SPECTROSCOPIC INVESTIGATION OF THE REACTION OF ACETIC AND ISOBUTYRIC ACIDS WITH TERTIARY AMINES

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The aim of the present research was a spectroscopic investigation of the structures of complexes of carboxylic acids with tertiary amines. As in preceding communications [1-5], major attention was directed to problems associated with the transfer of a proton from the acid to the amine — equilibrium between the molecular complex and the ion pair, the structures and spectroscopic features of each of these complexes, and the effect of intermolecular interactions on this equilibrium. The IR spectra of solutions of acetic and isobutyric acids in triethylamine and trioctylamine and of solutions of the acids and amines in various solvents were investigated. The investigations were carried out with an IKS-14A spectrometer. The accuracy in the determination of the frequencies was limited by the widths of the bands and frequently by considerable overlapping of them; as a rule, it was no less than 2-5 cm^{-1}

The band at ~1710 cm^{-1} has the maximum intensity in the 1500-1800 cm^{-1} region in the spectra of solutions of acetic and isobutyric acids in tertiary amines (Fig. 1). The frequency of the maximum of this band for acetic acid is 1712 cm^{-1}; this is characteristic for acid molecles that form a strong hydrogen bond with proton acceptors [6]. The shoulder at 1750 cm^{-1} is explained by Fermi resonance with a νC—C overtone at 870 cm^{-1} [7]. The band for isobutyric acid has the form of a poorly resolved doublet with components at 1700 and 1720 cm^{-1}. This doublet is typical for a stable molecular complex of isobutyric acid with piperidine [2], pyridine [8], dimethyl sulfoxide [9], and trimethylphosphine oxide. The integral coefficient of absorption of this band for both acids dissolved in triethylamine is $(2.5 \pm 0.3) \cdot 10^4$ liter/mole $\cdot cm^2$, i.e., lower by a factor of 1.7 that for the dimer [10, 11]. The decrease in the intensity of the νC = O band of the acids is again characteristic for stable molecular complexes of acids [6]. The band at ~1710 cm^{-1} can therefore be assigned to the acid-amine complex with an OH...N hydrogen bond. Consequently, most of the acid molecules in solution in a tertiary amine exist as a molecular complex with the amine.

The spectra (Fig. 1) also contain bands at 1560 and 1624 cm^{-1} in the interval characteristic for the $\nu_a CO_2^-$ vibration of the carboxylate ion [12, 13]. The presence of these bands indicates that a small portion of the acid molecules exist in solution in the form of ionic complexes formed as a result of transfer of a proton from the acid to the amine. The bands at 1560 and 1624 cm^{-1} can be interpreted on the basis of the following considerations:

1. The transfer of a proton from the carboxyl group to the nitrogen atom of the tertiary amine will inevitably lead to the appearance of an unsymmetrical carboxylate ion in the ion pair because of the existence of an $NH^+ \ldots O^-$ hydrogen bond [14].

2. The formation of 2 : 1 complexes containing two molecules of acid occurs readily in systems containing acid and amine [3, 15, 16].

3. The addition of a second acid molecule to the unsymmetrical ion pair will lead to a decrease in the $\nu_a CO_2^-$ frequency by ~40 cm^{-1} [14] (the concept of the symmetrical and asymmetrical vibrations of the carboxylate ion with nonequivalently charged oxygen atoms is used arbitrarily here). When the acid concentration in the amine decreases, the intensity of the band at 1624 cm^{-1} increases at the expense of the band at 1560 cm^{-1}. Raising the temperature will also lead to a change in the relative intensity of these bands in favor of the band at 1624 cm^{-1}. This provides a possibility for assignment of the band at 1624

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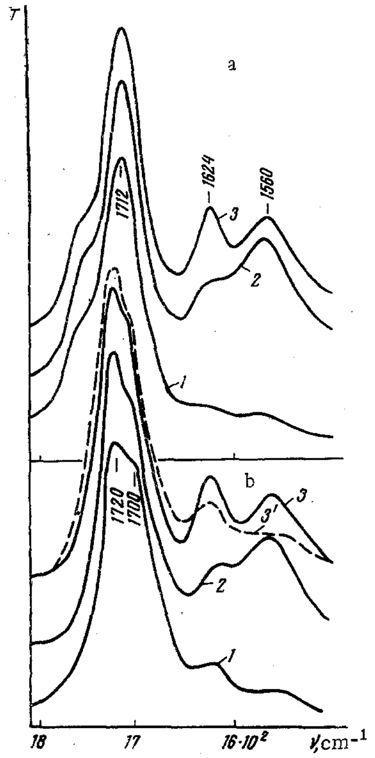


Fig. 1. Spectra of solutions of acetic (a) and isobutyric (b) acids in tertiary amines: 1) in triethylamine; 2) and 3) in trioctylamine. The acid concentrations were 0.5 (1, 2) and 0.15 mole/liter (3), the temperatures were 20°C (1, 2, and 3) and 80° (3'), and the layer thicknesses (d) were 45.7 μm (1 and 2) and 150 μm (3) (T is the absorption).

cm^{-1} to $\nu_a \mathrm{CO}_2^-$ in the ion pair formed by the carboxylate ion with the trialkylammonium cation and of the band at 1560 cm^{-1} to $\nu_a \mathrm{CO}_2^-$ in the acid anion in the 2 : 1 complex. One oxygen atom of the anion in this complex interacts with the NH group of the cation, while the other forms a hydrogen bond with the hydroxyl group of the second molecule of acid. In the limiting case of minimal disturbance (a solution of $\mathrm{R_4N \cdot CH_3CO_2}$ in $\mathrm{CCl_4}$), $\nu_a \mathrm{CO}_2^-$ of the acetate ion is 1575 cm^{-1} [17]. Symmetrical charging will lead to a decrease in $\nu_a \mathrm{CO}_2^-$; $\nu_a \mathrm{CO}_2^-$ value in a solution of $\mathrm{CH_3COOH}$ in $\mathrm{D_2O}$ containing an equivalent amount of KOH is 1560 cm^{-1}, i.e., it coincides with $\nu_a \mathrm{CO}_2^-$ in the 2 : 1 complex. However, an increase in the frequency in the ion pair is due to the unsymmetrical disturbance of the carboxylate ion on reaction with the $\mathrm{R_3NH^+}$ cation. The terminal C = O group of the second acid molecules gives a νC = O band at ~1710 cm^{-1}, which is superimposed on the νC = O band of the molecular complex of the acid with the amine [2].

Additional data on the presence of equilibria in the described systems can be obtained from the spectra at ~1200 cm^{-1}, where there is a characteristic band of a carboxyl group that is sensitive to intermolecular interaction. The frequency of the νC—O band [or, more accurately, νC—O with the participation of δ OH (see [18])] for the acetic acid dimer is 1291 cm^{-1} (solution in $\mathrm{C_2Cl_4}$). When the solution is heated, a band at 1180 cm^{-1}, which is intensifed at the expense of the band at 1291 cm^{-1} and consequently belongs to the monomer, appears. The frequency of the corresponding band for the isobutyric acid dimer is 1239 cm^{-1}, while the frequency of the monomer is 1180 cm^{-1}. When the complex of isobutyric acid with strong proton acceptors is formed, this band occupies an intermediate position between the monomer and dimer, and the frequency of the νC—O band increases, approaching the frequency of the dimer (1210, 1212, and 1225 cm^{-1}, respectively), in the order pyridine, dimethyl sulfoxide, and trimethylphosphine oxide as the hydrogen bond becomes stronger. A band appears in this same region at 1215 cm^{-1} in the spectrum of a solution of isobutyric acid in triethylamine. Similarly, the frequencies in the spectra of solutions of acetic acid in pyridine (1265 cm^{-1}) and trioctylamine (doublet at 1263 and 1252 cm^{-1}) are extremely close. This makes it possible to speak of the existence of a molecular complex in solutions of these acids in tertiary amines.

Thus equilibrium between two types of complexes of the acids with the amines — a molecular complex with an OH...N hydrogen bond and 1 : 1 and 2 : 1 ionic complexes — exists in solutions of the acids in amines. When the temperature is raised, the intensity of the bands of the ionic complexes decreases, and the νC = O band of the molecular complex increases, such that the equilibrium is shifted to favor the latter. This means that the ionic complex is energetically more favorable than the molecular complex. A comparison of the spectra of solutions of the acids in various amines shows that for both acids the equilibrium is shifted to favor the molecular complex on passing from trioctylamine to triethylamine, in conformity with the decrease in their proton-acceptor capacity [19]. Acetic acid in solution in triethylamine is present almost entirely as a complex with a hydrogen bond. This was noted in [20], but De Tar and Novak did not discuss the possibility of an equilibrium between the molecular complex and the ion pair. On the other hand, the opposite point of view, first formulated in [22], according to which the complex of acetic acid with triethylamine has an ionic structure, has been widely propagated (cf. [21]). In addition, in [22] no mention is made of the possibility of the simultaneous existence of two types of complexes, whereas the results of the present study definitively indicate that both secondary [2, 4] and tertiary amines react with carboxylic acids to give two types of complexes that are in equilibrium with one another.

The relative percentages of 1 : 1 and 2 : 1 complexes under comparable conditions depend substantially on the proton-donor capacity of the acid: while the 2 : 1 complex is formed only in the presence of excess acid in the case of the strong acids $\mathrm{C_3F_7COOH}$ and $\mathrm{CCl_3COOH}$ [14], in the case of monohaloacetic acids the equilibrium can be shifted completely to favor 1 : 1 complexes only in the presence of a three-fold

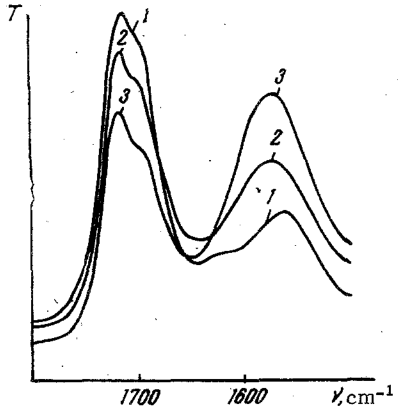


Fig. 2

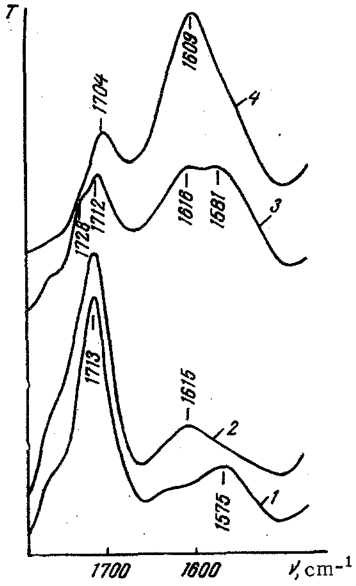


Fig. 3

Fig. 2. Spectra of equimolar solutions of isobutyric acid and triethylamine (0.5 mole/liter of each) in C_2Cl_4 containing: 0 (1), 0.5 (2), and 1.5 mole/liter (3) of methanol (d = 45.7 μm).

Fig. 3. Spectra of equimolar solutions of acetic acid and triethylamine (0.4 mole/liter of each) in C_2Cl_4 (1), $(CH_3)_2SO$ (2), CH_3CN (3), and $CHCl_3$ (4) (d = 45.7 μm).

excess of amine [23]. For weaker proton donors such as acetic and isobutyric acids, the 2:1 complex does not vanish even in a solution of these acids in the amine. This may be explained by the difference in the energies of addition of an acid molecule to the amine and to the 1:1 complex, which depends on the strength of the acid. A decrease in the proton-donor capacity of the acids in the examined series will lead to a decrease in the energy of their bonds with the amine, while a simultaneous increase in the electron-donor capacity of the anion in this series will lead to a certain increase in the strength of the OH...O hydrogen bond in the 2:1 complex.

The effect of the solvent on the molecular complex-ion pair equilibrium position is shown in Figs. 2 and 3. It is seen from Fig. 2 that the equilibrium position in a solution in C_2Cl_4 containing equimolar amounts of isobutyric acid and triethylamine does not differ qualitatively from that in a solution of the acid in the amine. The increase in the intensity of the band at 1560 cm^{-1} is explained by the more favorable conditions for the formation of a 2:1 complex as compared with the solution in the amine. The addition of an equivalent amount of methanol to the solution will lead to a decrease in the intensity of the $\nu C = O$ band and to an increase in $\nu_a CO_2^-$; this indicates a shift in the equilibrium to favor the ionic form. When the amount of methanol is increased, the equilibrium continues to be shifted, and the band of the isobutyrate ion remains the only one in the spectrum of a solution in pure methanol. The effect of methanol on the equilibrium position is easy to explain starting from the concepts of local intermolecular interaction. The formation of a $CH_3OH...O = C$ hydrogen bond with the carbonyl group of the acid in the acid-amine molecular complex causes an additional shift of the electron cloud of the carboxyl group toward the oxygen atom of the C = O group, which, as in the case of 2:1 complexes, facilitates transfer of a proton along the OH...N hydrogen bond. The same shift in the equilibrium is observed for the acid-secondary amine system under the influence of hydroxyl-containing proton donors [4]. The effect of chloroform on the equilibrium position is realized via this same mechanism, although, because of its lower proton-donor capacity as compared with methanol, the shift of the equilibrium to favor the ion pair is not as pronounced as in CH_3OH (Fig. 3; a similar pattern is also observed for isobutyric acid). One's attention is directed to the successive decrease in $\nu_a CO_2^-$ on passing from the free ion pair in solution in the amine or C_2Cl_4 (1624 cm^{-1}) to the ion pair participating in the hydrogen bond with chloroform (1609 cm^{-1}), with methanol (1573 cm^{-1}), and with a second molecule of acid (the 2:1 complex) (1560 cm^{-1}). This decrease reflects the gradual equalization of the C—O bonds in the acid anion as the charge on the second oxygen atom increases.

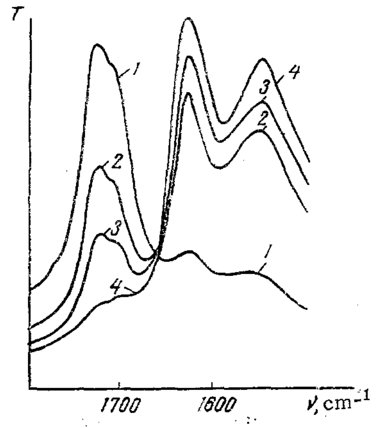
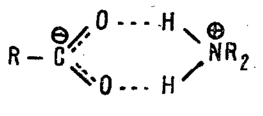


Fig. 4. Spectra of solutions of isobutyric acid (c = 0.5 mole/liter) in triethylamine in the presence of 0 (1), 0.5 (2), 1.0 (3), and 10 mole /liter (4) of diethylamine (d = 45.7 μm).

A portion of the acid molecules in a solution of an equimolar mixture of the acid and amine in acetonitrile form a hydrogen bond with the solvent molecules, as one can judge from the presence of a band at 1728 cm^{-1}, which is markedly overlapped with the band of the acid-amine molecular complex at 1712 cm^{-1}. The increase in the intensity of the $\nu_a CO_2^-$ bands as compared with the situation in an inert solvent indicates that in acetonitrile the equilibrium is shifted to favor ionic forms. In dimethyl sulfoxide (DMSO) solution, the $\nu C = O$ bands of the acid-amine complexes and of the acid-solvent complexes coincide in frequency because of the high proton-acceptor capacity of DMSO. For this reason, no appreciable amount of 2 : 1 complexes is formed in DMSO (Fig. 3). The increase in the intensity of the $\nu_a CO_2^-$ band as compared with a solution of the acid in triethylamine means that the equilibrium is shifted to favor the ionic form in solution in $(CH_3)_2SO$ as in CH_3CN.

It is appropriate to direct our attention to the different behavior of the complexes of carboxylic acids with secondary and tertiary amines in dipole solvents that are not proton donors. While the complex ⇌ ion pair equilibrium position in CH_3CN and $(CH_3)_2SO$ for the tertiary amines considered above is shifted to the right, the equilibrium position for the isobutyric acid-diisobutylamine complex in these solvents is practically the same as that for solution in an inert solvent [4]. It is difficult to give an exhaustive explanation for this, and one can only assume that the C = O group of the molecular complex of the acid with the tertiary amine is more susceptible to disturbance on the part of the dipole molecules of the solvent than in the case of the complex with a secondary amine, in which the carbonyl group participates in the hydrogen bond with the NH group of the amine [2].

Let us make a comparative estimate of the capacity of secondary and tertiary amines to act as proton acceptors during the formation of an ion pair in an inert solvent. It is clear from the results in [2, 3] that isobutyric acid on reacting with piperidine forms predominantly ion pairs at room temperature. The same pattern is also observed for isobutyric acid-diethylamine and isobutyric acid-dibutylamine systems. However, in solutions in tertiary amines isobutyric acid exists mainly in the form of a molecular complex. The character of the reaction of the acid with amines is graphically illustrated by the spectra of solutions of isobutyric acid in triethylamine containing different amounts of diethylamine (Fig. 4). Intense bands at 1620 cm^{-1} (δNH_2^+) and 1560 cm^{-1} ($\nu_a CO_2^-$) of the $C_3H_7CO_2^- \cdot H_2^+N(C_2H_5)_2$ ion pair appear in the presence of equimolar ratios of the acid and diethylamine, while the band at 1710 cm^{-1} from the molecular complex of the acid with triethylamine is markedly weakened. When the amount of $(C_2H_5)_2NH$ in solution increases, the spectrum rapidly becomes indistinguishable from the spectrum of a solution of the acid in pure diethylamine. This indicates the energetic advantage of the interaction of isobutyric acid with diethylamine as compared with triethylamine. In fact, in the case of the isobutyric acid-piperidine system it was found that the formation of an ion pair from free molecules is accompanied by the liberation of a substantially higher energy than in the formation of the molecular complex with a hydrogen bond [3]. In addition, aliphatic secondary amines form a stronger hydrogen bond with a standard proton donor than tertiary amines [19]. The existence of a second NH...O = C hydrogen bond in the acid-amine molecular complex is apparently the factor that stimulates the formation of an ion pair in the case of a secondary amine. This bond will lead to an increase in the electron density on the nitrogen atom and to a decrease in electron density on the OH group; this also facilitates transfer of a proton along the OH...N bond to form an ion pair.



In conclusion, we add that the region above 1800 cm^{-1}, in which the frequencies of the XH valence vibrations lie, proves to be of little use for the study of the equilibrium between the molecular complex and ion pair. The spectra of the same acid that forms a molecular complex (for example, complexes of isobutyric acid with pyridine, triethylamine, dimethyl sulfoxide, and trimethylphosphine oxide) and an ion pair (complexes of isobutyric acid with piperidine and dibutylamine) do not differ quantitatively in this region.

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