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DYNAMICS OF FORMATION AND BREAKING OF HYDROGEN BOND IN SOLUTIONS

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The life-time of hydrogen-bonded complexes in solution may be determined by two types of processes: I) the molecular exchange similar to that of ligands in metal donor-acceptor complexes, 2) the process of reverse proton transfer from the donor to the acceptor and backwards ("intracomplex tautomerism"), occuring but in some particular cases. The molecular exchange

$$A\text{-}H\ldots B' \;+\; B'' \rightleftharpoons A\text{-}H\ldots B'' \;+\; B'$$

where B' and B" are either different or similar molecules, may proceed via two different mechanism: the synchronous, with the formation of the activated complex of a complicated composition

$$A\text{-}H\ldots B' \;+\; B'' \rightleftharpoons A\text{-}H\genfrac{}{}{0pt}{}{\cdot B'}{\cdot B''} \rightleftharpoons A\text{-}H\ldots B'' \;+\; B'$$

and the step-like, with the breaking of one bond, followed by the formation of the second bond.

To establish the true mechanism of the process, the investigation of the molecular exchange kinetics in CHF_2Cl solutions was carried out at low temperature ($-100^{\circ} \div -170^{\circ}C$) by means of NMR. Within this range of temperature, in proton magnetic resonance spectra of systems, containing proton donors and proton acceptors, the signal of the proton, participating in hydrogen bonding, can split into signals, corresponding to complexes of different kinds. For example, in the spectrum of $CF_3COOH+HCON(CH_3)_2+(CH_3)_2O$ solutions (Fig.I), two OH-proton signals of the acid in complexes with ether $\delta=12{,}3$ ppm, and amide $\delta=18{,}2$ ppm, are observed. There are no dimers in detectable amounts under these conditions. It is to be noted that the two CHO-proton signals belonging to the free formamide molecule and to the molecule of formamide bonded with the acid have been detected.

In the spectra of systems, containing carboxylic acid and only one acceptor, at low concentrations two OH-signals are observed: the first corresponding to the I:I acid-acceptor complex, the second to the cyclic dimer. With the increase of the concentration, there also appear the signals of complexes, containing two acid

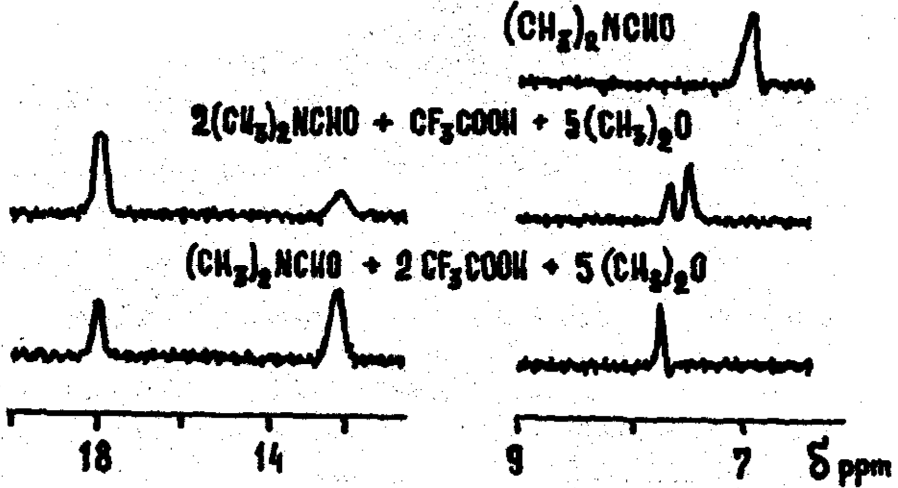

Fig.I. The spectra of the $CF_3COOH+(CH_3)_2NCHO+(CH_3)_2O$ solutions in CHF_2Cl at -155°C

molecules. It has been shown that, under these conditions, the proton exchange does not affect the line-shape.

In systems, containing the proton donor with the intramolecular hydrogen bond and the acceptor, the separate signals of the proton donor and the complex with the intermolecular donor-acceptor hydrogen bond are seen.

By means of the full line-shape analysis, the life-times of different forms were found, and, using the concentration dependence of life-times, were determined the rate orders of reactions. The process of the complex dissociation appeared to be monomolecular. The activation parameters of molecular exchange were calculated from the temperature dependence of rate constants. The activation energies proved to be close to the hydrogen bond energies in such complexes. The values of activation entropy are positive and also close to the entropy of hydrogen-bonded complexes. This suggests that the molecular exchange process is of a step-like character, i.e., the new bond forms only after the breaking of the previous one. In the transition state determining the rate of the exchange there is no interaction between the donor and the acceptor.

A peculiar case are the carboxylic acid-amine complexes, with the possible equilibrium between various molecular and ionic forms,

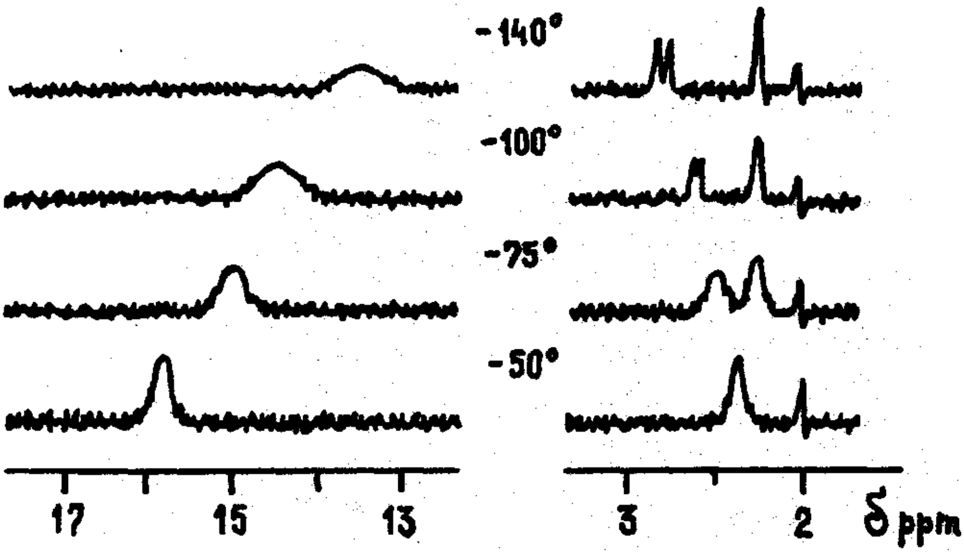

Fig.2. The spectra of the $CH_2ClCOOH$ (0,05 M) + $(CH_3)_3N$ (0,I2 M) solutions in CHF_2Cl.

In the spectra of $CH_2ClCOOH+(CH_3)_3N$ system (with excess of amine), the splitting of the trimethylamine signal into signals, belonging to the free amine and its complex with the acid, is observed at low temperature. With further decrease of temperature, the signal shifts to the low field and splits into a doublet, the splitting increased with the decrease of temperature up to -I20°C (the effective value of J rises from 2 to 5,5 Hz). Below -I20°C, there is no change in the spectrum (Fig.2). This means that the tautomeric conversion takes place in the complex on account of the reversible proton transfer. The molecular exchange between the complexes and free molecules going on slowly in NMR time-scale (the signals observed separately), the proton transfer is accomplished quickly even at temperature -I70°C (the observed signals of the complexes seen coalesced). With the decrease of temperature, the equilibrium shifts to the ionic form, and below -I20°C there is only an ionic form in the solution. The shift of the equilibrium is accompanied by a strong shift of the coalesced OH and NH^+ signal to the high field.

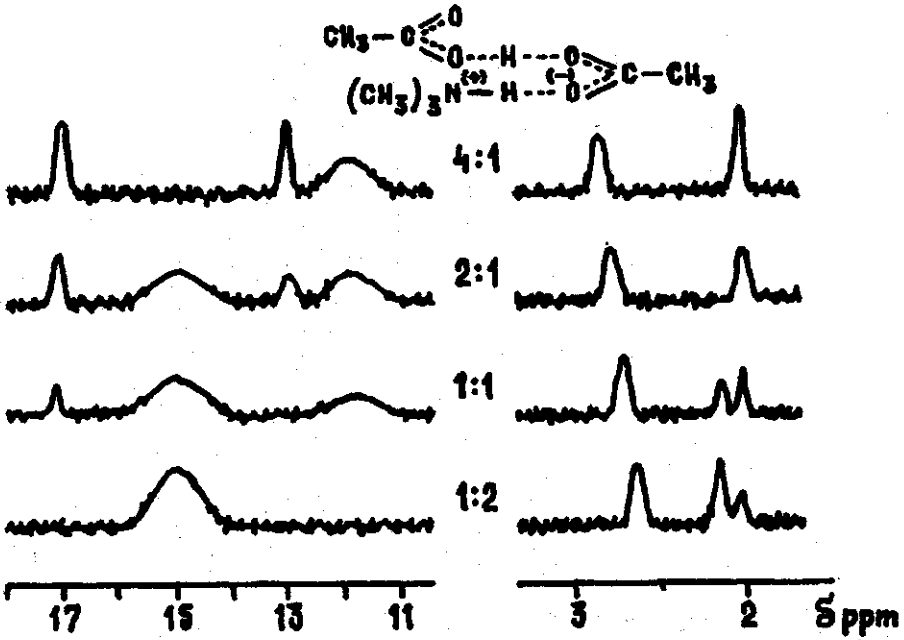

Fig.3. The spectra of the $CH_3COOH+(CH_3)_3N$ solutions at -I65°C.

In the acetic acid-trimethylamine system (excess of amine), even at the lowest temperature -I70°C, there is an equilibrium between the molecular and the ionic forms of the complex, as seen from the position of the signal of the trimethylamine bonded in the complex. The estimate of the lower limit of the proton transfer frequency may be made, using the line width of the movable proton. It is found to be $\nu >$ IO^5 sec^{-I} at -I70°C. In case of excess of the acid, a more complicated picture is observed (Fig.3). Besides the mentioned above OH/NH$^+$ signal of the I:I complex, there appear two more signals, having the same integral intensity. The low-field signal belongs to the OH-proton, while the high-field one to the NH$^+$-proton in the amine complex with two molecules of the acid. With further increase of the amount of the acid, the cyclic dimer signal ~I3 ppm also appears. The position of the 2:I complex signals does not depend on temperature, hence, no tautomeric proton transfer occurs in this complex. This is in accordance with the results of the infra-red study of the acid-amine systems.

With the decrease of pK_a of an acid, the calculated chemical shift of the signal, corresponding to the molecular form of the I:I complex, increases, which is related with the strengthening of the hydrogen bond. At the same time, the chemical shift of the NH^+-signal of the ionic form decreases, which corresponds to the increase of pK_B of the conjugated base (carboxylate-anion).