

SPECTROSCOPIC INVESTIGATION OF THE INTERACTION OF ISOBUTYRIC ACID WITH PIPERIDINE

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Studying intermolecular interactions in carboxylic acid-amine systems opens up the possibility of systematically investigating proton transfer in complexes with hydrogen bonding. The presence of an equilibrium between two types of complex (a molecular complex and an ion pair formed as a result of proton transfer through hydrogen bonding) is a criterion for the existence of two minima on the potential energy surface of the interaction between a proton donor and a proton acceptor [1]. The existence of this equilibrium was first recorded in [2], but no reference has been made to it in subsequent investigations of carboxylic acid-amine systems (for example, [3-5]). In the present communication, we will give the results of an investigation of the equilibria in systems containing isobutyric acid (IBA) and piperidine from their IR absorption spectra. The spectra were recorded on IKS-12 and IKS-14 instruments and the experimental technique was analogous to that described in [6].

It is logical to begin the interpretation of the spectra of the acid-piperidine system by considering the simplest case of solutions of the acid in the amine in which the probability of dimerization of the acid and formation of complexes containing more than one acid molecule is minimal. In the spectrum of a solution of IBA in piperidine (Fig. 1), bands are observed at 1560, 1620, and also 1410 cm^{-1} , which can be identified as the $\nu_{\alpha}\text{CO}_2^-$, δNH_2^+ , and $\nu_{\text{S}}\text{CO}_2^-$ of an acid-amine complex having an ion-pair structure. When the temperature is increased, the intensity of these bands is diminished, the barely noticeable absorption in the $\nu\text{C}=\text{O}$ region is strengthened, and a doublet band appears at 1700 and 1720 cm^{-1} [6]. As was shown in [6], the existence of dimers in solutions of IBA in dioxan and pyridine can be eliminated. Consequently, the band with its center at 1710 cm^{-1} in the spectrum of a solution of IBA in piperidine, which is a stronger proton acceptor, cannot belong to a dimer and the doublet at 1700 and 1720 cm^{-1} is therefore assigned to the $\nu\text{C}=\text{O}$ vibrations of the carbonyl group of an IBA molecule participating in hydrogen bonding between its hydroxyl group and the nitrogen atom of the piperidine. At each given temperature, the intensity of this band changes in proportion to the concentration of the acid, which provides grounds for ascribing this band to 1:1 complexes.

The interpretation of the 1560 and 1620 cm^{-1} bands can be confirmed by studying the spectra of solutions of the acid and piperidine in water and methanol. It can be seen from Fig. 2 that the $\nu\text{C}=\text{O}$ band at 1705 cm^{-1} in the spectrum of IBA in CD_3OD , which belongs to acid molecules bonded with alcohol molecules, decreases in intensity in strict proportion to the amount of piperidine added to the solution and disappears completely when the ratio of the components is equimolar. At the same time, the $\nu_{\alpha}\text{CO}_2^-$ band of the acid anion appears at 1560 cm^{-1} . The half width of the 1560 cm^{-1} band is 30 cm^{-1} and its integral absorption coefficient A is $7.5 \cdot 10^4$ liter/mole $\cdot \text{cm}^2$. The spectrum of a solution of IBA and piperidine in D_2O is completely analogous. In these solvents, the ion pairs are dissociated and the $\text{C}_3\text{H}_7\text{COO}^-$ and $(\text{CH}_2)_5\text{ND}_2^+$ ions participate in hydrogen bonds with the solvent molecules. This leads to the complete equalization of the CO bonds of the carboxylate ion. Under these conditions, the δNH_2^+ band at 1620 cm^{-1} is absent owing to hydrogen exchange with the solvent.

Consequently, in solutions of IBA in piperidine there is an equilibrium between two forms of the 1:1 IBA-amine complex, i. e., an ion-pair form and a form consisting of a molecular compound with hydrogen bonding, this equilibrium being strongly shifted towards the ion pair at room temperature. The spectroscopic criteria for the first type of complex are the $\nu_{\alpha}\text{CO}_2^-$ band at 1560 cm^{-1} , the $\nu_{\text{S}}\text{CO}_2^-$ band at 1410

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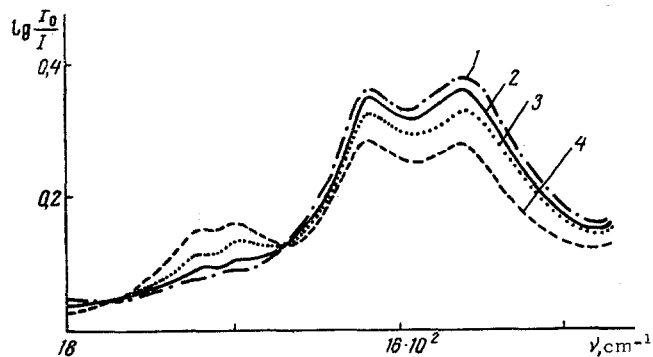


Fig. 1. Spectra of a solution (0.4 mole/liter) of IBA in piperidine: 1) 20; 2) 40; 3) 65; 4) 90°C.

cm^{-1} and the δNH_2^+ band at 1620 cm^{-1} , and the criterion for the second type of complex is the $\nu\text{C}=\text{O}$ doublet at 1700 and 1720 cm^{-1} . When the temperature is increased, the equilibrium is shifted towards the energetically more favorable form, which proves to be the molecular complex. The fact that the $\nu_{\alpha}\text{CO}_2^-$ frequency of the isobutyrate ion is the same in aqueous solution and in piperidine solution indicates its symmetrical structure in the ion pair, which is guaranteed by the formation of two $\text{NH}\cdots\text{O}$ hydrogen bonds in accordance with the hypothesis of [7]. The structure of these complexes can be represented in the following manner:



The molecular complex is not detected spectroscopically in aqueous or alcoholic solution. In the spectrum of an equimolar acid-piperidine mixture, the bands of molecular piperidine at 742 , 1111 , 1144 , 1189 , 1256 , and 1315 cm^{-1} are completely absent or are very weak and the bands at 940 and 1080 cm^{-1} characteristic of the piperidinium ion [8, 9] are visible.

In solvents with low dielectric constants, the components do not interact stoichiometrically to form ion pairs as they do in water and methanol. In solutions of an equimolar mixture of IBA and piperidine in mixed $\text{CD}_3\text{OD}-\text{CCl}_4$ solvents with different compositions, a $\nu\text{C}=\text{O}$ doublet at 1700 and 1720 cm^{-1} , and a band at 1620 cm^{-1} appear as the proportion of CCl_4 is increased, and the half width of the 1560 cm^{-1} band increases to $\sim 100\text{ cm}^{-1}$. In the spectra of solutions in C_2Cl_4 (Fig. 3) and dioxan, the $\nu\text{C}=\text{O}$ doublet is also observed, the position of the $\nu_{\alpha}\text{CO}_2^-$ band is unchanged, and its half width is $90-100\text{ cm}^{-1}$. The presence of the $\nu\text{C}=\text{O}$ band in these solvents means that part of the acid is present in molecular form. The large width of the $\nu_{\alpha}\text{CO}_2^-$ band is evidently characteristic of systems in which the ion pair is not dissociated. We should mention that in solutions in CHCl_3 , which is a weak proton donor, and also in the presence of excess acid, the half width of the $\nu_{\alpha}\text{CO}_2^-$ band is less than in CCl_4 , C_2Cl_4 , dioxan, and piperidine, but in all cases its position and integral absorption coefficient remain unchanged within the limits of experimental error: $A = (7.7 \pm 0.5) \cdot 10^4\text{ liter/mole} \cdot \text{cm}^2$.

Taking these facts into account, we can reach an interesting conclusion from an analysis of the spectra of solutions in acetonitrile, the dielectric constant of which is higher than that of methanol (36 and 33) but whose molecules cannot form hydrogen bonds as proton donors. When the concentration of IBA and piperidine in CH_3CN is 0.3 mole/liter each the spectrum in this region is very similar to the spectrum of the solution in CCl_4 , i. e., there is a $\nu\text{C}=\text{O}$ doublet and the half width of the $\nu_{\alpha}\text{CO}_2^-$ band is $\sim 80\text{ cm}^{-1}$. This means that the stoichiometric proton transfer from IBA to piperidine with dissociation of the ion pairs is due not so much to the high dielectric constant of the solvent as to the ability of its molecules to form hydrogen bonds as proton donors.

It has been shown in a number of works [2-5] that complexes with a $2:1$ composition and higher, i. e., containing more than one acid molecule, can be formed as a result of the interaction of acids with amines. Spectra of solutions of IBA and piperidine in C_2Cl_4 are shown in Fig. 3a. The IBA concentration here was kept constant while the piperidine concentration was changed so that the relative content of IBA and piperidine was $1:7$, $1:1$, and $1:0.5$. It can be seen that the intensity of the doublet centered at 1710 cm^{-1} increases as the amount of piperidine decreases. At the same time, the intensity of the $\nu_{\alpha}\text{CO}_2^-$ band at 1560 cm^{-1} and the δNH_2^+ band at 1620 cm^{-1} decreases. The same changes occur when the concentration of solutions of equimolar mixtures of IBA and piperidine is changed (Fig. 3b).

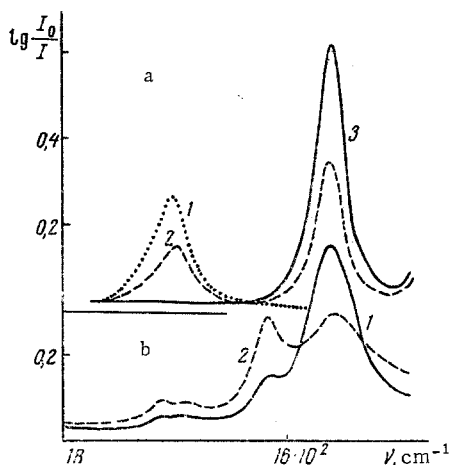


Fig. 2

Fig. 2. Spectra of solutions of IBA and piperidine in d-methanol, CCl_4 and their mixture: a) solution in d-methanol, IBA concentration 0.17 mole/liter, piperidine concentration: 1) 0; 2) 0.08; 3) 0.16 mole/liter; b) solution in CCl_4 , IBA and piperidine concentration 0.3 mole/liter, d-methanol concentration: 1) 0.3 mole/liter; 2) 0.

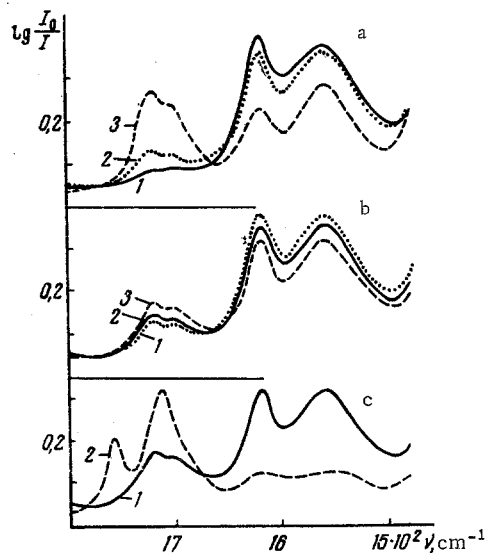


Fig. 3

Fig. 3. Spectra of solutions of IBA and piperidine in C_2Cl_4 : a) IBA concentration 0.4 mole/liter, piperidine concentration: 1) 2.8; 2) 0.4; 3) 0.2 mole/liter; b) equimolar mixtures of the acid and piperidine at concentrations of: 1) 0.4; 2) 0.14; 3) 0.025 mole/liter; c) equimolar mixture of the acid and piperidine (concentration 0.025 mole/liter) at temperatures of 20 (1) and 90°C (2).

We can conclude that the amount of complexes consisting of two acid molecules and one amine molecule, which are the products of the addition of an acid molecule to an ion pair, increases both when the proportion of piperidine is decreased and when the solution is diluted. This latter acid molecule evidently forms a hydrogen bond with the carboxylate ion, and the doublet at 1710 cm^{-1} belongs to its $\text{C}=\text{O}$ group. In spite of the fact that the frequencies and relative intensity of the components of the doublet are exactly the same for the acid molecule bonded with the ion pair and for the acid molecule forming the hydrogen bond with the amine, there can be no doubt about the existence of the 2:1 complexes. Since equilibrium (1) characterizes a monomolecular process, the ratio of the intensities of the band at 1560 (or 1620) cm^{-1} and the doublet at 1710 cm^{-1} must remain constant at a given temperature, irrespective of the composition of the system. It is therefore impossible to explain the increase in the intensity of the 1710 cm^{-1} doublet observed in Fig. 3 in terms of an increase in the number of 1:1 complexes with hydrogen bonding; it indicates an increase in the number of 2:1 complexes.

The doublet at 1700 and 1720 cm^{-1} serves as an analytical band for determining the concentration of 2:1 complexes. The number of these is proportional to the intensity of the doublet bands after deducting the contribution made by the $\nu\text{C}=\text{O}$ absorption of the IBA molecules associated with piperidine by hydrogen bonding. The integral absorption coefficient of the $\nu\text{C}=\text{O}$ doublet, both for the 2:1 complexes and for the IBA-piperidine complexes with hydrogen bonding, can be taken as $4 \cdot 10^4$ liter/mole $\cdot\text{cm}^2$, bearing in mind that it is 3.6 , 4.0 , and $4.3 \cdot 10^4$ liter/mole $\cdot\text{cm}^2$ for the IBA-dioxan and IBA-pyridine complexes and the acid dimer respectively [6, 10]. In the IBA-pyridine complex (with strong hydrogen bonding) the $\nu\text{C}=\text{O}$ band is also a doublet at 1700 and 1720 cm^{-1} , while in the dimer the carbonyl group itself participates in hydrogen bonding, which is evidently the reason for the further increase in its absorption coefficient. Experimental measurement of the absorption coefficient of the doublet involves a considerable error but gives, on average, a value close to $4 \cdot 10^4$ liter/mole $\cdot\text{cm}^2$.

In determining the concentration of 2:1 complexes from the $\nu\text{C}=\text{O}$ band, attention must be paid to the possibility of the existence of acid dimers, the $\nu\text{C}=\text{O}$ band of which is situated at 1707 cm^{-1} . The number of dimers can be calculated if the dimerization constant K_g of the acid is known and the number of

monomers has been measured from the ν_{OH} band at 3540 cm^{-1} . Such a calculation was carried out for the systems whose spectra are shown in Fig. 3, using the values of K_g and the integral absorption coefficient of the ν_{OH} band of the monomers obtained in [10]. It was found that even in the most dilute solution, containing 0.025 mole/liter each of IBA and piperidine, not more than 0.5% of the acid molecules are associated into dimers. At the same time, the proportion of IBA molecules taking part in hydrogen bonding with 1:1 complexes, i. e., the number of 2:1 complexes, is $\sim 20\%$. When the solution is heated, however, the $\nu_{C=O}$ band of the dimers appears between the components of the doublet, and the $\nu_{C=O}$ band of the acid monomers at 1757 cm^{-1} and the intensity of the $\nu_{\alpha}CO_2^-$ and δNH_2^+ bands diminish (Fig. 3c).

Thus, in solutions containing isobutyric acid and piperidine, an equilibrium is established between the free molecules of acid and amine, the dimers of the acid, two types of 1:1 acid-amine complex (a molecular complex with hydrogen bonding and an ion pair) and, finally, 2:1 complexes arising when a hydrogen bond is formed between an acid molecule and a 1:1 complex. The position of the equilibrium depends on the concentration of acid and amine in solution, the temperature, and the nature of the solvent.

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