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LOCALIZATION AND MOVING OF A PROTON INSIDE HYDROGEN-BONDED COMPLEXES IN APROTIC SOLVENTS

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ABSTRACT

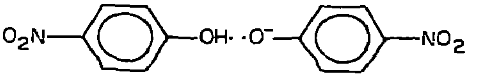
The results of the study of a number of molecular and ionic H-bonded complexes in freon solutions by ^{1}H NMR at 100—150 K are reported. It is shown that under these conditions the signals of OH(NH) protons belonging to various complexes, self-associates and free molecules are observed separately. The spin—spin coupling of the signals is frequently discernible. The fine structure makes it possible to distinguish between complexes with fast proton migration between two wells on the potential surface and those with the proton localized in one well (in particular, the central one). Several complexes with slow (in the NMR scale) proton migration have also been found.

The results of the study of the non-catalytic proton exchange kinetics between various molecules containing OH and NH groups in dilute solutions in aprotic solvents are considered. The exchange between the RCOOH and ROH molecules goes on via the intermediate formation of a cyclic ionic pair with two equivalent H-bonds even in non-polar solvents such as cyclohexane. For exchange between two RCOOH or ROH molecules a synchronous transfer of two protons in a cyclic molecular complex is likely.

INTRODUCTION

The interaction between strong proton donor and proton acceptor molecules in aprotic solvents is known to result in the formation of many kinds of complexes. They may be of more or less ionic character, may be simple ($AH\cdots B$, $A^-\cdots HB^+$) or complicated ($AH\cdots AH\cdots B$, $AHA^-\cdots HB^+$, BHB^+A^-), and involve one or more H-bonds. The shape of the potential energy surface, determining the distribution function of the proton in a hydrogen bridge, represents one of the most fundamental questions of hydrogen bonding. It has been ascertained experimentally that in most of the complexes examined the proton is localized in the only potential well situated in the coordinate region, corresponding to a typical molecular ($AH\cdots B$), or a typical ionic ($A^-\cdots HB^+$) complex. A large group of "tautomeric" complexes with the proton migrating between two wells on the potential surface (the equilibrium $AH\cdots B \rightleftharpoons A^-\cdots HB^+$) is also known [1—5]. In the case of asymmetrical complexes this tautomerism usually has pronounced manifestations in vibrational and electronic spectra. As both wells have comparable populations, two groups of bands are observed in the spectra, their relative intensities varying with equilibrium shift, which may be temperature dependent.

Some complicated complexes with "homoconjugated" ions, such as $[AHA]^-$ and $[BHB]^+$, are postulated to involve the proton localized in the potential well with a minimum corresponding to the central position of the proton. In this instance we prefer the term "central H-bond" to the conventional but ambiguous "symmetrical H-bond"; the latter has been used in different meanings by some authors. The existence of uncharged asymmetrical complexes $A^{\delta-}\cdots H\cdots B^{\delta+}$ is not impossible. These would have a structure intermediate between the molecular and the ionic, where the H-bond is similar to the central form. Distinguishing between the two alternatives, i.e. a symmetrical complex with proton migration, $AH\cdots A \rightleftharpoons A\cdots HA$, and a complex with a central H-bond $A\cdots H\cdots A$, is a very complicated problem and can very rarely be done unequivocally. Thus, in UV-spectra of the symmetrical complex



two distinct bands occur, one of them belonging to a transition in the phenol aromatic ring and the other to the similar transition in the phenolate ring [6]. In most cases the choice between the two alternatives is made on the basis of indirect evidence. Thus, a low frequency proton stretching vibration ν_H(600—1500 cm^{-1}) and a normal value of ν_H/ν_D of ca. 1.4 are believed to be the distinguishing features of the central H-bond [7—9]. Complexes with proton migration, following [10], should have anomalously low values of ν_H/ν_D, near unity, which seems to be ruled out by experiment (see, e.g. ref. 11). However, the use of the one-dimensional model, where energy is regarded as being determined by only one coordinate of the proton suggests that the conclusions of ref. 10 be treated with reserve. Thus, it has been shown [12], that taking into account the interaction of the stretching proton vibration with a low-frequency stretching vibration of the H-bond, the anomalous isotope effect can be explained satisfactorily without recourse to the double-well potential model. Calculations by means of non-empirical techniques of quantum chemistry have so far failed fully to solve the problem. Indeed, such calculations may be performed only for isolated complexes, while all the experimental data available hold for solutions and solids. However, it has been shown that even transfer from a non-polar solvent, such as CCl_4, to the gaseous phase can result in a qualitative change of the type of a complex [13, 14].

Thus, additional spectral data for complexes with proton migration and a central H-bond are needed. Still more complicated is identification of complexes with two minima on the potential surface, if the population of the second well is negligibly small. This is of special importance for tautomeric uncharged complexes, $AH\cdots B \rightleftharpoons A^-\cdots HB^+$. In this instance the wells would be of comparable population only if the ionic form was energetically preferable. An ionic pair, having a high dipole moment (ca. 10 D) would interact with the molecules of a solvent and make proton transfer possible causing a considerable increase in entropy (20—30 cal mol^{-1} deg^{-1} [15]). Taking the least value, in the case of two wells of equal depth, an estimate can be made for the relative population of the ionic well, exp $\Delta S/R \approx 10^{-3}$—$10^{-4}$. It is rather difficult to detect a tautomer in such a small quantity. In this connection, the results of the kinetic investigations of non-catalytic proton exchange between molecules capable of H-bonding are of interest. The probability of catalytic processes can be minimized by employing dilute solutions in pure inert solvents, where the electrolytic dissociation would not take place.

In the present paper an approach is developed which can give information concerning proton localization in H-bonding. This approach is based on the treatment of the spin—spin structure of an NMR proton signal which can be observed at low temperature. A number of experimental data on the kinetics of fast proton exchange between OH- and NH-containing molecules are considered with a view to establishing the possible involvement of H-bonded ionic pairs as disadvantageous in terms of energy.

RESULTS AND DISCUSSION

Study of proton migration inside H-bonded complexes by ^1H NMR at low temperature

Most spectroscopic papers on strong H-bonding and proton transfer have employed optical spectroscopy, the use of NMR being less common. As a rule, fast exchange processes average the signals of movable protons belonging to various complexes and free molecules, and deprive them of spin—spin structure. However, it has been demonstrated [15—19] that at 100—140 K the signals belonging to all the non-equivalent OH-groups can be observed separately. A mixture of CHF_2Cl and $CHFCl_2$, freezing at ca. 90 K, and of good solvent ability and low viscosity down to 100 K, seems to be about the only solvent convenient for this range. Line-widths of a complex in this solvent usually do not exceed 10 Hz at 100 K.

Figure 1 shows the spectra of solutions, containing $[(CH_3)_2N]_3PO$ and an excess of HCOOH at 120 K, where only the molecular complexes are present. At low total concentration, two signals belonging to the OH groups of the AH···B complex (δ = 14.6) and to the cyclic dimer of the acid (δ = 13.0) are seen. The signals are broadened by molecular exchange, having a marked speed at 120 K. At a total concentration about 0.6 mol l^{-1}, two more signals of the same intensity for any relative amount of the components appear. They can thus be attributed to a 2:1 complex, shown on Fig. 1. The low field signal is likely to be related to the proton connected with the P=O group, and the high field one to the proton connected with the carbonyl. As the OH···O=P signal of the 2:1 complex is shifted to lower field compared with the analogous signal of the 1:1 complex, it is reasonable to suppose that an H-bond becomes stronger on addition of a second acid molecule

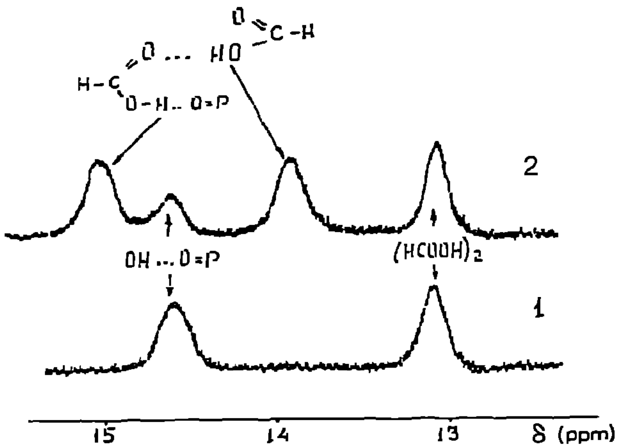


Fig. 1. The ^{1}H NMR spectra (60 MHz) of solutions containing $[(CH_3)_2N]_3PO$ and HCOOH in CDF_2Cl + $CDFCl_2$ at 120 K: 0.05 and 0.1 mol l^{-1} (1), 0.2 and 0.4 mol l^{-1} (2).

to the complex. Similarly, the OH···O=C bond in the 2:1 complex must be stronger than that in the cyclic dimer. It can be seen that NMR spectra at low temperature allow identification of all the complexes present and the measurement of the chemical shifts of various types of OH-protons.

The typical spectra of H-bonded ionic pairs, formed by trifluoroacetic acid with amines in the same solvent, are shown in Fig. 2. The spin—spin coupling of the signals with the ^{15}N nucleus shows that the complexes have an ionic structure. The single signal in the spectrum of the complex with $(CD_3)_2{}^{15}NH$ (2) does not, however, prove the two protons to be equivalent (as in I), as the possibility of fast exchange in II cannot be neglected. The fine structure of signals in the spectrum of complex with $CD_3{}^{15}NH_2$ (3) shows that the exchange must be very slow. The low-field multiplet is obviously to be attributed to the two H-bonded $^+$NH groups. The additional

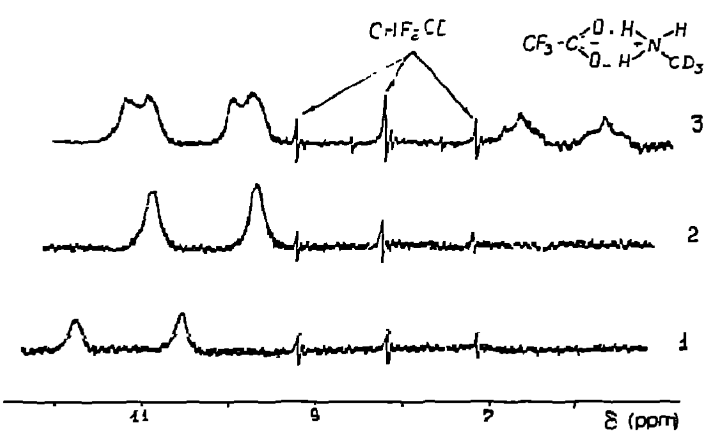
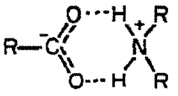


Fig. 2. The spectra of the solutions of the salts of CF_3COOH and $(CD_3)_3{}^{15}N$ (1), $(CD_3)_2{}^{15}NH$ (2) and $CD_3{}^{15}NH_2$ (3) in CDF_2Cl + $CDFCl_2$, 0.02 mol l^{-1}, (110 K).

splitting is accounted for by the spin—spin coupling with the "free" NH proton, the multiplet of the latter being observed at higher field. The spin—spin coupling and the relative intensities of the signals strongly support the cyclic structure I with equivalent hydrogen bonds



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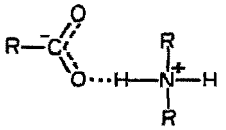
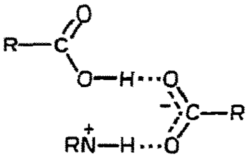


II

As will be seen, this is of importance in elucidating the mechanism of fast proton exchange between the molecules of carboxylic acids and alcohols in inert media.

In the presence of an excess of CF_3COOH, the low temperature spectra are of more complicated appearance. Figure 3 represents the spectra of solutions containing CF_3COOH and $(CD_3)_3{}^{15}N$ at 110 K. As the concentration of acid rises, the intensity of the doublet belonging to the 1:1 ionic pair decreases. A doublet at high field ($\delta = 7.7$) and a singlet at low field ($\delta = 18.5$) appear simultaneously. At a considerable excess of CF_3COOH, the signal $\delta = 12.8$, belonging to the cyclic dimer, is seen. The integral intensities of the doublet and the singlet being equal, they can be attributed to the $^+$NH and OH protons of the 2:1 ionic complex, respectively:



The OH···O H-bond must be very strong (probably, similar to the central bond), while the NH···O H-bond is weaker than that in the 1:1 ionic pair, the negative charge being distributed on four oxygen atoms.

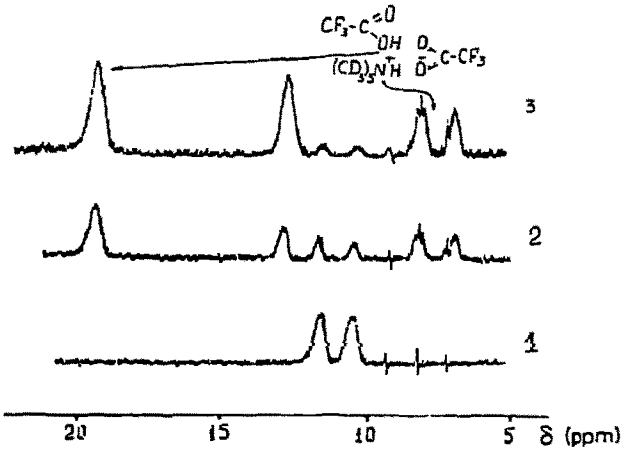


Fig. 3. The spectra of solutions containing $(CD_3)_3{}^{15}N$ and CF_3COOH at the concentrations: 0.03 and 0.02 mol l^{-1} (1); 0.02 and 0.04 mol l^{-1} (2); 0.02 and 0.06 mol l^{-1} (3) at 110 K.

Thus, the ^{1}H-NMR spectra at low temperature can provide valuable information as to the structure of molecular and ionic complexes.

The spectra of complexes with fast proton migration, $AH \cdots B$ (I) $\rightleftharpoons$ $A^- \cdots HB^+$ (II) can be easily treated if one of the A and B fragments, e.g. B, involves a nucleus of spin 1/2. Then, assume as a first approximation that H-bond formation does not alter the J_{BH} spin—spin coupling constant, $\Delta_{II} = J_{BH}$, where Δ_{II} is the observed coupling of the proton signal in the ionic form II. Similarly, in the same approximation, the spin—spin coupling cannot be transmitted through a H-bond: $\Delta_I = 0$.

Given the following conditions: (1) The lifetime of the complex is much greater than the value $(2\pi J_{BH})^{-1}$. (2) The lifetime of the proton inside the complex is much greater than the same value. (3) The average lifetimes of the I and II forms are much less than $(2\pi J_{BH})^{-1}$ and than the spin relaxation time T_2: $\tau_{I,II} \ll (2\pi J_{BH})^{-1} \ll T_2$. Then, the observed value of the coupling $\Delta = p_{II} J_{BH}$ (p_{II} is the population of state II).

In particular, in the case of a symmetrical complex with proton migration, $AH \cdots A \rightleftharpoons A \cdots HA$, the proton signal will be a triplet with $\Delta = 1/2\, J_{AH}$. Many experimental papers confirm the picture described in the cases of intramolecular proton migration [20, 21], where conditions (1) and (2) may be fulfilled at conventional temperature.

In the case of a complex with only one central (or close to the central) potential well, an interesting peculiarity may be observed. Since the spin—spin coupling between two A and H nuclei decreases strongly with increase of the internuclear distance A—H, a marked fall of the Δ value compared to J_{AH} is to be expected. Indeed, for the FHF^- ion the value Δ_{HF} was ca. $1/5\, J_{HF}$ [22]. Such a decrease in the spin—spin coupling value points to a considerable stretching of the A—H bond, and, therefore, indicates a central H-bond. Figure 4 represents the spectra of the solution containing CD_3COOH and an excess of $(CD_3)_3{}^{15}N$ (OH and NH signals on the left), or CD_3COOH and an excess of $(CH_3)_3{}^{14}N$ (CH_3 signals on the right). With a fall in temperature splitting of the signals of the CH_3 group into two occurs, the high field signal belonging to the molecules of free amine and the low field one to

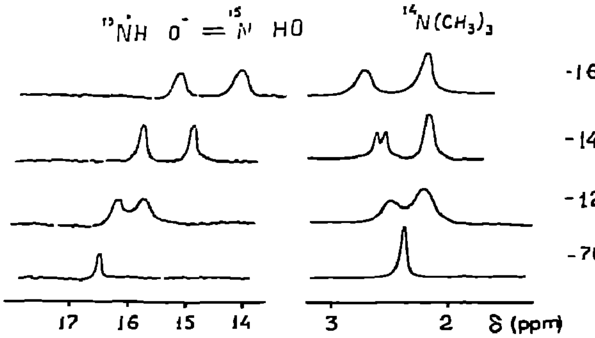


Fig. 4. The spectra of the solutions containing 0.05 mol l^{-1} CD_3COOH and 0.1 mol l^{-1} $(CD_3)_3{}^{15}N$ (on the left) or $(CH_3)_3{}^{14}N$ (on the right) in $CDF_2Cl + CDFCl_2$ at various temperatures.

the tautomeric complex [23]. The separation of the signals points to the slowing down of exchange processes; below 150 K the lifetime of the proton inside the complex is more than 0.5 s. In some temperature range the doublet structure of the CH_3 signal of the complex due to the spin—spin coupling with the movable proton should be seen. In the same range the spin—spin coupling of the signal of the movable proton with the ^{15}N nucleus occurs. As the temperature falls the $\Delta_{^{15}NH}$ value increases and tends to the value $J_{^{15}NH}$ characteristic of the ionic pair $(CD_3)_3{}^{15}NH^+ClO_4^-$ (75 Hz). Simultaneously, the shift of the averaged OH—^{15}NH proton to higher field is seen, since the chemical shift of the ^{15}N proton in the ionic pair is less than that of the OH proton in the molecular complex (this difference cannot be accounted for by a greater H-bond strength in the molecular complex, as the shielding of the proton in the "free" OH and ^{15}NH groups may differ considerably). The picture described can be interpreted only in terms of fast proton migration inside the complex.

Of special interest are the spectra of some complicated complexes with homoconjugated ions $(AHA)^-$ and $(BHB)^+$. Unfortunately, in most strong proton donors (phenols, carboxylic acids) the spin—spin coupling constants of OH proton with other nuclei are too small to be measured at low temperature, the phosphorus acids being an exception. Figure 5 (1) shows the OH signal of acid $(C_2H_5O)_2POOH$ involved in the molecular H-bonded complex $AH \cdots B$ with $(CH_3)_2SO$ at 110 K. The signal is a doublet, the value $J_{AH} = 24$ Hz being practically unchanged when either tetrahydrofuran or $(CH_3)_2NCHO$ are taken as acceptors. This value is probably close to J_{AH} in the free molecule of the acid, which is extremely difficult to estimate. Figure 5 (2) shows the same signal in a solution of pure $(C_2H_5O)_2POOH$ at low (ca. 10^{-3} mol l^{-1})

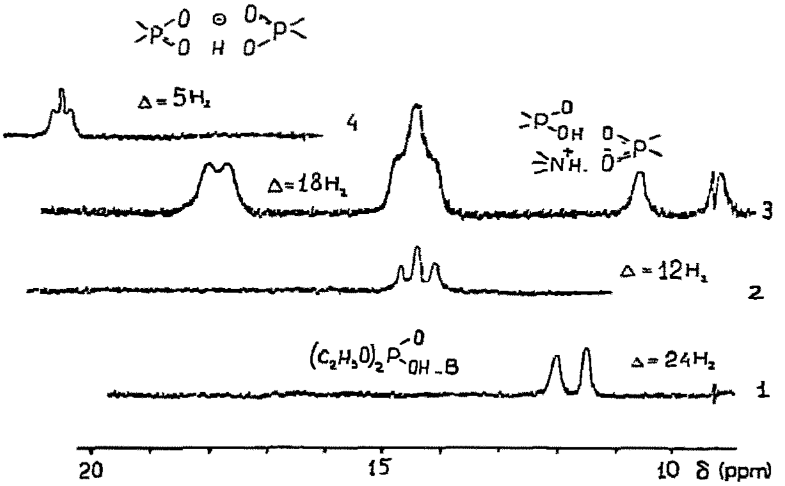
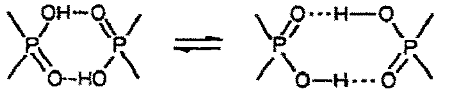


Fig. 5. The spectra of solutions in $CDF_2Cl + CDFCl_2$ (110 K) containing: (1) $(C_2H_5O)_2$-$POOH$ (0.005 mol l^{-1}) and $(CH_3)_2SO$ (0.05 mol l^{-1}); (2) $(C_2H_5O)_2POOH$ (0.002 mol l^{-1}); (3) $(C_2H_5O)_2POOH$ (0.02 mol l^{-1}) and $(CD_3)_3{}^{15}N$ (0.004 mol l^{-1}); (4) the salt $(C_2H_5O)_2$-$PO_2^-[N(C_4H_9)_4]^+$.

concentration at 110 K. Since it appears as a triplet with $\Delta = 12$ Hz, the acid must exist in solution as a cyclic dimer with fast migration of two protons



This dimer is very stable — in the IR spectrum no bands of free molecules can be found even at 10^{-3} mol l^{-1} and +80°C. Figure 5 (4) shows the spectrum of the homoconjugated ion, AHA^-, involved in an ionic pair with an almost spherical cation $(C_4H_9)_4N^+$. The occurrence of a triplet with a very small (5 Hz) value of Δ proves that there exists a central H-bond in the complex. Finally, Fig. 5 (3) shows the spectrum of a solution, containing $(CD_3)_3{}^{15}N$ and a great excess of the acid, all the molecules of amine being involved in the 2:1 ionic complex. In the spectrum the NH^+ group doublet ($\delta \cong 10$), and the triplet of the cyclic dimer ($\delta = 14.3$) are observed together with a low field doublet ($\delta = 17.7$), which can be attributed only to the OH proton of the 2:1 complex. The doublet character of the splitting and the high value of Δ (18 Hz) show the H-bond $OH\cdots O$ to be far from symmetrical. Thus, the second H-bond affects the anion and the disturbance causes the former to lose its central character.

Homoconjugated cations $(BHB)^+$ are usually formed if an anion is deprived of proton acceptor ability, i.e., for ionic pairs with very strong acids such as $HClO_4$. Figure 6 shows the spectrum of the 1:1 ionic complex of CF_3SO_2OH with $(CD_3)_3{}^{15}N$ at 110 K (1). With a great excess of amine the 1:2 complexes are formed (2). In this case the doublet of the NH^+ proton ($J_{BH} = 75$ Hz) is transformed into a triplet ($\Delta = 32$ Hz); thus, $\Delta \approx \frac{1}{2}J_{BH}$. This means that in accordance with [24] (but contrary to [25]) the potential surface of this homoconjugated cation includes two symmetrically situated wells, between which fast proton migration takes place.

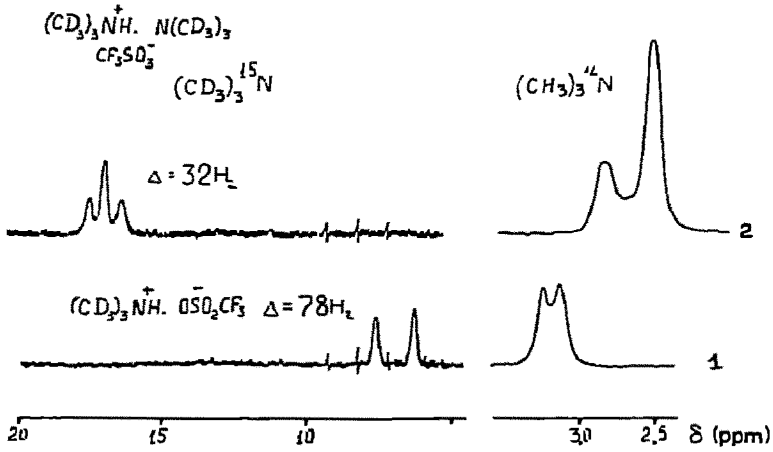


Fig. 6. The spectra of solutions in $CDF_2Cl + CDFCl_2$ (110 K) containing: (1) the salt $CF_3SO_2O^-[H^{15}N(CD_3)_3]^+$ (0.005 mol l^{-1}), (2) the same salt + $(CD_3)_3{}^{15}N$ (0.03 mol l^{-1}).

The kinetics of proton migration inside some H-bonded complexes

In the NMR spectra of tautomeric complexes with strong OH···N bonds the signals of the movable OH and NH^+ protons have never been observed separately, the proton migration being too fast even at 100 K ($\tau < 10^{-5}$ s). However, proton transfer in some complexes with weaker H-bonds, AH···N, is slower. The kinetics of proton transfer within complexes of a number of acids with triethylamine in CHF_2Cl have been studied [26, 27]. The acids were selected so as to display practically identical proton transfer ability (pK_a = 5—6) but wide variation in proton donor ability. Thus, the enthalpy of the complexes of these acids with $(CD_3)_2SO$ varies from 1 kcal mol^{-1} up to 9 kcal mol^{-1}. The complexes of these acids with triethylamine proved the molecular—ionic tautomerism, the enthalpy of ionic pairs varying within a narrow range (13—15 kcal mol^{-1}). This shows that the similar acidity of these acids is not a peculiarity of aqueous solutions only. The typical spectrum of a system with the molecular—ionic tautomerism (thiophenol—triethylamine in CHF_2Cl) is represented in Fig. 7. As the temperature falls, the α-methylene proton signal of amine is shifted to lower field and then splits into two signals; the low field one belongs to the tautomeric complex, its chemical shift being changed with the shift of the equilibrium. Simultaneously the movable $SH\cdots N \rightleftharpoons S^-\cdots HN^+$ proton signal is split into those belonging to molecular and ionic complexes. The shape and relative intensities of these signals do not depend upon concentration and are determined only by the frequency of proton migration and the equilibrium position. The line shapes may be used to obtain the lifetimes of the complexes and the kinetic characteristics of the proton migration. The spectra of all the systems, have a similar appearance, but the splitting occurs at various temperatures. In Table 1 the temperature values are given for a mono-molecular rate constant of proton transfer inside a complex of ca. 10^3 s^{-1}. There is a

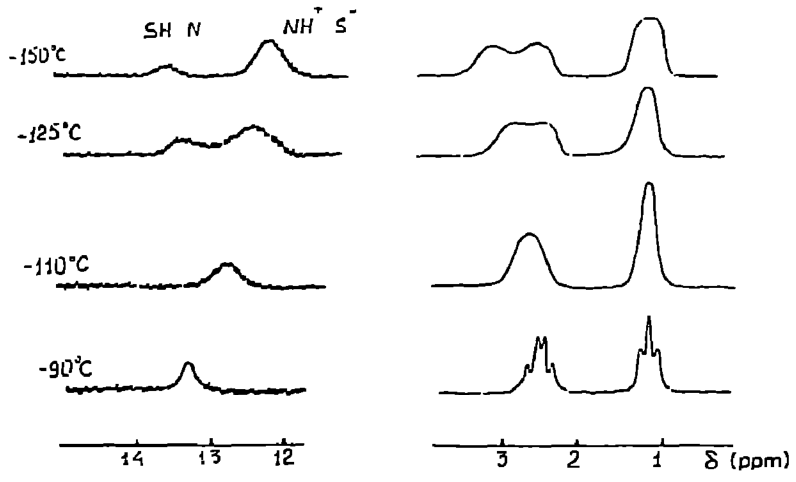


Fig. 7. The spectra of the solution containing C_6H_5SH (0.05 mol l^{-1}) and $(C_2H_5)_3N$ (0.1 mol l^{-1}) in CHF_2Cl at various temperatures.

TABLE 1

The enthalpy values of H-bonded complexes of acids with $(CD_3)_2SO$ and the kinetic characteristics of proton transfer inside the complex of acids with $(C_2H_5)_3N$

Acid	pK_a	ΔH_{DMSO} (kcal mol^{-1})	T (°C)	$E^{\neq}$ (kcal mol^{-1})
$(CH_3)_3CCOOH$	5.1	9.6	<-180	—
CH_3NHNO_2	5.1	7.0	-145	2.2
C_6H_5SH	6.2	5.2	-115	3.4
$(CF_3)_2CHNO_2$	5.3	4.4	-55	4.7
$CH_3CH(NO_2)_2$	5.1	2.2	$+42$	7.9
$(CF_3)_2CHCOOCH_3$	6.2	~ 1	$>+70$	>10

slow decrease of the proton donor ability of an acid with increase of temperature. In the same range an increase in activation energy is observed. Thus, the proton donor ability of an acid, while not influencing its proton transfer ability, determines the proton transfer kinetics. This result seems not to be trivial, explaining the uncommon kinetic properties of CH-acids, which can usually form only very weak hydrogen bonds.

For a long time it has been known that "active" solvents, such as alcohols, strongly affect the rates of proton transfer from CH-acids. The interaction between 1,1-dinitroethane and trioctylamine in various solvents has been studied [28]. In Table 2 the enthalpy values of the molecular and ionic complexes are given, as well as the kinetic characteristics of proton transfer inside the complex. With increasing solvent dielectric constant, decrease of molecular complex enthalpy and increase of ionic pair enthalpy are observed. In methanol no molecular complexes were found. Thus there is no marked change of the kinetic characteristics of the mono-molecular process with different solvents. However. the rate of the bimolecular process of proton transfer from an acid to a base decreases strongly in this range. This indicates that the influence of a solvent may be explained by the change of transfer inside the complex being unaffected.

TABLE 2

The thermodynamic and kinetic characteristics of the complexes of 1,1-dinitroethane with trioctylamine in various solvents

Solvent	ϵ	ΔH_{MC} (kcal mol^{-1})	ΔH_{IP} (kcal mol^{-1})	k_H^{298} (s^{-1})	k_D^{298} (s^{-1})	$E^{\neq}$ (kcal mol^{-1})
C_6D_{12}	1.8	4.8	11.3	27	11	7.4
CCl_4	2.2	4.5	11.5	25	9	7.4
$CDCl_3$	4.8	3.0	12.0	19	7	7.9
CD_2Cl_2	9.0	3.0	12.7	20	16	7.6
CD_3CN	37.5	2.2	13.0	13	5	8.0

$$\mathrm{XH} + \mathrm{Y} \overset{K}{\rightleftharpoons} \mathrm{XH\cdots Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X\cdots HY}$$

fast slowly

$k + Kk_{-1}$, where k is the bimolecular rate constant.

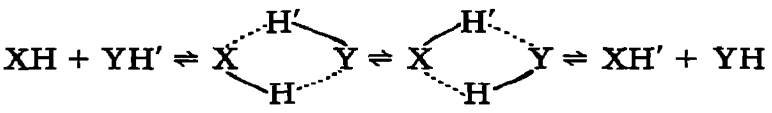
The fast proton exchange in inert media

The process of proton exchange in "inert" media (such as cyclohexane, CCl_4, and a gaseous phase) is considerably different from that in "active" media (binary mixtures, concentrated solutions, solutions in protic solvents). In active media it is, as a rule, an ionic process, where an acid—base catalysis and electrolytic dissociation play an important part. A typical example of proton exchange catalysed by a base B is the following

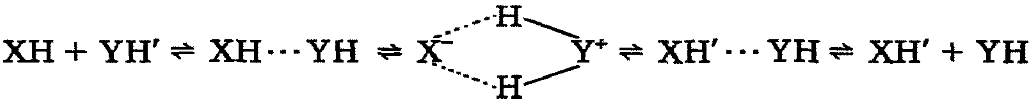
$$\mathrm{XH} + \mathrm{B} \rightleftharpoons \mathrm{X}^-_{\mathrm{sol}} + \mathrm{HB}^+_{\mathrm{sol}} \overset{\mathrm{ROH'}}{\rightleftharpoons} \mathrm{XH'}$$

In this case there is, in fact, no exchange between different molecules, but between a molecule and a medium. As for inert media, one can study the exchange between individual molecules, e.g. in hydrogen-bonded complexes. It is clear that molecular self-association can disturb this process considerably. The difference between the mechanisms may be illustrated by the case of proton exchange between alcohol and water [29, 30]. In CCl_4 solutions this is a molecular non-catalytic process (which may be proved by its independence of the presence of admixtures). In the binary alcohol—water mixture the molecular mechanism has a low probability, since it requires two molecules to be released from the net of hydrogen bonds. Therefore, in the mixture, thoroughly purified from acidic and basic impurities, proton exchange has a rate at least three orders of magnitude less than in CCl_4. Exchange catalysed by an acid or a base will not be considered here.

As originally noted by Brodsky [31], the ability of an XH group to participate in the fast proton exchange is determined, first of all, by having lone pairs. Indeed, the exchange between CH— or SiH— groups without lone pairs is usually slow and requires rather high values of activation energy and the presence of a catalyst. The exchange between OH— or NH— groups is very rapid and needs practically no activation energy. It was supposed that in this case synchronous ("cooperative") transfer of several protons occurs inside a hydrogen-bonded cyclic complex, i.e.



or inside a complex of more complicated structure, e.g. including three molecules. The advantage of such a mechanism is that it does not require considerable activation energy. However, the process of cyclic complex formation is less favorable than that of the linear complex, from the point of view of energy or entropy and only a very small amount of such complexes may be present in solution. It is evident that the stability of a cyclic complex is determined by both the proton donor and proton acceptor ability of the molecule. If two groups with lone pairs have markedly different proton donor and proton acceptor abilities, the formation of the cyclic complex may prove too unfavorable. Then, the mechanism involving the successive transfer of two protons in a linear complex will be favored, a cyclic ionic pair with two equivalent hydrogen bonds being formed as an intermediate of the reaction



$$XH + YH' \rightleftharpoons XH\cdots YH \rightleftharpoons X^{-}\begin{matrix}\cdots H \diagdown \\ \cdots H \diagup\end{matrix}Y^{+} \rightleftharpoons XH'\cdots YH \rightleftharpoons XH' + YH$$

As shown above, such ionic pairs are formed, e.g. on the interaction between the molecules of carboxylic acids and secondary amines. This process differs considerably from the ionic one, as it does not involve the breaking of an ionic pair (electrolytic dissociation), and, therefore, is able to take place in inert media (proton transfer with ionic pair formation has been found even in cyclohexane solution). For the cyclic ionic pair to be formed the presence of lone pairs is also required. When studying proton exchange in inert media some experimental criteria are necessary for the true mechanism to be chosen in a particular case. The transitional state of the "ionic pair" mechanism must have a large dipole moment, while the transitional state of the "synchronous" mechanism must have a dipole moment less than that of the linear complex $XH\cdots YH'$. In particular, in the case of homomolecular proton exchange the dipole moment is equal to zero. Therefore the exchange having an ionic pair mechanism would be accelerated by (1) transfer from the gaseous phase to a solution; (2) increase of the dielectric constant of the solvent; (3) imposing a strong external electric field. The synchronous proton transfer however, is bound to slow down under these conditions.

The influence of dielectric permeability on proton exchange between the CD_3OH and $(CH_3)_3COH$ molecules, on the one hand and between CD_3OH and CH_3COOH molecules, on the other hand, was examined by dynamic NMR [32]. Solvents unable to form H-bonds of any considerable energy, i.e. hydrocarbons and their halogen derivatives, were chosen. The process was found to be first order with respect to both components, $V = k\,[XH]\cdot[YH]$, which shows that the elementary act proceeds in a complex of composition 1:1. The kinetic parameters of the exchange are given in Table 3. With increasing ϵ of the solvent, the rate of the exchange between two alcohol molecules decreases, while the rate of the exchange between the molecules of CD_3OH and CH_3COOH is increased. Taking CH_2Cl_2 in place of CCl_4, the activation energy of the exchange between CD_3OH and $(CH_3)_3COH$ is essentially unchanged, probably owing to the temperature coefficient of the diffusion. The activation energy of the exchange between CD_3OH and CH_3COOH, which is markedly higher than that of the diffusion in CCl_4,

TABLE 3

Solvent effects on proton exchange with the participation of methanol

Solvent	ϵ_{solv}	$(CH_3)_3COH$		CH_3COOH	
		k (l mol^{-1} s^{-1})	$E^{\neq}$ (kcal mol^{-1})	k (l mol^{-1} s^{-1})	$E^{\neq}$ (kcal mol^{-1})
C_6H_{12}	2.0	960	—	—	—
CCl_4	2.3	850	1.8	4800	5.6
C_6H_6	2.3	480	—	—	—
$CHCl_3$	4.7	420	—	—	—
C_6H_5Cl	5.6	80	—	11000	—
CH_2Cl_2	8.9	150	2.1	65000	2.2
$C_6H_4Cl_2$	9.9	120	—	90000	—

is 2.5 times lower in the more polar CH_2Cl_2, suggesting a different exchange mechanism in these two cases. It is supposed that the transitional state of the exchange between two alcohol molecules is a cyclic molecular complex with a low dipole moment, while that of the CD_3OH—CH_3COOH exchange is close to an ionic pair. To confirm this, the influence of a strong electric field on the proton exchange rate between CD_3OH and CH_3COOH in CCl_4 was examined using a described technique [33]. The registration was made using the infra-red absorption bands of the components. At an electric field strength of about 10^5 V cm^{-1}, a marked increase in rate of ca. 6% was observed, which corresponds to a dipole moment increase of ca. 7 D. Thus, the transitional complex in question must be close to a typical ionic pair. However, most reactions of the proton exchange in inert solvents probably have a molecular mechanism, ionic pairs taking no part in the process.

In review [34] some experimental data on the kinetics of the proton exchange between OH— and SH— containing molecules in CCl_4 solutions have been analyzed. In particular, it was found that the elementary process goes on in a binary 1:1 complex. In Table 4 the kinetic characteristics of the exchange are shown. It can be seen that the exchange with the more acidic SH-group is about 4 orders slower than with the OH-group. The exchange with the SH-group (the acidic component of the reaction) is retarded with increasing basicity of the other component $CH_3OH > (CH_3)_3COH > (C_2H_5)_2NH$. That indicates that the ionic pair stability is not correlated with the exchange rate. The conclusion is that the proton exchange rates are determined by the ability of an XH-group to form hydrogen bonds as a donor and an acceptor, simultaneously. This is believed by the authors [34] to be the main justification of the molecular mechanism with a cooperative transfer of protons in a binary cyclic complex. Unfortunately, such cyclic complexes were not observed directly.

Some exchange processes were examined in a gaseous phase and in hexane solutions at low concentrations. It was found that the exchange between HHal molecules (Hal = Cl, Br) in a gaseous phase is too slow to be measured by means of NMR (under the conditions of thorough purification from the Lewis' acid admixtures). This agrees with the very low proton acceptor capacity of these molecules, and, therefore, with the low stability of cyclic complexes. In Table 5 the rate constants of the exchange between $(CD_3)_2NH$ and CD_3OH molecules are given. These values may be considered as confirmation of the cooperative mechanism. Indeed, if the ionic pair mechanism had taken place, the transfer from a gas to a solution should have resulted rather in rate increase than in its decrease.

While there is an effective criterion for deciding whether the proton exchange mechanism is molecular or ionic (e.g. the transfer from a solution to a gas), there is no such criterion for the limiting stage of the process. It has been assumed [35, 36] that the complex dissociation stage is the slowest stage of proton exchange. However, the values of the lifetimes of even very stable hydrogen-bonded complexes at room temperature were found to be about 10^{-10} s, the characteristic times of most rapid proton exchange processes, examined by NMR, being 10^{-4} s. Therefore, the breaking of unstable cyclic complexes cannot be the slowest stage of most proton exchange reactions under these conditions. However, the exchange between carboxylic acids which form strong 8-membered cyclic dimers becomes measurable by NMR at temperature below —130°C [37]. The lifetime of OH-protons in the cyclic dimer $(HCOOH)_2$ was found to coincide with the dimer lifetime, the proton transfer being considerably faster. The OH-signal below —140°C is a triplet with an effective coupling constant equal to half of that in HCOOH molecule. Were the proton transfer slow (on the NMR scale), the signal would be a doublet with a complete value of a coupling constant. Thus, the rate of proton exchange between the cyclic dimers of HCOOH is limited by the breaking of H-bonds. This process has a high activation energy, ca. 10 kcal mol^{-1}. It may be that all three kinds of processes (complex formation, proton transfer and complex dissociation) could be the limiting stage of the proton exchange, depending on the electronic structure of interacting molecules and of the medium.

TABLE 4

The rate constants (at 25°C) and the activation energy values of the proton exchange between $t\text{-}C_4H_9SH$ and CH_3OH with various molecules in CCl_4

Molecule	$t\text{-}C_4H_9SH$		CH_3OH	
	k^{298}, l mol^{-1} s^{-1}	$E^{\neq}$, kcal mol^{-1}	k^{298}, l mol^{-1} s^{-1}	$E^{\neq}$, kcal mol^{-1}
C_6H_5OH	0.1	4.5	240	2.1
H_2O	—	—	250	1.5
CH_3OH	0.07	3.0	380	1.5
$(CH_3)_3COH$	0.04	5.0	850	1.8
$(C_2H_5)_2NH$	0.011	6.0	150	1.4
$(C_3H_7)_2NH$	0.008	8.0	100	—

TABLE 5

The kinetic parameters of homomolecular (NH—NH) and heteromolecular (NH—OH) proton exchange in the gas phase and in solution in C_6D_{12}
(α is the reaction order with respect to amine, β the reaction order with respect to alcohol; k^{303}, bimolecular rate constant; $E^{\neq}$, activation energy)

	$(CD_3)_2NH$—$(CD_3)_2NH$		$(CD_3)_2NH$—CD_3OH	
	Gas	Solution	Gas	Solution
α	1.9	2.0	1	1.0
β	—	—	1.1	1.1
k^{303} (l mol^{-1} s^{-1})	84	47	260	140
$E^{\neq}$ (kcal mol^{-1})	1.4	2.0	1.0	1.8

The exchange reactions going on in weak four-membered bimolecular cyclic complexes can be divided into two types: (1) exchange with participation of SH or PH groups, requiring activation energy of about 5—8 kcal mol^{-1}, (2) exchange between OH or NH groups, where the temperature coefficient is close to that for the diffusion process (1—2 kcal mol^{-1}). According to ref. 38, the comparatively slow reactions (1) must be limited by the elementary act of the cooperative proton transfer. In this case the dissociation rate of complexes is many orders higher than the exchange rates which hence cannot determine them. Rather high values for activation energy cannot be in agreement with the postulation of complex formation as the limiting stage (this process is certain to have no potential barrier [39]). In the case of fast processes (2) the situation is more complicated. The kinetic isotope effect of fast proton exchange between methanol and water in CCl_4 has been examined to find the limiting stage [29]. The NMR ^1H and ^2D technique and kinetic IR spectroscopy were used. The rate turned out to increase a little in the range OH—OH, OH—OD, OD—OD, which is not in agreement with the supposition of proton transfer as the determining stage. The authors believed that cyclic complex formation limited the rate. This process could be very slow because of the extremely small values of its equilibrium constant ($k = Kk_{diss}$, where K is the equilibrium constant and k_{diss} is the dissociation rate constant which cannot be more than that of diffusion). In this case, although the rate is not determined by diffusion, the activation energy is determined by it.

It can be seen that fast proton exchange is a rather complicated process and so far incompletely investigated. It can have various mechanisms, but in inert media most reactions proceed via proton transfer in cyclic molecular or ionic complexes with two hydrogen bonds.

Summing up, we conclude that low temperature NMR spectroscopy, particularly in combination with optical kinetic spectroscopy, is useful in solving important questions concerning the structure and dynamics of hydrogen-bonded complexes. Among the latter are problems of proton localization inside a hydrogen bridge and, in some cases, of the reverse proton transfer rate between the potential wells. It is hoped that the development of low-temperature NMR spectroscopy on other nuclei (^{15}N and ^{17}O) will open new perspectives in this field.

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