

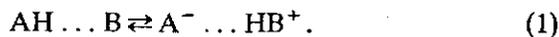
The Hydrogen Bond and Proton Transfer in Trifluoroacetic Acid-isoquinoline Complexes. The Effect of the Medium

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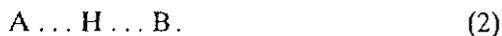
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Spectroscopic investigations of proton transfer in systems with a strong hydrogen bond in solutions have made it possible to record the existence in these systems of complexes of various structures and compositions in equilibrium with one another and with free molecules (see the review [1]). The authors of Refs. [1]–[3] suggest that the type of the experimentally observed equilibrium be used as the characteristic of the potential energy surface of the proton donor-proton acceptor system. It was assumed by the authors of the works cited that there exist two possible types of evolution of the potential surface upon smooth change of the proton-releasing and proton-accepting abilities of the interacting molecules. In the first case, as the interaction is intensified, at the surface, apart from the minimum corresponding to a stable molecular complex with a hydrogen $AH \dots B$ bond, there appears a second minimum corresponding to an $A^- \dots HB^+$ ion pair. The second minimum is gradually deepened, while the first one gradually disappears. The system thus passes through a tautomeric equilibrium of the following type:



Another type of evolution consists in that the only minimum at the

surface, while being shifted along the reaction coordinate, passes through all the possible states of the system from a molecular complex to an ion pair, the minimum in the intermediate region corresponding to a complex with a quasisymmetrical hydrogen bond:



It was, however, shown at a later time [4], [5] that the proton transfer is accompanied by a reorganization of the solvation shell of the solvent which surrounds the complex. In order to describe such a situation adequately, it is necessary to use the concept of the free-energy surface of a complex-solvent system rather than the concept of the potential energy surface of an isolated complex consisting of two molecules [6]. The concept of two types of surface evolution may be retained. However, such an evolution may occur not only upon change of the properties of the proton-donor and -acceptor molecules themselves but also upon change of the properties of the solvent and also upon change of temperature.

Judging by the data of Refs. [7]–[10], for carboxylic acid-amine systems the variation of the proton-donor or -acceptor ability of the acid and amine leads to an evolution of the first type associated with equilibrium (1). The purpose of the present work is to determine spectroscopically the structure of complexes and the character of the evolution of the free-energy surface in the trifluoroacetic acid (I)-isoquinoline (II) system upon variation of the properties of the solvent. The difficulty of such an investigation is that in solutions of carboxylic acids with proton acceptors, apart from 1:1 complexes which are actually the objects studied, there are also always present the acid dimers and complexes, in which there are two or more acid molecules per acceptor molecule.

EXPERIMENTAL

In the present work we used a series of solvents having different properties—carbon tetrachloride, benzene, toluene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, butyl chloride, chloroform, acetonitrile, water. The concentration of the solutions was varied over

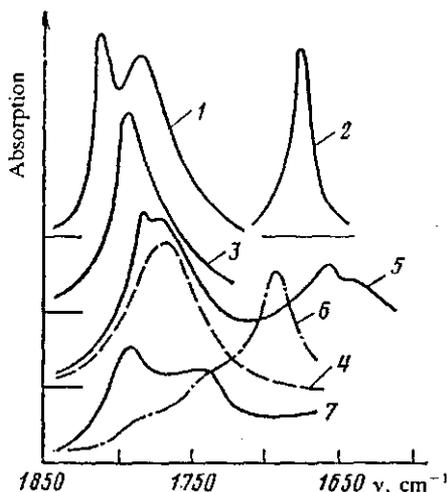


FIGURE 1 The IR absorption spectra of solutions of trifluoroacetic acid in the following solvents: (1) CCl_4 (4.8×10^{-3}); (2) D_2O (3.2×10^{-2}); (3) CH_3CN (7.0×10^{-2}); (4) I + II in CCl_4 ($4.8 \times 10^{-3} + 1.5 \times 10^{-2}$); (5) I + II in CCl_4 ($9.6 \times 10^{-3} + 3.7 \times 10^{-3}$); (6) I + II in CH_3CN ($1.4 \times 10^{-1} + 2.1 \times 10^{-1}$); (7) I + II in CH_3CN ($4.0 \times 10^{-2} + 1.3 \times 10^{-2}$). The concentration is given in mol/liter.

as wide ranges as allowable by the transparency of the solvents and the solubility of the complex.

The IR spectra were recorded on an UR-20 spectrophotometer. We used standard-type cells with fluorite windows. The solution concentration in different experiments was varied from 10^{-4} to 10^{-1} mol/liter and the thickness of the absorbing layer from 2 to 0.01 cm.

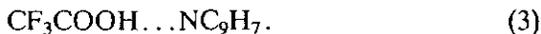
The solvents were purified and dried using standard procedures. Isoquinoline was distilled under vacuum.

RESULTS AND DISCUSSION

The nature of the bond in complexes with carboxylic acids is often determined spectroscopically in the region of $1500\text{--}1800\text{ cm}^{-1}$, which covers the valence vibration band of the carbonyl group of the acid, $\nu(\text{C}=\text{O})$, and the antisymmetric valence vibration band of the carboxylate anion, $\nu_a(\text{CO}_2^-)$, which arises upon elimination of

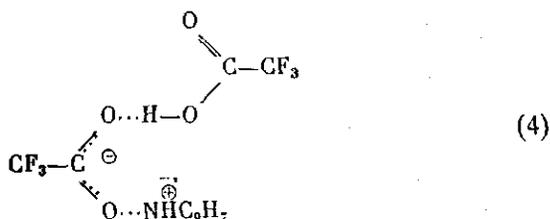
the proton. The frequency $\nu_a(\text{C}=\text{O})$ of the free (monomeric) acid molecule in nonpolar aprotic solvents of the CCl_4 type is 1810 cm^{-1} . When trifluoroacetic acid (I) is involved in the hydrogen bond as a proton donor, the value of this frequency decreases (to 1778 cm^{-1} in the acid dimer) (Fig. 1). The $\nu_a(\text{CO}_2^-)$ frequency of the trifluoroacetate ion is usually located (depending on the conditions) in the region of $1650\text{--}1700\text{ cm}^{-1}$. Figure 1 shows this band in the spectrum of a solution of I in heavy water. When isoquinoline (II) is added to such a solution, there appear a series of narrow bands with frequencies appreciably different from the frequencies of the skeleton vibrations of isoquinoline itself in this region. Some of the most intense bands ($1400, 1615, 1660\text{ cm}^{-1}$) can also be observed in the spectrum of the isoquinoline solution in CHCl_3 in the presence of HCl. Obviously, these bands belong to the isoquinolinium cation. Thus, the spectra of aqueous solutions provide information on the bands of the ionic forms of the acid molecules studied.

Figure 1 also presents the spectrum of a solution of I and II in CCl_4 . In the presence of excess isoquinoline, when the concentrations of the acid monomers and dimers and also of the complexes containing more than one acid molecule are low, apart from the isoquinoline bands (not shown in Fig. 1), the spectrum shows only the 1765 cm^{-1} band, which presumably belongs to the I-II complex of 1:1 composition. The fact that this band lies below the dimer band is evidence that the hydrogen bond in the complex is very strong, but the complex may still be considered molecular:



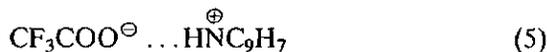
A band typical of the anion in the region of $1650\text{--}1660\text{ cm}^{-1}$ (the weak narrow band of the cation at 1660 cm^{-1} can be seen against its background) appears only when the acid fraction in the solution is increased, i.e. when its concentration exceeds the isoquinoline concentration. The band near 1770 cm^{-1} does not disappear. Beginning with a certain concentration of the acid, its intensity increases in the same direction as does the intensity of the 1650 cm^{-1} band and is overlapped with the bands of the dimer and monomer. Such concentration changes in the spectrum have been observed earlier for carboxylic acid-aliphatic amine systems and served as evidence of the formation of acid-amine complexes of 2:1 composition [7].

Addition of a second molecule of the acid enhances the interaction of the first acid molecule with isoquinoline, thereby leading to a proton transfer; associated with this is the appearance of the 1650cm^{-1} band (a low value of the $\nu_a(\text{CO}_2^-)$ frequency is also characteristic of the anion in the 2:1 complex); the terminal C=O group of the second acid molecule makes a contribution to the 1770cm^{-1} band:



In principle, in the presence of a large excess of the acid a third, fourth, etc. acid molecule may be added to such a complex. Indeed, the measurement of the intensity of the $\nu(\text{OH})$ band of the acid monomer (3505cm^{-1}) at acid and isoquinoline concentrations of 1.8×10^{-2} and 0.32×10^{-3} mol/liter, respectively, made it possible to estimate, after the monomer concentration was determined and the number of dimers calculated from the known dimerization constant [11], the concentration of the acid bound with isoquinoline. It turned out that the latter exceeds at least 4 times the total concentration of isoquinoline under the conditions indicated.

A different picture is observed in the spectra of solutions in a polar solvent (acetonitrile) (Fig. 1). In this case, with isoquinoline present in excess there is a 1695cm^{-1} band of the trifluoroacetate ion in an ion pair of 1:1 composition:



and two weak bands, at 1795 and 1745cm^{-1} , whose intensity increases with increasing acid fraction in the solution. In the presence of an excess of the acid these two bands predominate, while the band at 1695cm^{-1} disappears. The band at 1795cm^{-1} is due to the absorption of trifluoroacetic acid molecules linked to the solvent via a hydrogen bond; an identical band is observed in the absence of

isoquinoline. The band at 1745 cm^{-1} is located approximately in the middle between the bands of the molecular and ionic forms of the acid. Such a band has been recorded earlier in the trifluoroacetic acid-aniline system in CH_3CN [12]. Its appearance is associated with the fact that the structure of the 2:1 complexes in acetonitrile differs from the structure described above for CCl_4 . In a strongly polar solvent such complexes undergo dissociation (at least partly) with the formation of the cation and the *bis*-trifluoroacetate anion with a symmetrically arranged proton:



It is such complexes that are characterized by an "intermediate" value of frequency. Complexes having a more complex composition (3:1, 4:1, etc.) in CH_3CN are not evidently formed in appreciable amounts.

The most significant point is the difference in structure between complexes of 1:1 composition; according to what has been said above, we have a molecular complex with a strong hydrogen bond in the case of CCl_4 and an ion pair with a transferred proton in CH_3CN . It was therefore interesting to record the spectra of such a complex in solvents more polar than CCl_4 but less polar than

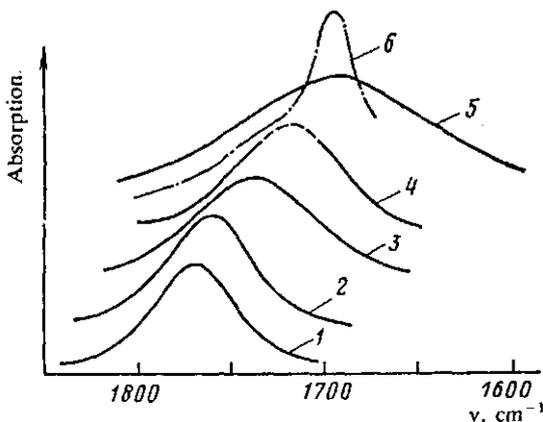


FIGURE 2 The band of the I + II complex of 1:1 composition in the IR spectra of solutions in CCl_4 (1), toluene (2), *o*-dichlorobenzene (3), nitrobenzene (4), chloroform (5), and acetonitrile (6).

CH₃CN. It was found that in the presence of excess isoquinoline there is observed a band at 1760 cm⁻¹ in toluene, a 1750 cm⁻¹ band in chlorobenzene, a band at 1735 cm⁻¹ in *o*-dichlorobenzene, and a band at 1715 cm⁻¹ in nitrobenzene (Fig. 2). In all these solvents the band has a much larger width than the bands of the monomer and dimer of trifluoroacetic acid or the band of the anion in aqueous solution. The band in the chloroform solution is especially strongly broadened ($\Delta\nu_{1/2} \approx 150 \text{ cm}^{-1}$). Its maximum lies at about the same frequency as in the acetonitrile solution (at 1695 cm⁻¹). Noticeable differences between the spectra of the solutions in CHCl₃ and CH₃CN appear only in the presence of a large excess of the acid, since the spectrum and structure of the 2:1 complex in chloroform are the same as in other, not too polar solvents. This is evidenced by the presence of bands at 1660 and 1780 cm⁻¹ which are typical of the structure of compound (4).

Thus, the examination of the IR spectra of trifluoroacetic acid complexed with isoquinoline in the proportion of 1:1 shows that as the properties of the solvent are changed, the band of the complex in the region of 1800–1650 cm⁻¹ gradually changes its position from the position typical of the $\nu(\text{C}=\text{O})$ of the acid (the solution in CCl₄) to that typical of the $\nu_a(\text{CO}_2^-)$ of the trifluoroacetate anion (solutions in chloroform and acetonitrile), passing through the intermediate frequencies close to the frequency of the *bis*-trifluoroacetate ion with a symmetrical hydrogen bond (solutions in chlorobenzene, *o*-dichlorobenzene, etc.).

Hence, the structure of the complex and the nature of the interaction between the partners are also changed. The complex in CCl₄ is a molecular complex with a hydrogen bond; in toluene, chlorobenzene, and dichlorobenzene it has a structure intermediate between the molecular and ionic structures; finally, the complexes in chloroform and acetonitrile are ion pairs with a transferred proton. The dielectric constant ϵ of the solvents listed increases approximately in the same sequence, though no unique correspondence between the values of ϵ and the ionicity of the complex is observed.

From the spectra it follows that the structure of the complex in aromatic hydrocarbons ($\epsilon = 2.28; 2.38; 5.62$ for benzene, toluene and chlorobenzene, respectively) is closer to the ionic structure than in butyl chloride ($\epsilon = 7.39$). At the same time, the spectra in chloroform ($\epsilon = 4.39$) are close to those in acetonitrile ($\epsilon = 36.2$). This is,

however, not surprising, since the dielectric constant, which is a macroscopic quantity, does not reflect all the specific features of the interaction of a given solvent with the complex. With aromatic solvents, their high polarizability evidently plays a significant role; the stabilization of the ionic forms in chloroform is favored by the proton-releasing ability of its molecules, as has been noted in Ref. [13]. Complexes of trifluoroacetic acid with pyridine in CHCl_3 are also ion pairs [14].

No two bands which could be assigned to the molecular and ionic forms of the 1:1 complex are observed simultaneously in any of the solvents considered; otherwise the existence of the tautomeric equilibrium (4) could have been deduced. Hence, in the isoquinoline-trifluoroacetic acid system the evolution of the free-energy surface occurs, depending on the properties of the solvent, through the shift of the only minimum along the reaction coordinate via a state corresponding to the "intermediate" complex. At the same time, the adducts of the acid with isoquinoline of 2:1, 3:1, etc. compositions in all the solvents contain isoquinoline and at least one of the acid molecules in an ionic form. Accordingly, their spectra vary insignificantly in going from one solvent to another. The only exception is acetonitrile, in which, as noted above, two molecules of trifluoroacetic acid that enter into the composition of the 2:1 complex form a *bis*-trifluoroacetate ion.

The conclusions made in the present paper are also confirmed by the results of an investigation of the electronic spectra of adducts of trifluoroacetic acid with isoquinoline in the region of the 1L_b band of isoquinoline.

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