH]}{[AH\cdots B]} \approx Kk_{ass}^{-1}\left(\frac{[AH]_0}{[B]_0} - 1\right) \qquad (2.6)$$

because equilibrium (2.5) is strongly shifted to the left, and, with an excess of AH, the concentration [B] is small compared to [AH] and [AH · · · B]. It is clear that information could be obtained only about the dissociation velocity, since finding k_{ass} would require a very accurate value of the equilibrium constant, K, to be known. The lifetime of the complex proved to depend strongly on temperature. Thus at 130 K, $\tau_{AH\cdots B} = 3.4\times10^{-2}$ s; at 150 K, $\tau_{AH\cdots B} = 4\times10^{-4}$ s; at 170 K, $\tau_{AH\cdots B} = 1.8\times10^{-5}$ s. The activation energy was found to be $\Delta E_{diss} = 8.7$ kcal mol^{-1}, which is close to the enthalpy of this complex (9.6 kcal mol^{-1} in CCl_4, Kuopio *et al.*, 1976). It is worth emphasizing that if the data obtained were extrapolated to room temperature, the lifetime of the complex would be estimated as 10^{-9} s, which means that it is likely to be determined by diffusion.

The equilibrium between *ortho*-substituted phenols with strong intramolecular hydrogen bonding and their complexes with proton acceptors has been studied at 110–200 K in CHF_2Cl (Denisov *et al.*, 1977). Intramolecular hydrogen bonding in a proton donor molecule hinders self-association and proton exchange, which makes it possible to observe the simple process (2.5). Figure 2.5 shows the spectra of a solution of *o*-nitrophenol and 2,4,6-trimethylpyridine. As the temperature falls, the hydroxyl signal is shifted to the lower field (which corresponds to the equilibrium shift towards the intermolecular hydrogen bonding) and, then, is split into two. With no acceptor, only the high-field signal is observed, while with excess of acceptor only the low-field signal is left. With an excess of the phenol the lifetimes of the complex measured are independent of concentrations, and the lifetimes of the intramolecular hydrogen bond are inversely proportional to the acceptor concentration. A two-stage mechanism was

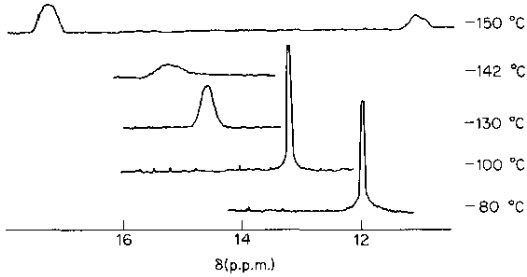
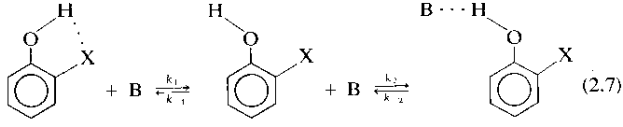


Figure 2.5 ^{1}H NMR spectra of the *o*-nitrophenol (0.06 mol l^{-1}) + 2,4,6-trimethylpyridine (0.04 mol l^{-1}) system in CHF_2Cl

suggested, involving the total breaking of one hydrogen bond followed by the formation of the other:



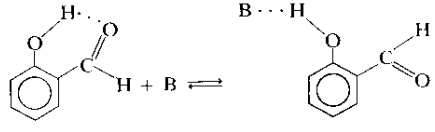
(2.7)

The lifetimes of the forms with intra- and intermolecular bonding are

$$\tau_{\text{intra}} = k_1^{-1}\left(1+\frac{k_{-1}}{k_2[\text{B}]}\right), \qquad \tau_{\text{inter}} = k_{-2}^{-1}\left(1+\frac{k_2[\text{B}]}{k_{-1}}\right) \tag{2.8}$$

the observed reaction orders being in accordance with (2.8), if $k_2[\text{B}] \ll k_{-1}$.

If salicylic aldehyde were taken as proton donor, the kinetics of the process could be studied using both OH and CHO group signals. The CHO signal is very sensitive to the breaking of the intramolecular hydrogen bond, due to the simultaneous rotation of this group through 180°:



(2.9)

The lifetimes measured by these two signals proved practically the same, which confirms that proton exchange has no influence upon the spectra. The activation parameters are given in Table 2.1. The difference between the activation energy values of the forward and backward reactions is close to

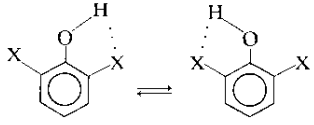
Table 2.1 Enthalpy change ΔH and activation parameters ΔE_{diss}, ΔS_{diss} of the forward and backward reaction (2.9).*

No.	Phenol + acceptor	$-\Delta H$ (kcal mol^{-1})	ΔE_{diss}^{inter} (kcal mol^{-1})	ΔE_{diss}^{intra} (kcal mol^{-1})	ΔS_{diss}^{inter} (e.u.)	ΔS_{diss}^{intra} (e.u.)
1.	2-Nitrophenol + collidine	6.0±0.3	13.2±0.6	6.8±0.6	+20	+6
2.	2-Nitrophenol + hexamethapole	5.1±0.3	11.9±0.6	6.7±0.6	+19	+6
3.	2-Formylphenol + collidine	5.0±0.3	12.8±0.6	8.0±0.5	+17	+2.5
4.	2-Formylphenol + hexamethapole	3.2±0.3	11.4±0.7	8.1±0.6	+16	+2.3
5.	2-Acetylphenol + hexamethapole	0.3±0.1	10.6±0.6	10.8±0.6	+19	+5

* Nos. 1–4 in CHF_2Cl, No. 5 in a mixture of $C_2H_5Cl + CH_2Cl_2$

the enthalpy of the process determined independently. In addition, the activation energy of breaking an intramolecular hydrogen bond is unchanged, when various acceptors are used, which confirms mechanism (2.7).

The hindered internal rotation in molecules of 2,6-disubstituted phenols, involving the breaking of intramolecular hydrogen bonds, was examined by Koelle and Forsen (1974), and Golubev and Denisov (1975):



(2.10)

The substituents X, become non-equivalent when process (2.10) is slow (Figure 2.6), which makes it possible to use their signals for determining the rate. The activation parameters of the internal rotation, given in Table 2.2,

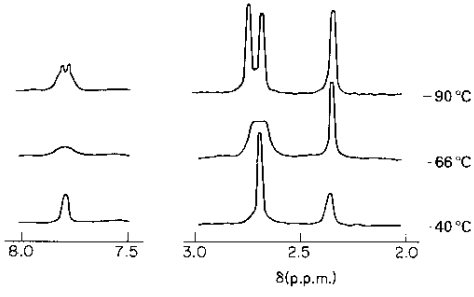


Figure 2.6 ^1H NMR spectra of 2,6-diacetyl-4-methylphenol in CHF_2Cl at various temperatures

Table 2.2 Kinetic characteristics of the hindred internal rotation in 2,6-disubstituted phenols

No.	Phenol	ΔE_{diss} (kcal mol^{-1})	ΔS_{diss} (e.u.)
1.	2,6-Dicarbomethoxyphenol	9.0 ± 0.4	-1.4 ± 0.5
2.	2,6-Diacetyl-4-methylphenol	10.5 ± 0.4	-2.0 ± 0.5
3.	2,6-Diformylphenol	7.1 ± 0.2	-21 ± 1

turn out to be close to the respective values for the OH $\cdots$ X bonds, breaking in the presence of an acceptor. Thus the conclusion that an acceptor molecule does not take part in the first stage of process (2.7) is supported.

Molecular exchange of the type (2.1) has been thoroughly investigated by means of DNMR under conditions of excess of one of the proton acceptors. This excess can often depress the formation of more complicated complexes. In the paper by Fratiello *et al.*, (1973), spectra of mixtures of $(CF_3)_2CHOH$ or p-FC_6H_4OH molecules with triethylamine in diethyl ether were obtained. The complexes of the donor with amine and ether were in equilibrium. The activation energy of the process leading to collapse of the signals was very high ($\sim$15 kcal mol^{-1}), which proves that proton exchange does not occur. The kinetics of molecular exchange (reaction 2.1) between complexes of carboxylic acids with different proton acceptors have been investigated, one of the acceptors being varied and the other being a molecule of diethyl ether (Golubev and Denisov, 1976). Splitting of the signals was observed in the temperature range 120–60 K. It was found that the lifetime of the complex, $RCOOH \cdots O(C_2H_5)_2$, is independent of the nature of the second acceptor, and is determined by its concentration only. Therefore, it was supposed that this exchange is monomolecular, dissociation of the complex being the velocity-limiting stage:

$$AH \cdots B' + B'' \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AH + B' + B'' \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} AH \cdots B'' + B' \qquad (2.11)$$

The rate of the forward reaction is

$$V = k_1[AH \cdots B']\frac{k_2[B'']}{k_2[B''] + k_{-1}[B']} = k_1[AH \cdots B']\left(1 + \frac{k_1[B']}{Kk_{-2}[B'']}\right)^{-1}$$

$$= k_1[AH \cdots B']\left(1 + \frac{k_1}{k_{-2}}\frac{[AH \cdots B']}{[AH \cdots B'']}\right)^{-1}, \qquad (2.12)$$

where K is the equilibrium constant of the exchange (2.1). A similar equation may be written for the rate of the inverse process. The average lifetime of a molecular form X being equal to $[X]V^{-1}$, the monomolecular

dissociation velocity constants k_1 and k_{-2} can be obtained from the lifetimes observed, $\tau_{AH\cdots B'}$, $\tau_{AH\cdots B''}$, by means of the equations:

$$\tau_{AH\cdots B'} = k_1^{-1}\left(1+\frac{k_1[AH\cdots B']}{k_{-2}[AH\cdots B'']}\right),$$
$$\tau_{AH\cdots B''} = k_{-2}^{-1}\left(1+\frac{k_{-2}[AH\cdots B'']}{k_1[AH\cdots B']}\right). \qquad (2.13)$$

The values k_1 and k_{-2} can be determined from the plots $\tau_{AH\cdots B'} = f([AH\cdots B']/[AH\cdots B''])$. The lifetimes of complexes determined by hydrogen bond dissociation and formation processes, are $t_{AH\cdots B'} = k_1^{-1}$; $t_{AH\cdots B''} = k_{-2}^{-1}$. In Table 2.3 t values of HCOOH and CF_3COOH complexes with various acceptors, at 170 K, are given together with activation parameters of the exchange. Denisov *et al.* (1976) emphasized that the activation entropy values are positive, resulting in very high values of the pre-exponential factors in the Arrhenius equation (10^{15}–10^{18} s^{-1}). This means that the hydrogen bond in an activated complex is much weaker compared to the initial state. In the case of some bimolecular mechanisms, e.g.

$$AH\cdots B'+B'' \rightleftarrows AH:\begin{matrix}B'\\ \vdots\\ B''\end{matrix} \rightleftarrows AH\cdots B''+B'$$

a decrease of entropy in the transitional state would be expected rather than an increase.

Golubev (1977) examined the possible contribution of proton exchange to the observed averaging of signals of trifluoroacetic acid complexes when an excess of one of the two acceptors was present. The CHO signal in the $(CH_3)_2NCHO$ molecule appeared to be rather sensitive to the formation of a hydrogen bond with strong proton acceptors. The kinetics of the molecular

Table 2.3 Kinetic characteristics of hydrogen-bonded complexes in CHF_2Cl

No.	Acceptor	$t^{170\,K}\times 10^5$ (s)	ΔE_{diss} (kcal mol^{-1})	ΔS_{diss} (e.u.)
	1. Complexes of HCOOH			
1.	$(C_2H_5)_2O$	0.17±0.03	7.6±0.3	12.0±0.6
2.	$(CH_3)_2SO$	0.9±0.2	8.9±0.6	16±1
3.	$(CH_3)_2NCHO$	3.0±0.5	9.6±0.6	18±1
4.	$[(CH_3)_2N]_3PO$	3.5±0.7	10.2±0.8	21±1.5
	2. Complexes of CF_3COOH			
1.	$(CH_3)_2O$	0.6±0.1	8.7±0.6	16±1
2.	$(C_2H_5)_2O$	1.7±0.2	9.8±0.3	20±1
3.	$(CH_2)_4O$	5.6±0.7	10.2±0.8	20±1
4.	$(CH_3)_2SO$	12±2	10.8±0.8	22±1.5
5.	$(CH_3)_2NCHO$	16±4	11.2±1	24±1.5
6.	$[(CH_3)_2N]_3PO$	43±8	11.9±1	26±1.5

exchange (2.1) between the complexes of CF_3COOH with $(CH_3)_2NCHO$ and $(CH_3)_2O$ was studied, the lifetimes being determined using either OH or CHO signal shape. As the proton exchange cannot affect the CHO signal shape, the good correspondence of the times obtained proved the proton exchange rate in this case to be negligibly small. The step-like mechanism of the molecular exchange was confirmed.

Summing up, one can say, that the monomolecular process, $AH \cdots B \rightleftarrows AH + B$, while requiring comparatively high activation energy, is the most profitable way of breaking either inter- or intramolecular hydrogen bonds.

2.3 Reversible Proton Transfer Inside Hydrogen-Bonded Complexes

Proton transfer is the simplest and, at the same time, one of the most important chemical reactions. The study of this process, as well as of more complicated reactions, involving proton transfer as one of the stages, has attracted the attention of a great many investigators (Caldin and Gold, 1975). However, a similar process in inert solvents has not been well studied so far, probably, in view of its minor practical importance. Since reactions with the participation, or formation, of ions are, to a much greater extent, affected by the solvent in comparison with pure molecular processes, the acid–base interaction in inert media may differ considerably from the 'common' reaction in solvents strongly solvating the ions. It is known that, in this case, interaction between comparatively weak partners results in the formation of a molecular complex with a hydrogen bond, $AH \cdots B$, while interaction between strong partners results in the formation of a close ionic pair, $A^- \cdots HB^+$, with interionic hydrogen bonding. Dissociation of an ionic pair into free ions in solvents, like hydrocarbons and their halogen derivatives, is extremely disadvantageous. Thus the reaction is always a process of complex formation, with a hydrogen bond between molecules contributing much to the energy balance of the reaction. Hydrogen bonding affects the kinetics of proton transfer even more considerably.

The structure of the binary complex in the case of intermediate interaction energy and the gradual alteration of this structure with increasing complex formation energy are problems of special importance. These problems have been dealt with in a number of experimental works, carried out mainly by IR, UV, and NMR spectroscopy. It was in 1956 that Barrow, having analysed the IR spectra of complexes of pyridine with carboxylic acids in $CHCl_3$ in the region of skeleton vibrations, stated that the interaction with CH_3COOH proceeds no further than the formation of molecular complexes, but, with CCl_3COOH and CF_3COOH, results in proton transfer and the formation of an ionic pair. In the intermediate cases, $CH_2ClCOOH$ and $CHCl_2COOH$, the complex formed is tautomeric: $AH \cdots B \rightleftarrows A^- \cdots HB^+$. This conclusion was, at first, doubted (Davis, 1968), but later

confirmed by Gusakova *et al.* (1970). In a number of papers (e.g. Vinogradov and Linnel, 1971) the assumption of a tautomeric proton transfer inside a complex was made in order to explain the structure of the stretching vibration band, ν_{XH}. However, the question of the shape of this band seems to be rather obscure in the spectroscopy of hydrogen bonding (Hadzi and Bratos, 1976). It may be determined by many factors having no direct relation to proton migration (Fermi resonance, interaction with low-frequency vibrations of hydrogen bond, etc.). At present, there is not a single case known when the ν_{AH} band structure observed could be referred without any doubt to proton tunnelling in a double-minimum potential well.

In later works it has been shown that reliable identification of a tautomeric structure of a complex is a difficult task requiring a study of each complex over a wide range of the spectrum. Equilibrium between a molecular complex and an ionic pair of $OH\cdots N \rightleftarrows O^- \cdots HN^+$ type has been found from the IR spectra in the region of skeletal vibrations of partner molecules (Gusakova *et al.*, 1972, Lindemann and Zundel, 1977), in the region of low-frequency intermolecular vibrations of the hydrogen bond (Denisov *et al.*, 1973), from UV spectra (Baba *et al.*, 1969; Hudson *et al.*, 1972), and from NMR spectra at low temperatures (Golubev *et al.*, 1977a). In the last work, by the way, it has been stated that the frequency of the reversible proton transfer in the $OH\cdots N$ complexes is above $10^5\,s^{-1}$, even at a temperature of $-170\,°C$. Proton transfer in complexes with $CH\cdots N$ bonding, studied by IR spectroscopy (Golubev and Denisov, 1977) and NMR spectroscopy (Golubev *et al.*, 1978), appeared to be much slower.

Thus the fact of proton migration in hydrogen-bonded complexes in inert media is not in doubt. It has been safely established for a comparatively large number of compounds, in particular, for complexes of acids of rather different types with aliphatic and aromatic amines. However, not even a single case of molecular–ionic tautomerism has been reported for a complex with an oxygen atom as a proton acceptor. In analysing some data obtained by a number of authors (Hadzi, 1965; Matrosov and Kabachnik, 1977), one can suppose that, in the case of complexes with strong $OH\cdots O$ hydrogen bonding, their structure is altered gradually with the rise of the interaction energy, from the molecular, $AH\cdots B$, to the ionic, $A^- \cdots HB^+$. In the intermediate case, the spectral characteristics of such complexes resemble those of 'symmetrical' hydrogen bonding which have been observed in complex ions, like FHF^-, and bimalcate ion, whose potential surface of interaction has only one minimum corresponding to the central position of the proton. Thus for such complexes (e.g. complexes of CF_3COOH with some oxides) a very low ν_{OH} frequency and a very high chemical shift of the OH proton are typical. A number of frequencies in these complexes are intermediate between those characteristic of the intrinsic molecular and ionic complexes. One may assume the structure of complexes with extremely

strong manifestation of hydrogen bonding to be intermediate between molecular and ionic, $A^{\delta-} \cdots H \cdots B^{\delta+}$, with a 'quasi-symmetrical' hydrogen bond.

So, from the experimental data available, one may conclude that, as the interaction energy grows, the potential energy surface of proton donor–acceptor interaction may be altered at least in two ways. Figure 2.7 shows a schematic cross-section of this surface along the reaction coordinate (note, that this coordinate does not coincide with that corresponding to the position of the proton between the two nearest nuclei, since, on proton transfer, a change occurs in the bond lengths and the angles of A and B fragments). To the left of the hachured area there is a region, corresponding to a molecular complex; to the right is the region of ionic pairs. In case I, at low energy, only one minimum is seen. When interaction is intensified, another minimum appears, corresponding to the ionic pair, which deepens more rapidly than the first one (Denisov and Schreiber, 1974). At very high energy of complex formation, the potential barrier, dividing these two wells, disappears, and the complex formed will be of ionic structure. In case II, along with the deepening of the only well, a simultaneous shift to the region of an ionic complex occurs. In the intermediate case the hydrogen bond is quasi-symmetrical. The primary criterion of the type of proton potential function is to be found in equilibria observed in the system. However, if the presence of the molecular–ionic tautomerism proves the existence of at least two minima, the absence of an experimentally observed tautomerism is not sufficient proof of the absence of the second well. For example no equilibria have ever been reported for which an ionic pair would be more profitable

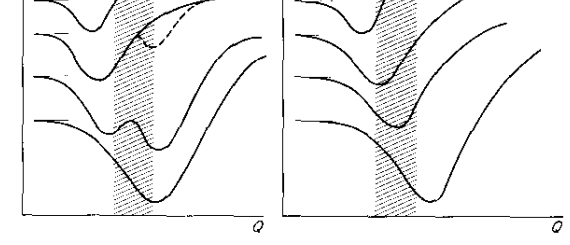


Figure 2.7 Two types of cross-sections of potential surfaces of interaction between a proton donor and a proton acceptor along the reaction coordinate Q

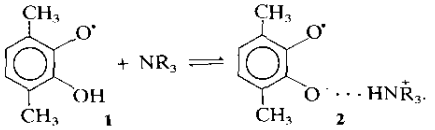
than a molecular complex. This is only natural, since the ionic complex with a large dipole moment, 10–15 D, strongly affects the arrangement of the solvent molecules around itself. This accounts for the fact that proton transfer is accompanied by a strong decrease in entropy (of 20–30 e.u.). Therefore, the equilibrium constant of the endothermal proton transfer would be comparatively small, hampering detection of an ionic pair. However, the existence of a second minimum, lying above the first, may strongly influence the kinetics of proton exchange (Bureiko *et al.*, 1979). To identify the potential function type correctly in cases where the tautomerism (i.e. two groups of bands related to molecular and ionic complexes, respectively) is not clearly seen in the spectra, it is necessary to turn to the finer spectroscopic features of the complexes, either with a migrating proton, or with a quasi-symmetrical hydrogen bond. These involve, for example, isotopic effects in IR and NMR spectra (Gunnarson *et al.*, 1976; Shapet'ko *et al.*, 1976), as well as a considerable decrease in the spin–spin coupling constants of the proton, $A^{\delta-} \cdots H \cdots B^{\delta+}$, with nuclei of the fragments, A and B, in comparison with the structures, AH and HB^+ (Fujiwara and Martin, 1974).

Where a double-well potential function exists, the question naturally arises of the frequency of proton migration inside a complex. As early as 1948, Sokolov made an assumption that this process is an elementary act of acid–base interaction. Formation of an intermediate hydrogen-bonded complex was considered to be the first stage of proton transfer, though such complex cannot always be observed immediately, in active solvents. However, repeated attempts to determine the rates of exothermal proton transfer inside any $OH \cdots N$ complex in studying the kinetics of interaction between two molecules AH and B, have failed. (It is worth mentioning that the rate of an analogous endothermal process is not so interesting in terms of kinetics, since its potential barrier cannot be lower than the energy of the process, and, consequently, its rate may be hindered by purely thermodynamic causes. Most reactions, known as 'reactions, controlled by proton transfer', are slow enough, since this transfer is unprofitable in terms of thermodynamics.)

Caldin *et al.* (1973) studied the kinetics of the interaction between a number of phenols and amines in chlorobenzene by means of microwave jump and detected the ionic pair by UV absorption. The velocities varied from 0.01 to 0.1 of the diffusion limit; the rate constants did not correlate with the equilibrium constants, and were determined by steric factors. This has led the authors to the conclusion that formation of an ionic pair is limited by the stage of hydrogen-bonded complex formation (which has been found by its UV absorption) rather than by proton transfer. The rate of this process is less than the diffusion limit due to an entropy factor, i.e. due to the need for collision of two definitely orientated polyatomic molecules. A similar conclusion was drawn by Ivin *et al.* (1971), in studying the

influence of solvent viscosity on the kinetics of ion-pair formation from 2,4-dinitrophenol and amines.

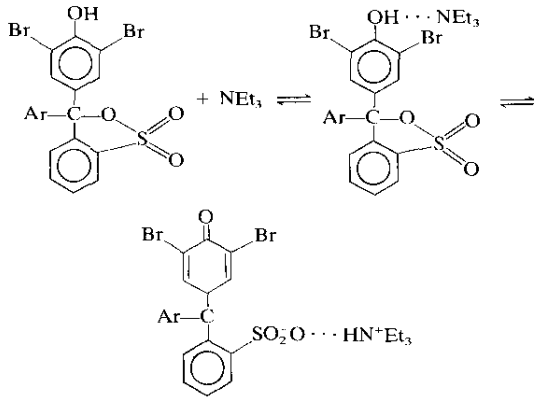
Recently, the kinetics of proton transfer from free radicals, like **1**, to various amines, in a low-polar solvent, has been intensively investigated by means of ESR (Masalimov *et al.*, 1976, 1977a,b):



(2.14)

In molecule, **1**, superfine coupling with the OH proton can be observed, and this disappears in ionic pair, **2**. When both forms are present in solution, some broadening of the signal is observed, which can be used to determine the rate of the process. Unfortunately, the monomeric free radical, **1**, cannot be distinguished from the molecular hydrogen-bonded complex by ESR, and the authors have not discussed the possibility of its intermediate formation. Thus it is hard to say, to which stage the kinetic characteristics are related (specific rates being about 10^8 l mol^{-1} s^{-1}). However, the activation parameters of the forward and backward reactions being rather close to the similar values for forming and breaking of complexes with strong hydrogen-bonding (section 2), one may suppose that it is this process which is rate limiting. This conclusion is supported by a weak dependence of the forward reaction velocity upon the basicity of the amines used.

Crooks and Robinson (1970, 1971) determined the rates of interaction between the bromphenol blue molecule and amines:



This process was found to proceed via two stages. The formation of a hydrogen-bonded complex (seen in the UV spectrum) was accomplished at the usual rate, while the proton transfer inside the complex was extremely retarded (down to $10^2\,s^{-1}$!). The authors tried to explain this strange fact by the unfavourable orientation of the molecules in the reaction complex, and by the weak solvation of the transitional state. However, in this case, absorption in the visible spectral region cannot appear immediately on proton transfer, but appears only after the formation of a quinoide structure, which requires the sulton ring to be broken. Thus it is obvious, that the rates observed have no relation to proton transfer, but are determined by the C—O bond breaking.

We believe that so far there have been no direct measurements made of proton migration frequency inside any OH · · · N complex. In Grunwald's (1966) review an analysis of a good deal of indirect evidence concerning the rates of various processes involving extremely fast proton transfer has been made. The conclusion was drawn that, in some cases, the frequency of proton migration inside a complex can reach $10^{13}\,s^{-1}$. Indeed Kreevoy (1965), for example, observed broadening of some bands in Raman spectra of solutions, containing CF_3COOH and the CF_3COO^- ion, compared with the same bands in solutions of pure CF_3COOH or CF_3COONa. This could be accounted for by proton migration with a frequency of about $10^{13}\,s^{-1}$, in an extremely strong complex, $CF_3COOH \cdots \bar{O}COCF_3$. However, in the IR spectra of complexes of carboxylic acids with amines, referred to above, these bands are not broadened. Thus it can be stated that, in these cases, the frequency must be below $10^{12}\,s^{-1}$ (but above $10^9\,s^{-1}$, since the bimolecular proton transfer is controlled by diffusion). It is obvious, that such an immense frequency value could only be reached either due to a very small potential barrier or a high probability of proton tunnelling. It may be supposed, that in complexes with a strong OH · · · N hydrogen bond both possibilities are combined. Indeed, the formation of a strong hydrogen bond must constrict strongly interacting molecules, which results in a lowering and narrowing of the barrier. It must be mentioned, that so far there has been no strict proof of proton tunnelling in OH · · · O or OH · · · N complexes.

In tautomeric complexes with weaker hydrogen bonding the proton migration frequency is much lower. Ulashkevich *et al.* (1977) and Golubev *et al.* (1980) have used ^1H NMR to study the kinetics of such a process in complexes with NH · · · N, SH · · · N, and CH · · · N hydrogen bonds. Figure 2.8 shows the spectrum of a solution containing CH_3NHNO_2 ($pK_a = 5$), and triethylamine in CHF_2Cl. (The occurrence of reversible proton transfer in the system is proved by IR spectra.) At low temperatures, splitting of the signal of the α-methylene group of the amine is observed, as well as that of the movable proton. The relative intensity and the lineshape of NH signals do not depend on concentration, therefore, the averaging of the signal involved is sure to be determined by the monomolecular process. The

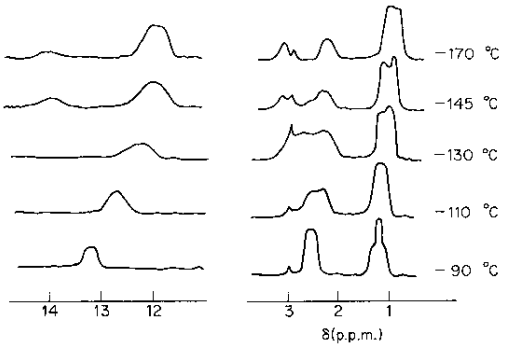


Figure 2.8 ^{1}H NMR spectra of a solution containing CH_3NHNO_2 (0.03 mol l^{-1}) and $(CH_3CH_2)_3N$ (0.1 mol l^{-1}) in CHF_2Cl at various temperatures

low-field signal belongs to the NH group of the molecular complex (with excess amine, at low temperatures, there are practically no free CH_3NHNO_2 molecules). The high-field signal belongs to the NH^+ group of the ionic pair, its intensity increasing as the temperature decreases. The monomolecular rate constant for proton transfer ranges from 500 s^{-1}, at 120 K, to 30,000 s^{-1}, at 170 K. The spectrum of the thiophenol–triethylamine complex (Figure 2.9)

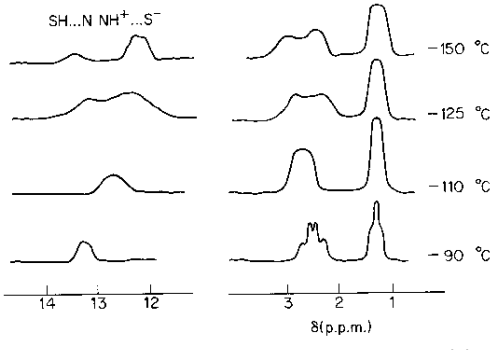


Figure 2.9 ^{1}H NMR spectra of a solution containing C_6H_5SH and $(CH_3CH_2)_3N$ in CHF_2Cl at various temperatures

has a similar appearance, though the splitting of the $SH \cdots N \rightleftarrows S^- \cdots HN^+$ signal takes place at a higher temperature. The rate of proton transfer inside complexes with $CH \cdots N$ hydrogen bonding may be varied within a wide range, but, generally, it is lower than in the similar complexes of NH and SH acids. Table 2.4 gives data concerning complexes of different types of acids with triethylamine. These acids have very similar acidities ($pK_a = 5$–6), but differ most strikingly in their proton–donor abilities, the value of which may be judged by the energy of their hydrogen bonding with dimethylsulphoxide. Since the rates of proton transfer in the tautomeric complexes of these acids are within the interval of characteristic NMR frequencies at various temperatures, they cannot be directly compared with each other. So, the temperature is given, at which the monomolecular rate constant is equal to $10^3\ s^{-1}$. It can be seen that, as the energy of hydrogen bonding increases, the rate increases greatly, while the activation energy falls. It is noteworthy, that CH acids do not seem to be a particular case of 'pseudo-acids', and low rates of deprotonization appear to be directly related to their weakness as proton donors in hydrogen bonding. The considerable influence of the strength of hydrogen bonding on the rate of proton migration seems very natural. At a fixed enthalpy of formation, ΔH_2, for the ion pair, and with an increase in hydrogen bonding energy, ΔH_1, the energy barrier falls since the transitional state, $[A^{\delta-} \cdots H \cdots B^{\delta+}]$, is stabilized (Table 2.4). Also, the minima on the potential energy surface are brought together on account of 'constriction' of A and B fragments by the proton (Figure 2.10). As a result, the probability of proton migration must increase considerably. One can suppose that in the limiting case of very strong hydrogen bonding, the potential barrier may disappear altogether, with the resulting potential function having only one minimum. At intermediate values of ΔH_2, the corresponding complexes could be described by the structure, $A^{\delta} \cdots H \cdots B^{\delta+}$, with a 'quasi-symmetrical' hydrogen bond.

Table 2.4 The enthalpy values of hydrogen-bonded complexes of acids with $(CD_3)_2SO$ and kinetic characteristics of proton transfer inside the complexes formed with $(CH_3CH_2)_3N$

No.	Acid	pK_a	$-\Delta H_{DMSO}$ (kcal mol^{-1})	t(°C)	ΔE_1 (kcal mol^{-1})
1.	$(CF_3)_3COH$	5.5	11.8	<-180	
2.	$(CH_3)_3CCOOH$	5.1	9.6	<-180	
3.	CH_3NHNO_2	5.1	7.0	-145	2.2
4.	C_6H_5SH	6.2	5.2	-115	3.4
5.	$(CF_3)_2CHNO$	5.3	4.4	-55	4.7
6.	$CH_3CH(NO_2)_2$	5.1	2.2	$+42$	7.9
7.	$(CF_3)_2CHCOOCH_3$	6.2	<1	$+70$	10

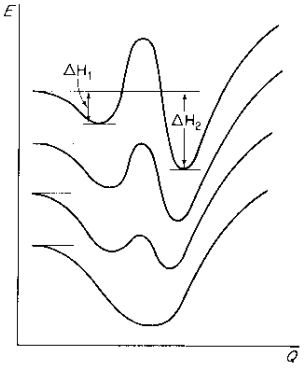


Figure 2.10 The possible evolution of a reaction path profile for proton transfer with an increase of the hydrogen bonding energy, ΔH_1

2.4 Proton Exchange in Hydrogen-Bonded Systems

In systems containing molecules with AH and BH groups capable of hydrogen bond formation as proton donors and proton acceptors, proton exchange takes place in hydrogen-bonded complexes. Therefore, some useful information about the processes of forming and breaking of these complexes, and the proton transfer processes in them, can be expected from a study of the proton exchange kinetics. It should be noted that here, as in previous sections, special attention is paid to proton exchange between molecules in inert media, where it is possible to exclude, or at least to minimize, all other reaction paths except the proton exchange in the hydrogen-bonded complexes.

The information available on the kinetics of proton exchange processes embraces practically all classes of molecules capable of forming hydrogen bonds. The following methods are often used for the investigation of proton exchange: chemical methods and optical spectroscopy for the study of labelled compounds, NMR spectroscopy; some work has been carried out using ESR (Prokofiev *et al.*, 1974). For an investigation of proton exchange under the conditions mentioned above, kinetic IR spectroscopy (Denisov *et al.*, 1968) is very convenient. Combined with the stopped-flow method (Bureiko and Denisov, 1974) it permits investigation of proton exchange in

solutions (see Figure 2.11) with a half-exchange period as little as a few milliseconds.

In spite of the broad variety of physical and chemical properties of the molecules studied, and the wide range of characteristic times of proton exchange (from some milliseconds to several hours), one may conclude from the available experimental data that the ability of a molecule to form a hydrogen bond determines the kinetic characteristics of proton exchange with its participation. Tables 2.5 and 2.6 list some values of rate constants, k, and activation energies, ΔE.

In comparing different classes of compounds, it will be obvious that the exchange of the proton of the thiohydrylic group of thiols with all the partners studied is accomplished much more slowly than exchange of the proton of the hydroxylic group of similar alcohols. The ability of the SH group to form hydrogen bonds as a proton donor and a proton acceptor is considerably lower than that of the hydroxylic group. Since the acidity of thiols is greater than that of alcohols, one may conclude that, in this case, the proton exchange rate is determined by the ability of the molecule to form hydrogen bonds rather than by its acidic properties.

Supposing (see section 2.1) that proton exchange takes place in intermediate cyclic complexes, of the type, R—A$\diagdown\!\!\diagup^{\mathbf{H}}_{\mathbf{H}}$B—R′, then the kinetics of the process must depend on the strengths of both AH $\cdots$ B and BH $\cdots$ A bonds, i.e. on the proton donor and proton acceptor abilities of

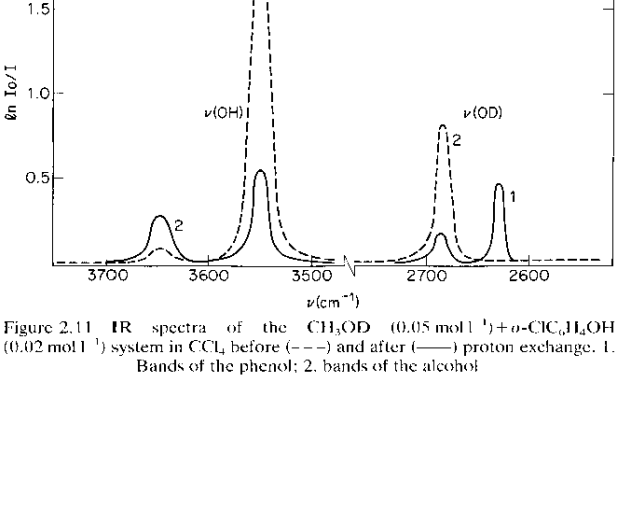


Figure 2.11 IR spectra of the CH_3OD (0.05 mol l^{-1}) + o-ClC_6H_4OH (0.02 mol l^{-1}) system in CCl_4 before (– – –) and after (——) proton exchange. 1. Bands of the phenol; 2. bands of the alcohol

Table 2.5 Kinetic parameters of proton exchange processes in CCl_4 solutions obtained by kinetic IR spectroscopy*

No.	System	k**(l mol^{-1} s^{-1})	ΔE(kcal mol^{-1})
	I. Carboxylic acid–ethanol		
1.	CF_3COOH	4.8×10^{4}	4.2
2.	CCl_3COOH	3.6×10^{4}	4.8
3.	$CHCl_2COOH$	2.4×10^{4}	3.4
4.	$CH_2ClCOOH$	6.8×10^{3}	4.3
5.	CH_3COOH	3.5×10^{3}	4.5
6.	$HCOOH$	1.3×10^{3}	5.0
7.	$(CH_3)_3CCOOH$	1.0×10^{3}	5.7
	II. Phenol–methanol		
8.	4-ClC_6H_4OH	320	2.0
9.	C_6H_5OH	240	2.1
10.	2-ClC_6H_4OH	65	3.3
11.	2,4,6-$Cl_3C_6H_2OH$	37	3.1
	III. Alcohol–water		
12.	CD_3OH	270	1.7
13.	C_2H_5OH	240	1.9
	IV. Secondary amine–ethanol		
14.	$C_6H_5NHCH_3$	240	1.8
15.	$(C_2H_5)_2NH$	150	1.5
16.	(iso-$C_4H_9)_2NH$	80	3.1
	V. Carboxylic acid–isobutanethiol		
17.	iso-C_3H_7COOH	2.1	13.0
	VI. Phenol–butanethiol		
18.	4-$NO_2C_6H_4OH$	0.21	3.0
19.	4-ClC_6H_4OH	0.13	4.2
20.	C_6H_5OH	0.10	4.5
21.	4-$CH_3C_6H_4OH$	0.023	5.0
	VII. Alcohol–butanethiol		
22.	CF_3CH_2OH	3.0×10^{-2}	—
23.	CH_3OH	7.0×10^{-2}	3.0
24.	C_2H_5OH	2.2×10^{-2}	5.0
25.	iso-C_3H_7OH	0.9×10^{-2}	5.5
26.	t-C_4H_9OH	0.4×10^{-2}	5.0
	VIII. Amine–t-butanethiol		
27.	$C_6H_5NHCH_3$	0.1	8.0
28.	$C_6H_5NHC_2H_5$	0.08	8.0
29.	$(C_6H_5)_2NH$	0.1×10^{-2}	6.0
30.	$(C_2H_5)_2NH$	1.1×10^{-2}	6.0
31.	$(C_3H_7)_2NH$	0.8×10^{-2}	8.0
32.	(iso-$C_4H_9)_2NH$	0.4×10^{-2}	8.0

Table 2.5 (*Continued*)

No.	System	k**(l mol^{-1} s^{-1})	ΔE(kcal mol^{-1})
	IX. Heterocyclic amine–methanol		
33.	Pyrrole	1.2×10^{-4}	8.0
34.	Indole	4.5×10^{-4}	11.0
35.	Carbazole	0.3	14.0

* R.m.s. deviations in Tables 2.5 and 2.6 are 5–20%.
** At 20 °C.

each molecule. Experimental data have shown (Table 2.5) that the maximum values of the rate constants of the proton exchange with alcohols, or thiols, were found for carboxylic acids (Denisov and Smolyansky, 1968, Bureiko and Lange, 1978). The reaction becomes slower for phenol derivatives (Bureiko *et al.*, 1972), still slower when water (Bureiko *et al.*, 1977a) or alcohols are used, and is further retarded for secondary amines (Bureiko *et al.*, 1971; Bureiko and Denisov, 1973a). In C_6H_6, the proton exchange rate of $(C_3H_7)_2PH$ with methanol ($k = 0.01$ l mol^{-1} s^{-1}) is greater than the k value for the $(C_3H_7)_2PH+(C_2H_5)_2NH$ system (Ryltsev *et al.*, 1980). As a rule, the sequence of decreasing proton donor ability in a series of compounds is the same. A similar dependence has been obtained for the gas phase by Denisov and Tokhadze (1972) and Bureiko and Denisov (1973b).

The same regularity is observed in studying the influence of proton donor ability on the rate of proton exchange in a series of compounds of one class. As a rule, an increase in the proton donor ability of the AH group in such a series results in an increase of k. This means that the influence of the growth of proton donor ability on the exchange kinetics is greater than the simultaneous decrease of proton acceptor ability. In a series of RAH molecules,

Table 2.6 Solvent effect on the proton exchange rate involving the participation of methanol (obtained by ^{1}H NMR spectroscopy)

No.	Solvent	ε_{solv}	k*(l mol^{-1} s^{-1})	
			$(CH_3)_3COH$	CH_3COOH
1.	C_6H_{12}	2.02	900	
2.	CCl_4	2.28	850	4.8×10^3
3.	C_6H_6	2.28	480	
4.	$CHCl_3$	4.70	420	
5.	C_6H_5Cl	5.62	80	1.1×10^4
6.	CH_2Cl_2	8.90	150	6.5×10^4
7.	$C_6H_4Cl_2$	9.93	120	9.0×10^4

* At 27 °C.

the proton donor and proton acceptor abilities are changed in different directions by varitaion of the substituent, R. Therefore, in cyclic complexes formed by the BH molecule with a number of partners, RAH, an increase in the strength of one hydrogen bond will be accompanied by a decrease in the strength of the other. At the same time, the total energy of the complex, determining the depth of the potential well (Figure 2.2), does not change in the series as obviously as the energy of each of the two bonds.

The dominating influence of the proton donor ability on the rate of proton exchange is not yet fully understood. There are deviations from this experimental dependence, for example, the rate constant for proton exchange in the trifluoroethanol–butanethiol system (Table 2.5) is less than that for methanol-butanethiol, although the proton donor ability of CF_3CH_2OH is considerably greater than that of CH_3OH since it contains electronegative substituents. A decrease in k is also observed, on the transfer from *N*-alkylanilines to $(C_6H_5)_2NH$, a still stronger proton donor (Table 2.5). These facts may be considered as an indication of the influence of decrease in proton acceptor ability of the A atom in the AH group, and of the cyclic structure of proton exchange intermediates. It should be noted that, contrary to alcohols and aliphatic amines, an increase of the proton donor ability of diphenylamine and *N*-alkylanilines is brought about not by the inductive effect, but by conjugation of an electron lone pair of the N atom with the ring π electrons. This conjugation, and that in amide molecules also, is responsible for the decrease of the proton acceptor ability of the N atom, which, in the case of heterocyclic amines (systems IX, Table 2.5), results in a decrease of the exchange rate and even in a change of mechanism for the process (Belozerskaya *et al.*, 1970).

In the proton exchange of phenol derivatives with methanol (9–11 in Table 2.5), the reaction was retarded as proton donor ability of the molecule increased. This series of molecules is of interest also for studying the influence of intramolecular hydrogen bonding (in 2-chlorophenol and 2,4,6-trichlorophenol) on the rate of the process. The results of Forsen and Hoffman (1963) and Bureiko *et al.* (1975) testify to the fact that formation of an intramolecular hydrogen bond by the AH group proton is accompanied by a considerable decrease in the rate of proton exchange.

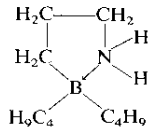
The experimental data available confirm the conclusion that the rate of the molecular proton exchange processes of the type considered is determined by the same peculiarities of electronic structure which control the hydrogen bonding ability of the functional groups of the molecules (Bureiko *et al.*, 1976, 1977b).

The value of another kinetic parameter of proton exchange process, i.e. the activation energy, ΔE, is not as sensitive as the k values to a change in molecular structure. ΔE for various classes of molecules ranges from 1.5 to 14 kcal mol^{-1}, but in most cases, for molecules of one class, the activation

energy varies only slightly. Most surprising is the fact that ΔE values are so small compared to the energy of breaking bonds. However, nothing can be said so far about the influence of the electronic structure of the molecules on the $\Delta E^{\neq}$ value, i.e. the barrier height measured from the bottom of the potential well (Figure 2.2). This value might be found experimentally through direct measurement of the cyclic complex concentration, and this may be looked upon as one of the most interesting problems to be studied in the future.

The importance of hydrogen bonding in proton exchange kinetics is supported also by a study of the influence, on the kinetics of the process, of solvents capable of forming hydrogen bonded complexes with the molecules concerned. The addition of proton acceptor compounds (acetone, DMSO, THF, dioxane) to inert solvents results in a decrease in the proton exchange rate (Tewari and Li, 1970; Denisov and Semenova, 1972). This has been discussed by Denisov and Tokhadze (1975) in terms of the dynamic characteristics of hydrogen bonding (see section 2.1). The influence of hydrogen bonding is seen clearly by comparing the results of a proton exchange study in alcohol–water systems in dilute CCl_4 solutions (Bureiko *et al.*, (1977a), and in binary mixtures (e.g. Paterson and Spedding, 1963; Tewari and Li, 1970). In the latter case, the k values are smaller by two orders of magnitude, while ΔE is markedly higher than in the case of proton exchange, at component concentrations of 10^{-2}–10^{-3} mol l^{-1}. This can be attributed to the effect of a network of hydrogen bonds in the binary mixtures hampering the formation of cyclic complexes between alcohol and water molecules.

In investigating the role of hydrogen bonding in proton exchange processes, consideration of the reaction mechanism and its limiting stage are extremely important. The data above are consistent with the supposition that the first stage involves proton transfer in the cyclic intermediate. For such a complex to form, the A atom and the B atoms must have lone pairs of electrons. The NMR investigation of amine–dinitroethane systems has shown that proton transfer in them is rapid, while the rate of proton exchange is very low. This fact is naturally related to the electronic structure of a carbon acid molecule. We have obtained another remarkable result in studying proton exchange involving the (3-aminopropyl)dibutylborane molecule, by means of kinetic IR spectroscopy. This molecule possesses a proton donor ability comparable with that of aliphatic alcohols (Iogansen *et*



al., 1971), but, on account of the lone pair of the N atom involved in coordination to the boron atom, it loses its proton acceptor function completely. While the k values for alcohol–alcohol and alcohol–amine systems in CCl_4 are of the order of 100–400 l mol^{-1} s^{-1}, the rate constants for proton exchange between aminoborane and methanol, or secondary amines, in the same solvent are 3–4 orders of magnitude lower. Such a result points to a cyclic rather than linear structure for the intermediate.

Experimental measurements of the order of reaction with respect to each component a supposition as to the number of molecules involved in the first stage of the process to be made. In all cases of proton exchange in solution, the reaction order is close to unity. Hence, the process can be seen as bimolecular, i.e. the first step of proton exchange takes place in the cyclic complex formed by two hydrogen bonded molecules. That the reaction proceeds in the cyclic bimolecular intermediates has been accepted by Huyskens and Zeegers-Huyskens (1961) and Limbach (1977), also.

What can be said as to the mechanism of such a process? An assumption of synchronous transfer of two protons in the cyclic complex was made by Brodsky (1949). The mechanism of such cooperative process may be represented by the scheme:

$$AH + BH^* \rightleftharpoons A\begin{matrix}H\\ \cdots\\ H^*\end{matrix}B \rightleftharpoons A\begin{matrix}H\\ \cdots\\ H^*\end{matrix}B \rightleftharpoons AH^* + BH \qquad (2.15)$$

In solutions, other reaction mechanisms via binary complexes are possible (Grunwald and Meiboom, 1963). An alternative mechanism is a sequential transfer of two protons in a linear complex, where the intermediate has the form of a cyclic ionic pair with two equal hydrogen bonds:

$$AH + BH^* \rightleftharpoons AH \cdots BH^* \rightleftharpoons$$

$$A\begin{matrix}H\\ \cdots\\ H^*\end{matrix}B^+ \rightleftharpoons AH^* \cdots BH \rightleftharpoons AH^* + BH \qquad (2.16)$$

Such a process would not involve the stage of breaking of the ionic pair (i.e. the electrolytic dissociation) and, therefore, could go on in an inert medium (section 2.3). Investigation of the possible proton exchange mechanisms is a promising field.

A study of the influence of the dielectric permeability of a solvent on the proton exchange rate may be a help in choosing between mechanisms (2.15) and (2.16). The results reported by Bureiko *et al.* (1979) indicate that, as ε_{solv} increases, the rate of proton exchange in alcohol–alcohol system decreases, while, for alcohol–acetic acid system, the proton exchange rate

rises considerably (Table 2.6). The authors explain this dependence by the cooperative mechanism (2.15) in the former case, and by the ion-pair mechanism (2.16) in the latter. On formation of the transitional state of mechanism (2.16), a great increase of the dipole moment, as compared to the initial state, must follow. Therefore, when ε is increased, the rate of proton exchange must be also increased. However, on formation of the transitional state of the cooperative mechanism, which resembles in structure the symmetrical cyclic complex, the dipole moment decreases, and this would result in the opposite effect. This very dependence has been observed experimentally.

Speaking of intermediate cyclic structures, it should be clearly understood that the cyclic model of the binary complex, formed by two non-linear hydrogen bonds, is less expedient than the linear structures, in terms of energy and entropy. Although, so far there is no direct experimental evidence to support the existence of four-membered cyclic hydrogen-bonded dimers, still the results of quantum mechanical calculations (Kollman and Allen, 1972) show that, in some systems, such a complex does possess energy, considerably exceeding the thermal energy, and is stable under some variations of geometrical parameters.

Very few experimental investigations of proton exchange processes have been carried out in the gas phase. The available data show that the reaction mechanism may be quite different for different systems, though the dependence of the rate of the process on the hydrogen-bonding abilities of the molecules seems to be the same. In all cases in solution, and for amines, alcohols, hydrogen halides, and phosphines (Ryltsev *et al.*, 1980) in the gas phase, proton exchange processes are bimolecular. In the homogeneous reaction of thiol a trimolecular reaction was observed with one thiol molecule and two molecules of the second component participating in the first step (Bureiko *et al.*, 1977b). The results obtained were interpreted by Denisov and Tokhadze (1972) who postulated a two-step reaction: (a) formation of a bimolecular hydrogen-bonded complex, and (b) proton transfer either in this complex activated by a third molecule, or in the trimolecular cyclic complex. In the condensed phase, the energy, ΔE, required for transition over the potential barrier, is obtained by the system from interaction with the solvent. Although such a two-step mechanism must occur in a solvent as well, it does not influence the kinetic characteristics because of almost continuous energy exchange of the complexes with the medium.

The problem of the limiting stage of proton exchange processes is still not clear. As seen from (2.15) and (2.16), the rate of the reaction may be determined by the time taken to form or break the intermediate, or by the time for proton transfer in this complex. So one can imagine that all the cases may be realized for different molecular systems under various conditions.

We know of only one system where breaking of the intermediate could be the determining stage of proton exchange: it is the proton exchange between carboxylic acid dimers forming strong eight-membered rings. In studying proton exchange of HCOOH, Denisov and Golubev (1977) concluded that the rate of the process was limited by the breaking of hydrogen bonds.

Large activation energies, ΔE, for proton exchange reactions involving thiol are not in accordance with the supposition that in this case the formation of hydrogen-bonded intermediates is the limiting stage, the activation energy of this process being very low (Tokhadze, 1975). The opinion was expressed (Denisov and Smolyansky, 1968) that the first step of cooperative proton transfer in the intermediate complex determines the kinetics of proton exchange in such systems. For proton exchange between alcohols, amines, water, which are probably also characterized by the cooperative mechanism, the rate constants, k, are considerably greater, while the activation energies, ΔE, are close to ΔE of the diffusion. By studying the kinetic isotope effect in a methanol–water system in CCl_4, Bureiko *et al.* (1977a) deduced that the proton exchange rate is determined by the stage of cyclic complex formation. This process may be very slow due to the extremely small value of the equilibrium constant. In this case, although the rate of the reaction is not determined by diffusion, the activation energy can, in fact, be determined by it. The problem of the limiting stage in different mechanisms of proton exchange processes is open to further investigation.

Summing up, one can say that we are still far from a full understanding of the nature of the proton exchange processes in hydrogen-bonded systems. There is little doubt that the ability of exchanging molecules to form hydrogen bonds influences the kinetic characteristics of the proton exchange. The evidence available testifies to a molecular mechanism via formation of cyclic intermediates (mostly, bimolecular ones) in an inert medium. The cooperative mechanism of proton transfer is the simplest model of the reaction. Its realization in a pure form is most probable in systems with symmetrical intermediates. If the hydrogen-bond forming abilities of component molecules differ greatly, then the step-like mechanism via formation of the hydrogen-bonded ion pair may be correct. In nature, a whole variety of intermediate reaction paths may exist for different molecular systems.

A better insight into the mechanism of proton exchange molecular processes may be obtained by a further spectroscopic study of the cyclic complexes, determination of their lifetimes, investigation of the dynamics of successive steps of the process by various physical and chemical methods and techniques, and by theoretical calculations of the potential surfaces of the interaction.

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