INVESTIGATION OF SYSTEMS WITH REVERSIBLE PROTON TRANSFER IN COMPLEXES WITH HYDROGEN BONDS BY PMR SPECTROSCOPY AT LOW TEMPERATURES

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In studies of the interaction between molecules of various OH acids and amines in fairly inert aprotic solvents by the methods of optical spectroscopy it was found that the simultaneous presence of ionic and molecular complexes in solution is possible in certain cases [1, 2]. These complexes exist in equilibrium with one another and sometimes with complexes with a composition more complicated than the 1:1, which usually have an ionic structure. Since the PMR spectra of these systems generally show signals that are averaged over all the species, the interpretation of these spectra is very difficult. In [3] it was shown that at temperatures on the order of −100 to −150°C in the PMR spectra of solutions containing carboxylic acids and various acidic proton acceptors (there is no proton transfer in these systems), the signals which correspond to different complexes can be observed individually, i.e., the process of molecular exchange is slow. In the present work the spectra of systems in which intracomplex tautomerism can be detected by the methods of IR spectroscopy were obtained at low temperature. Solutions of carboxylic acids RCOOH [R = $(CH_3)_3C$—, CH_3—, CH_2Cl—, $CHCl_2$—, and CF_3] and trimethylamine $(CH_3)_3N$ in Freon 22 (CHF_2Cl) were investigated. The operations involved in the purification, drying, and dosing of the substances and the preparation of the solutions were carried out with the aid of a glass vacuum apparatus. The trimethylacetic acid and monochloroacetic acid were dried in hexane solutions by Zeolite 5A, and then the solvent was driven off in a vacuum, and the substances were subjected to sublimation at 20-40°C. The compounds with low vapor pressures (acetic acid, trifluoroacetic acid, trimethylamine, and Freon) were dried after standard purification procedures in the gaseous phase by zeolites directly in the apparatus and then distilled into ampuls, which were placed in the cooled detector of a JEOL C-60 spectrometer. While the spectra of the previously studied systems without reversible proton transfer are practically independent of the extent of purification of the compounds at temperatures below −110°C, the spectra of solutions containing amines can be radically altered in the presence of impurities, especially water, which induces proton exchange.

The spectra obtained have a significantly different form, depending on the ratio between the concentrations of the acid and the amine. Figure 1 shows the temperature dependence of the spectrum of the $CH_2ClCOOH—N(CH_3)_3$ system with a threefold excess of the amine. When the temperature is lowered, the signal of trimethylamine is shifted to a weaker field and split into two signals. The signal in the stronger field belongs to the free molecules of trimethylamine, and it is not altered when the temperature is lowered further. The weak-field signal continues to be displaced down to −120°, the doublet splitting being observed. The effective value of the spin—spin coupling constant increases from 2 to 5.5 Hz. Below −120° the position and magnitude of the spin—spin splitting of this signal do not depend on the temperature and coincide with the corresponding values for the methyl signal of trimethylammonium perchlorate solution in Freon.

In parallel to the displacement of the signal of $(CH_3)_3N$ there is an upfield shift of the signal of the mobile proton, but no splitting of this signal is observed. Below −120° the position and half-width of this signal also cease to vary. The spectra presented show that there are simultaneously two equilibria in the system, viz.,

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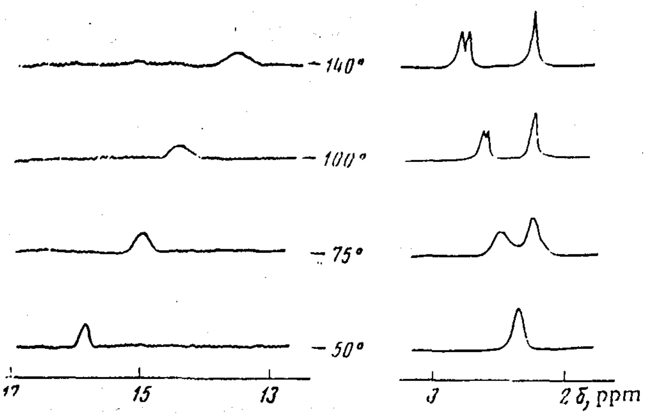


Fig. 1. Proton magnetic resonance spectra of a solution of $CH_2ClCOOH$ (0.1 mole/liter) + $(CH_3)_3N$ (0.3 mole/liter) in CHF_2Cl at different temperatures.

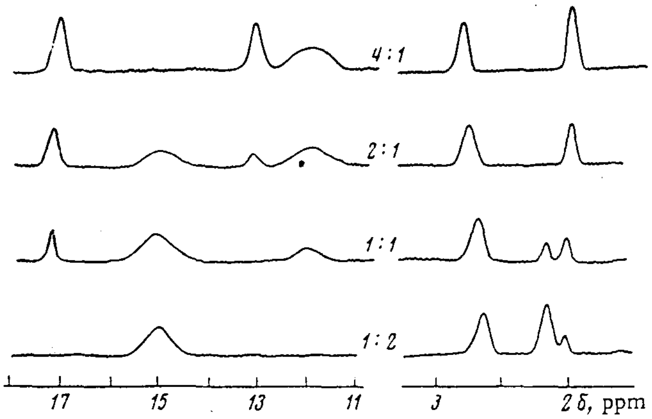


Fig. 2. Proton magnetic resonance spectra of the $CH_3COOH + (CH_3)_3N$ system in CHF_2Cl with various ratios between the concentrations of the acid and the amine (t = —165°C). The signal near 2 ppm belongs to the methyl group of the acid, and the spin—spin splitting of the signal of the cation is not observed below —150°C.

$$AH+B \rightleftharpoons AH \ldots B, \tag{1}$$

$$AH \ldots B \rightleftharpoons A^- \ldots HB^+. \tag{2}$$

At low temperatures process (1) is slow, and process (2) (reversible proton transfer) is fast, since no splitting of the signal of the mobile proton is observed. The half-width of this signal is determined by the incomplete averaging of the ^1H—^{14}N spin—spin splitting owing to the quadrupole relaxation and increases with increasing relative concentrations of the ion pair in which the proton is bound to a nitrogen atom [when equilibrium (2) is shifted to the right, there is an increase in the averaged value of the ^1H—^{14}N spin—spin interaction constant]. At temperatures below —120° the solution contains only ion pairs and free trimethylamine molecules. At about —150° there is broadening of all of the signals of the ionic complex, while the signals of the free molecules and of the solvent remain narrow. Under the same conditions there is no broadening of the signals of the molecular complexes formed by the carboxylic acids with the oxygen acceptors. This may indicate that there is a dipole—dipole association between the ion pairs which have dipole moments up to about 10 D, as well as a decrease in the rotational mobility of the aggregates formed in the solution. If acetic acid or trimethylacetic acid is taken as the proton donor, equilibrium (2) is observed even at the lowest

TABLE 1. Parameters of the Molecular and Ionic Complexes Formed between Carboxylic Acids and Trimethylamine

Acid	pK_a	δ_{mc}, ppm	δ_{ip}, ppm	$-\Delta H$, kcal/mole
$(CH_3)_3CCOOH$	5,05	16,5	14,9	5,0
CH_3COOH	4,75	16.8	14.4	5,7
$CH_2ClCOOH$	2,86	17,2	13,5	7,6
$CHCl_2COOH$	1,25	17,5	12.7	9,0
CF_3COOH	0,23	–	11,1	–

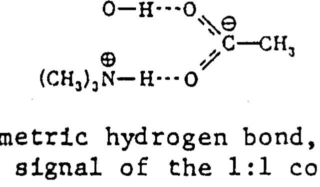
temperature, as we can see from the chemical shift of the signal of trimethylamine bound in the complex. Since in that case the low-field signal of the OH^- and NH^+ groups remains averaged, it may be concluded that the transfer of the proton is rapid (the lifetime of the state is $\tau < 10^{-4}$ sec at –170°C).

The position of the signal of $(CH_3)_3N$ bound in the complex is a function only of the relative concentration of the ionic and molecular species, the chemical shifts of the individual species being known and being independent of the proton donor. Thus, the equilibrium constant of monomolecular process (2) can be determined at each temperature. The chemical shifts of the signals of the OH^- and NH^+ protons are not known individually, but they can be determined when we have the dependence of the chemical shift of the mobile proton on the equilibrium constant:

$$\delta=\delta_{mc}\frac{1}{1+K}+\delta_{ip}\frac{K}{1+K}. \qquad (3)$$

These values, which were calculated according to the least-squares method, are presented in Table 1. It is seen that as the strength of the acid increases, the chemical shift of the molecular complex increases (the energy of the OH...N hydrogen bond increases), and the chemical shift of the ion pair decreases. This is natural, since in the ion pair the $NH^+...O^-$ hydrogen bond appears between a conjugate base and a conjugate acid. The plots of the averaged value of δ as a function of the pK_a of the acid calculated from Eq. (3) at a fixed temperature have the shape of curves with a maximum (this is consistent with the experimental data in [4]). However, the position of the maximum is strongly dependent on the temperature and is determined by the competition between several factors (the different dependences of δ_{mc}, δ_{ip}, and K on pK_a) rather than the highest hydrogen-bond energy in a given system. Table 1 also presents values of the enthalpy of the reversible proton-transfer reaction (2), which were determined from the temperature dependence of the equilibrium constants. This parameter also increases with increasing pK_a of the acid.

The spectra become more complicated when there is an insufficient excess of the amine or an excess of the acid. Figure 2 presents spectra of the $CH_3COOH–N(CH_3)_3$ system (–165°C) with various ratios between the concentrations of the components. When the relative amount of the acid is increased, the signal of the mobile proton decreases in intensity, and two other signals, which always have the same integral intensity, appear (δ = 17.3 and δ = 11.8 ppm). A signal at δ = 13.2 ppm, which belongs to cyclic dimers of the acid [3], also appears then. The signal at δ = 17.3 ppm apparently belongs to the OH proton of the 2:1 complex



which forms a very strong, nearly symmetric hydrogen bond, and the δ = 11.8 ppm belongs to the NH^+ proton in this complex. When the signal of the 1:1 complex is not present, i.e., only the 2:1 complexes and the dimers are present in the solution, the position and magnitude of the spin–spin splitting of the trimethylamine signal are not dependent on the temperature and correspond to the ionic species. Thus, in the 2:1 complexes the tautomerism associated with the reversible proton transfer is absent. As the strength of the acid is increased, the OH and NH^+ signals of the 2:1 complex diverge, i.e., when the $NH^+ \ldots O^-$ hydrogen bond is weakened, the $OH \ldots O^-$ bond becomes stronger and approaches the symmetric bond (as in the $[(RCOO)_2H]^-$-$[NR_4']^+$ complexes).

It should be noted that if we have only the value of the chemical shift of the signal of the mobile proton (at room temperature this signal is averaged with the signals of the complexes with compositions more complicated than the 1:1), it is impossible to uniquely determine the type of complexation in the system. Similarly, it was previously noted that the type of complexation (molecular, ionic, with intracomplex tautomerism) is practically impossible to establish from the IR spectra in the region including the stretching vibrations of XH, and in investigations of acid—amine systems it is necessary to study the spectra in the regions including the skeletal vibrations of the molecules of the proton donor and acceptor [5]. The bands of these vibrations, like the parameters of the signals of protons which do not directly form hydrogen bonds, are strongly dependent on the type of complex and are only scarcely dependent on the strength of the hydrogen bond in it, while the frequency and intensity of the band for the stretching vibration of the XH bond and the chemical shift of the proton on the XH group are mainly determined by the strength of the hydrogen bond.

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