

HYDROGEN BONDING AND PROTON TRANSFER IN CARBOXYLIC
ACID-AMINE SYSTEMS. SPECTROSCOPIC INVESTIGATION OF THE
EQUILIBRIUM BETWEEN A MOLECULAR COMPLEX AND AN ION PAIR

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Of particular interest in studies of strong hydrogen bonding in media of low dielectric constant is the case in which there is an equilibrium between a hydrogen-bonded molecular complex ($A-H \cdots B$) and an ion pair ($\bar{A} \cdots H^+ - B$), formed by transfer from a proton donor to an acceptor. Spectroscopic investigation of this type of equilibrium yields information regarding the parameters of the potential function of the proton in the hydrogen bond. This is also of interest in connection with quantitative calculations of the simplest systems in which proton transfer takes place [1].

The actual existence of equilibria of the type $A-H \cdots B \rightleftharpoons \bar{A} \cdots H^+ - B$ has been demonstrated by Barrow [2]. In his investigation of the IR absorption spectra of complexes of pyridine with carboxylic acids in $CHCl_3$, Barrow found that pyridine interacts with acetic acid to form a molecular compound with a hydrogen bond and with trichloroacetic acid to form an ion pair, while in the intermediate case (with mono- and dichloroacetic acid) an equilibrium between these forms exists. The system $CHCl_2COOH^-$ pyridine in C_6H_6 was also studied by dielectric-constant measurements. These authors [3] obtained results fundamentally in agreement with those of Barrow [2] but Gough and Price [4] concluded that a molecular complex is formed. The object of the present work was to investigate quantitatively the IR spectra of the systems described by Barrow [2] and to measure the thermodynamic characteristics of the complex. Moreover, in a search for new systems in which there is an equilibrium due to transfer of a proton, we studied the interaction of a specific proton donor (isobutyric acid) with amines differing in proton-acceptor power (pyridine, trioctylamine, triethylamine, diethylamine, and piperidine). Spectra of the binary systems and of their solutions in $CHCl_3$ and C_2Cl_4 (0.1-1.6 mole/liter) were recorded with UR-20 and IKS-12 instruments. The sample temperature was held constant within $\pm 1^\circ C$.

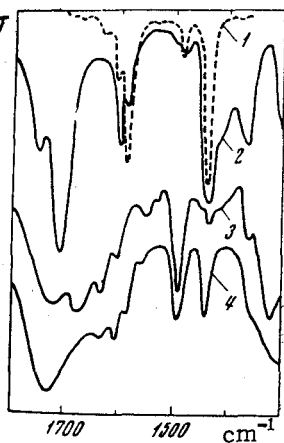


Fig. 1. Spectra of $CHCl_3$ solutions (0.5 mole/liter) of: 1) C_5H_5N ; 2) $C_5H_5N + CH_3COOH$; 3) $C_5H_5N + CCl_3COOH$; 4) $C_5H_5N + CHCl_2COOH$. Cell thickness 0.1 mm.

The most interesting region of the spectrum is that lying between 1300 and 1800 cm^{-1} , which contains bands due to skeletal vibrations of the pyridine molecule, bands due to the carbonyl group of the acid, and bands due to the pyridinium and acid ions. When a hydrogen bond was formed, there was practically no change in the frequency of the 1440 cm^{-1} band of pyridine, but the band at 1585 cm^{-1} (like those at 605 and 991 cm^{-1}) shifted to a higher frequency. Precisely the same picture was observed for the spectrum of the solution of pyridine and CH_3COOH in $CHCl_3$ (Fig. 1). all of these bands were essentially absent in the presence of CCl_3COOH , but bands appeared at 1490 and 1635 cm^{-1} , which are characteristic of the pyridinium ion. The presence of ν_s and ν_a of CO_2^- (1320 and 1675 cm^{-1}) confirmed our conclusion that ion pairs were formed. The spectrum of the solution of pyridine and $CHCl_2COOH$ in $CHCl_3$ (Fig. 1) showed a band at 1490 cm^{-1} , a band assigned to the carboxylate ion, and a band at 1440 cm^{-1} . The absence of any free pyridine bands and the shift of the 1585 cm^{-1} band to 1603 cm^{-1} indicate the following equilibrium, in agreement with Barrow [2]:

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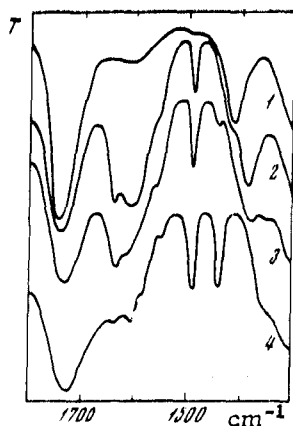
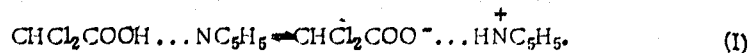
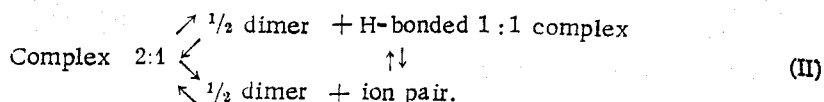


Fig. 2. Spectra of CHCl_3 solutions containing 0.6 mole/liter CHCl_2COOH and $\text{C}_5\text{H}_5\text{N}$ in the following concentrations (in moles/liter): 1) 0; 2) 0.1; 3) 0.3; 4) 0.6. Cell thickness 0.1 mm.

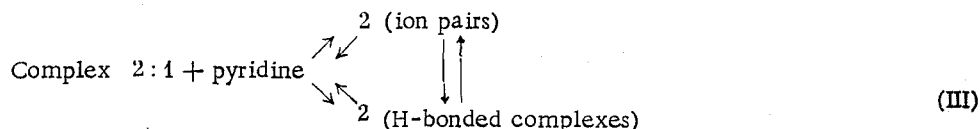


The spectrum of pyridine and CH_2ClCOOH was similar, but the ion bands were significantly weaker.

The above information relates to equimolar concentrations. However, addition of a second molecule of acid to the ion pair or hydrogen-bonded 1:1 complex is possible in excess acid. In this case, one would expect that the hydrogen bond would be so strengthened as to lead to proton transfer [5, 6]. Indeed, the changes in the spectra of CHCl_3 solutions of CHCl_2COOH containing different amounts of pyridine (Fig. 2) showed that all 2:1 complexes exist in ionic form, as previously noted by others [2, 7]. At the 2:1 concentration ratio, in addition to bands due to the 2:1 ionic complex the spectrum showed the weak band at 1440 cm^{-1} assigned to pyridine in a molecular complex, and the band increased in intensity with dilution. It may be concluded that at the stoichiometric concentration ratio, 2:1 complexes are partially dissociated into the 1:1 complex and the dimer of the acid:



A further increase in $\text{C}_5\text{H}_5\text{N}$ concentration increased the intensity of the band due to the hydrogen-bonded complex, and in place of ν_s 1380 and ν_a 1600 cm^{-1} of the dichloroacetate ion in the 2:1 complex, bands appeared at 1360 and 1645 cm^{-1} due to this ion in a 1:1 pair. Finally, the form of the spectrum was almost completely determined by equilibrium (I) when the concentrations were equimolar. The presence of a very weak band at 1585 cm^{-1} indicated the presence of a small amount ($\sim 5\%$) of free pyridine molecules and, consequently, the existence of the equilibrium



greatly shifted to the right.

Measurement of the intensities of the 1440 and 1490 cm^{-1} bands (assigned to the hydrogen-bonded complex and the ion pair) at different ratios of acid to pyridine made possible determination of the absorption coefficients of these bands and calculation of the equilibrium constant $K = C_1/C_2$, where C_1 is the concentration of the ion pair and C_2 is the concentration of H-bonded complex. At absolute concentrations of acid and pyridine in the solution of less than 0.7 mole/liter, the value of K is independent of absolute concentration and is $K_{20^\circ} = 1.2 \pm 0.3$. The heat of reaction (I) $\Delta H = 3.6 \pm 0.8 \text{ kcal/mole}$ was determined from the temperature dependence of the intensities of the 1440 and 1490 cm^{-1} bands over the range of 10 - 50°C . The accuracy of the intensity measurements was limited by the presence in all spectra of a strong background absorption with a maximum in the region from 1100 to 1500 cm^{-1} . Figure 3 shows the 1440 and 1490 cm^{-1} bands at the two extreme temperatures. It is significant that the number of ion pairs increased with a decrease in temperature. This implies that the form with the transferred proton is the most favored energetically.

K began to increase with an increase in concentration at absolute concentrations greater than 0.7 mole/liter, and $K_{20^\circ} \approx 7$ at acid and pyridine concentrations of 1.6 moles/liter. The corresponding shift in equilibrium (I) can be ascribed to association of the ion pairs which begins at the higher concentrations. The cause of association could be dipole-dipole interaction [8], since the dipole moment of such ion pairs is quite high [9].

The spectra of solutions of isobutyric acid in piperidine showed bands at 1560 and 1410 cm^{-1} , which are assigned to ν_a and ν_s vibrations of the carboxylate ion. In addition, there was a band at 1620 , which is assigned to δNH_2^+ deformation vibrations of the dialkylammonium ion [10]. No bands that could be assigned to the carbonyl group appeared in the region above 1620 cm^{-1} . Consequently, interaction of the acid with piperidine occurs via transfer of the proton of the carboxyl group to the nitrogen atom with the formation of an ion pair. The spectra of

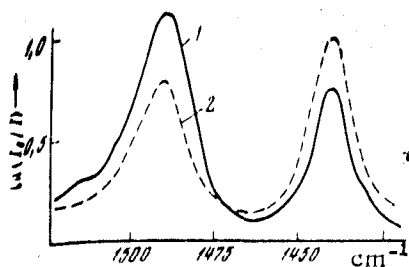


Fig. 3. Temperature dependence of bands due to the pyridinium ion and pyridine in a molecular complex. 1) 12°; 2) 48°C.

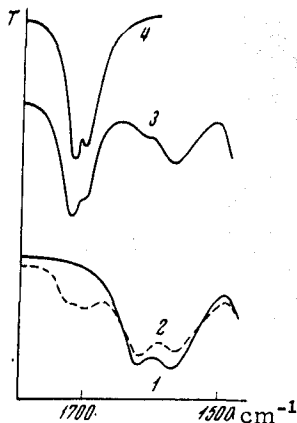


Fig. 4. Spectra of solutions of $(\text{CH}_3)_2\text{CHCOOH}$ in amines (0.4 mole/liter). 1) In $(\text{CH}_2)_5\text{NH}_4$; 2) in $(\text{CH}_2)_5\text{NH}$ at 90°C; 3) in $(\text{C}_8\text{H}_{17})_3\text{N}$; 4) in $\text{C}_5\text{H}_5\text{N}$. Cell thickness 0.046 mm. Curves 1, 3 and 4 at 20°.

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solutions of $(\text{CH}_3)_2\text{CHCOOH}$ in the less basic diethylamine, trioctylamine, and triethylamine contained ion bands at these same frequencies, and, in addition, a doubler appeared at 1710 cm^{-1} . The intensity of this band increased from $(\text{C}_2\text{H}_5)_2\text{NH}$ to $(\text{C}_8\text{H}_{17})_3\text{N}$ to $(\text{C}_2\text{H}_5)_3\text{N}$, and the ion bands simultaneously decreased in intensity (Fig. 4). The band at 1710 cm^{-1} is assigned to a carboxyl group with its hydroxyl involved in hydrogen bonding. It is clear, therefore, that solutions in these amines contain acid-amine complexes formed by hydrogen bonding in addition to the ion pair. The spectra of solutions of the acid in a weaker base, pyridine, contains no ion bands - only the band at 1710 cm^{-1} appears, and it is identical to the band in the spectra of solutions in alkylamines. This indicates that in pyridine interaction does not proceed further than formation of a hydrogen bond.

Thus, at room temperature pyridine forms only the molecular compound, piperidine forms only the ion pair, and alkylamines form an equilibrium mixture of both. When the temperature of the solution of the acid in piperidine was raised, the 1710 cm^{-1} band appeared, and the intensity of the ion pair band decreased (Fig. 4). Heating of solutions of the acid in other amines led to an increase in the intensity of the 1710 cm^{-1} band and a decrease in the intensity of the ion pair band. The intensity of the 1710 cm^{-1} band did not depend on temperature in the case of pyridine. This shift in the equilibrium indicates that, as in the interaction of dichloroacetic acid with pyridine, the less energetically favored form is the hydrogen-bonded complex.

The picture is more complex in the case of solutions of $(\text{CH}_3)_2\text{CHCOOH}$ and $(\text{CH}_2)_5\text{NH}$ in C_2Cl_4 , in which a decrease in the absolute concentrations of the components or a decrease in the fraction of amine resulted in formation of 2:1 ionic complexes in equilibrium with the two types of 1:1 complexes.

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