A SPECTROSCOPIC STUDY OF THE INTERACTION OF ISOBUTYRIC ACID WITH PYRIDINE AND DIOXAN

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UDC 543.42:539.196.3

There are many papers (see [1] for review) on the spectroscopy of hydrogen bonds formed by carboxylic acid with proton donors; only in a few cases have measurements been made of the energy of the complexes formed by the acids with electron donors. The problem is complicated by the need to take account of acid dimerization, because even very dilute solutions (one too dilute to be examined spectroscopically) contain appreciable proportions of dimers. Lindberg [2] made the first attempt to measure equilibrium constants and energies of formation for mixed complexes (benzoic acid–dioxan in CCl_4) via IR spectra. He used his values for the dimerization constants of the acid in CCl_4 at 26 and 50°C to deduce from his spectroscopic values the energy of formation of the mixed complex at these temperatures, $\Delta H = 6.2$ kcal/mole. However, this quantity has been doubted in subsequent work [3, 4], in which the dimerization constants of benzoic acid in CCl_4 have been found to be very different [2]. Measurements have been made of the energy of complexes of acids with π donors [5, 6], while the energy of complexes for formic and acetic acids with pyridine have [7] been determined from the Raman spectra without allowance for acid association.

There is a need for such data in relation to systems in which there is equilibrium between the molecular complex and the ion pair formed by intermolecular photon transfer [8]. Also, quantitative examination of such systems may assist in constructing the potential function for a proton in a hydrogen bond.

We have examined the interaction of isobutyric acid with dioxan and pyridine via IR spectra; we processed the results via our data of [9], in which the dimerization of the acid was measured. The spectra were recorded with an IKS-12 instrument with LiF and NaCl prisms. We used cells having CaF_2 windows

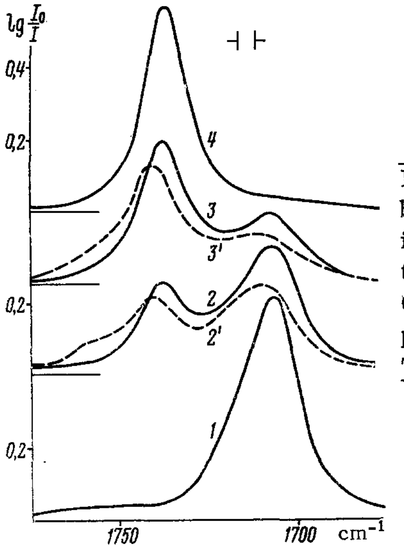

Fig. 1. The $\nu C=O$ band of isobutyric acid (0.0635 M) in CCl_4 in presence of dioxan at concentrations (M) of: 1) 0; 2 and 2') 0.54; 3 and 3') 1.38; 4) 11.75; temperature (°C): 1-4) 20; 2' and 3') 73.5. d = 0.0146 cm.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 14, No. 5, pp. 860-866, May, 1971. Original article submitted March 31, 1970; revision submitted July 30, 1970.

TABLE 1. Equilibrium Constants K for Hydrogen Bonding of Isobutyric Acid to Dioxan and Pyridine

Spectral region	°C	Equilibrium constant K, liter/mole	
		dioxan	pyridine
ν_{OH} of acid in CCl_4	20	27,3 ± 1,8	225 ± 10
	38,5	16,4 ± 1,1	113 ± 2
	53,5	12,1 ± 0,6	60 ± 6
	73,5	8,1 ± 0,5	31 ± 4
ν_{13} of pyridine in C_2Cl_4	20	—	215 ± 35
	100	—	18 ± 3
	ΔH (kcal/mole)	4,6 ± 0,3	7,5 ± 0,4

and fitted with electrical heaters. The temperature was measured by a thermocouple whose junction was placed in a hole drilled in one of the windows. The band areas were determined by planimetry.

Isobutyric Acid–Dioxan. The interaction may be described qualitatively via the spectra for the $\nu C=O$ region of the acid (Fig. 1). The $\nu C-O$ region is unsuitable for this purpose on account of marked overlap of the absorption bands of the components. When dioxan is added to a solution of the acid in CCl_4, the strength of the dimer band at 1707 cm^{-1} is reduced and a new band appears at 1737 cm^{-1}, which belongs to $\nu C=O$ in the acid with the hydroxyl group linked to the dioxan. If the acid is dissolved in pure dioxan, bands other than this do not persist, because in such a solution virtually all the acid molecules are linked to the dioxan, and there are no monomeric and dimeric molecules of the acid. The half-width of the 1737 cm^{-1} band is 15.5 cm^{-1}, while the integral absorption coefficient is $A = 3.5 \cdot 10^4$ liter/mole-cm^3, i.e., is intermediate between the A for $\nu C=O$ in the monomers and dimers [9], as is the position of this in the spectrum. Also, A is not dependent on temperature; as the temperature is raised, the intensities of the dimer and mixed-complex bands are reduced, while a band appears for the monomer at 1757 cm^{-1}. The addition of dioxan to a solution of the acid in CCl_4 reduces the intensity of the νOH band for the monomer at 3540 cm^{-1} as a result of formation of mixed complexes. There are no other absorption bands in this region, so one can make reliable quantitative estimates of the equilibrium. The spectrum of the acid in dioxan has the νOH band of the mixed complex with complex structure, the center lying at 3140 cm^{-1}. The bands for the monomer and dimer are absent under these conditions.

Isobutyric Acid–Pyridine. Detailed descriptions have been given [10, 11] of the changes in the spectrum of pyridine when the hydrogen bond is formed. The ν_{13} band is convenient for measurement (symbols as in [12]), which lies at 1574 cm^{-1} and relates to skeletal modes of the ring, and which shifts to higher frequencies when the hydrogen bond is formed. Isobutyric acid reduces its intensity and produces a band at 1591 cm^{-1}, which is superimposed on the weak ν_4 band of pyridine (Fig. 2). The A for ν_{13} is $2.3 \cdot 10^3$ liter/mole-cm^2, which does not alter when the complex with the acid is formed; as in dilute solution, a rise in temperature causes a dissociation of the complex.

Bands of the acid sensitive to hydrogen bonding are $\nu C-O$ (more precisely, $\nu C-O$ and δOH [13]), $\nu C=O$, and νOH. Figure 2 shows a spectra of the acid in solutions for the $\nu C-O$ region. The 1237 cm^{-1} $\nu C-O$ band relates to the acid dimer, and this undergoes a distinct low-frequency shift to 1210 cm^{-1} in the

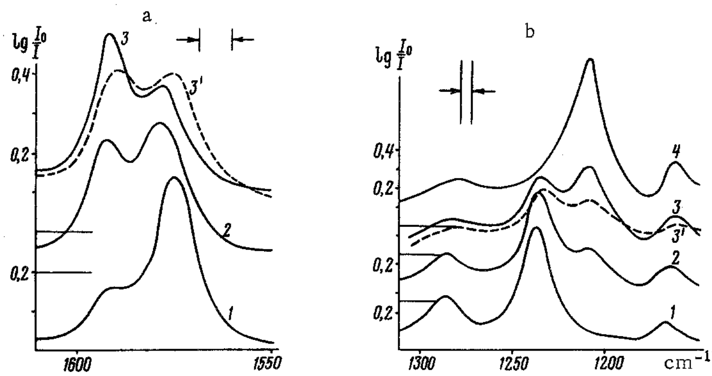

Fig. 2. a) The ν_{13} band of pyridine (0.49 M) in C_2Cl_4 in the presence of isobutyric acid (M): 1) 0; 2) 0.2; 3 and 3') 0.49; t, °C: 1, 2, 3) 20; 3') 100; d = 0.0146 cm. b) the $\nu C-O$ of isobutyric acid (0.25 M) in CCl_4 in the presence of pyridine (M): 1) 0; 2) 0.101; 3, 3') 0.253; 4) 0.778; t, °C: 1, 2, 3, 4) 20; 3') 100; d = 0.0146 cm.

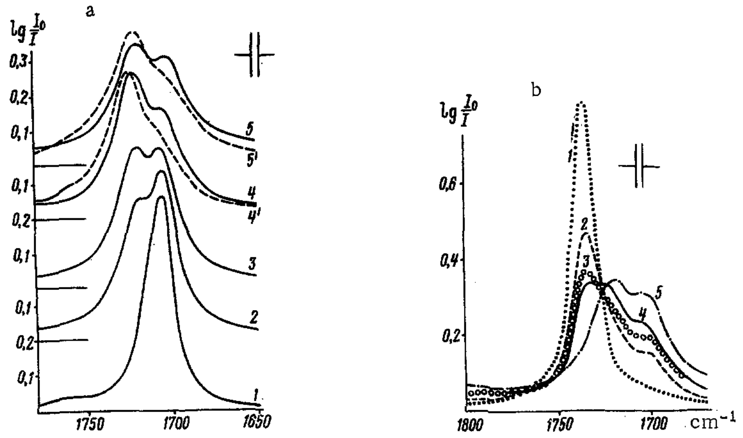

Fig. 3. The $\nu C=O$ band of isobutyric acid in the presence of pyridine: a) in CCl_4, acid (M): 1) 0.0635; 2, 3, 4, 4', 5, 5') 0.09; pyridine (M) 1) 0; 2) 0.18; 3) 0.27; 4, 4') 0.9; 5, 5') 12.4; t, °C: 1, 2, 3, 4, 5) 20; 4', 5') 73.5; d = 0.0146 cm; b) in dioxan, acid 0.09 M, pyridine (M): 1) 0; 2) 0.9; 3) 1.685; 4) 2.63; 5) 12.4; d = 0.0146 cm.

presence of pyridine on account of formation of the complex, and the integral absorption coefficient increases from $1.3 \cdot 10^4$ liter/mole-cm^2. Unfortunately, the solvent absorbs strongly in thick layers, so it was impossible to measure A for $\nu C-O$ in the acid monomer. Figure 2 shows that an acid concentration of 0.25 M is completely complexed by a threefold excess of pyridine in the solution, in fact virtually all the molecules being bound to the pyridine.

The composition of the complex was elucidated by recording spectra in the ν_{13} region of pyridine and the $\nu C-O$ region for the acid in solution in C_2Cl_4, the solutions containing equimolecular amounts of the two compounds. Graphical separation on the bands was used, and the integral absorption coefficients are known, so it was possible to deduce the proportion of pyridine bound to the acid and independently the proportion of acid molecules bound to the pyridine. Acid and pyridine concentrations of 1.5 M gave both these quantities as 0.7 ± 0.1, so the complex has a 1 : 1 composition. The residual 30% of the acid is present as dimers, while the proportion of monomers is negligibly small. An excess of pyridine (in the limit, a solution of the acid in pyridine) would allow one to displace the equilibrium completely towards the side of the mixed complex.

The interaction of the acid with pyridine produces substantial changes in the carbonyl-band region, although this group does not participate directly in forming the hydrogen bond to the pyridine. When pyridine is added to a solution of the acid in CCl_4, a new band at 1720 cm^{-1} appears, whose intensity increases at the expense of the dimer 1707 cm^{-1} band (Fig. 3a). However, the 1707 cm^{-1} band does not vanish even when there is a considerable excess of pyridine, and it persists when the acid is dissolved in pure pyridine (curve 5), in which the $\nu C=O$ band of the acid is represented by a doublet with components at 1707 and 1720 cm^{-1}. The integral absorption coefficient of the doublet band does not differ from A for the acid dimers in CCl_4 and is not dependent on temperature. Although the low frequency component of the doublet coincides in position with the dimer band, the above argument shows that this band in the presence of considerable excess of pyridine cannot belong to the dimer and resembles the 1720 cm^{-1} band in being ascribable to complexes of the acid with pyridine.

Further evidence for this is the temperature dependence of the intensity; the equilibrium shifts towards dimers and free pyridine as the temperature is raised, and the intensity of the 1237 cm^{-1} dimer band increases (curve 3' of Fig. 2b), as does the 1574 cm^{-1} band of free pyridine (curve 3' of Fig. 2a). On the other hand, the 1707 cm^{-1} band becomes weaker as the temperature is raised in the presence of excess pyridine. Also, the relative intensities of the components of the doublet are dependent on temperature, which forces us to ascribe these bands to different configurations of the complex formed by the acid with pyridine in a 1 : 1 ratio. The complex character is observed also for the new $\nu C=O$ band when pyridine interacts also with propionic and trimethylacetic acid, so it cannot be ascribed to rotational isomerism arising from rotation around the C–COOH bond. The $\nu C=O$ band is split when the isobutyric acid also interacts

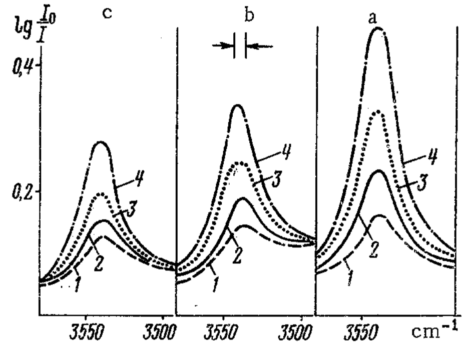

Fig. 4. Spectra in the νOH region for 0.09 M isobutyric acid in CCl_4: a) above, b) with 0.83 M dioxan, c) with 0.27 M pyridine; t, °C: 1) 20; 2) 38.5; 3) 53.5; 4) 73.5; d = 0.206 cm.

with aliphatic amines and the carboxylate ion, i.e., it is of fairly general character for strong hydrogen bonds. It may be that such complexes have a transform accompanying the cis configuration of the C = O and OH groups relative to the C – O bond. The doublet structure of the new νC = O band of isobutyric acid with pyridine is seen also in solution in dioxan, where dimers cannot be present (Fig. 3b). The position of the components of the doublet here is as for the solution in CCl_4.

In the νOH region, the acid–pyridine complex has a broad composite band peaking at about 2520 cm^{-1} and a band at 1960 cm^{-1}, i.e., there is a pattern typical of a strong hydrogen bond, as discussed in [14]. Nevertheless, there has been an assignment [15] of the 1960 cm^{-1} band for solutions in CCl_4 of palmitic and meristic acids in the presence of pyridine as due to the ion pair $RCOO^-\ldots HN^+C_5H_5$, and conclusions have even been drawn on the equilibrium constants for the formation of this pair. Our evidence is that isobutyric acid forms a 1 : 1 complex with pyridine in an inert solvent or when the acid dissolves in pyridine, and this is a molecular compound with a hydrogen bond. The bands for the carboxylate ion and the pyridine ion are not observed under these conditions. It is stated [16] that pyridine interacting with acetic acid in $CHCl_3$ also does not go further than producing hydrogen-bonded complexes.

Equilibrium Constant and Hydrogen-Bond Energy. The behavior in the systems with dioxan and pyridine can be described simply in terms of acid dimerization and formation of a 1 : 1 complex; the corresponding equilibrium constants are

$$K_d = \frac{c_d^a}{(c^a)^2}, \tag{1}$$

$$K = \frac{c^{ab}}{c^a c^b}, \tag{2}$$

where c^a and c_d^a are the concentrations of acid monomer and dimer, c^{ab} is the concentration of the mixed complex, and c^b is the concentration of the free molecules of proton acceptor (pyridine or dioxan). Previous spectroscopic measurements have given K_d for the acid in CCl_4 for the range 20-70°C; K can therefore be determined from c^a, the concentration of free acid molecules. Then c_d^a is calculated via K_d and (1), while $c^{ab} = c_0^a - 2c_d^a - c^a$, $c^b = c_0^b - c^{ab}$, where c_0^a and c_0^b are the total concentrations of the acid and pyridine respectively. Finally, (2) becomes

$$K = \frac{c_0^a - 2c_d^a - c^a}{c^a\,[c_0^b - (c_0^a - 2c_d^a - c^a)]}. \tag{3}$$

By measuring K at various temperatures one readily gets the energy of the hydrogen-bonded complex.

It is not convenient to determine c^a via the new OH band; Fig. 4 shows spectra in the region of absorption for the monomer, which illustrates the changes that occur in this band when dioxan or pyridine is introduced or the temperature is varied. We use these systems in CCl_4, with the acid concentration varying from 0.01 to 0.1 M, pyridine from 0.08 to 0.3 M and dioxan from 0.5 to 1.5 M. In each case we measured the integral intensity B of the νOH band at 3540 cm^{-1} and calculated the c^a via $A = 1.5 \cdot 10^4$ liter/mole-cm^2 from [9]. To calculate c_d^a we used [17] equation (1) in the form $c_d^a = B_2K_d/d^2A^2$ (d is thickness), because K_d/A^2 is known more accurately than K_d and A separately. Table 1 gives the mean K for each temperature. An independent measurement was made for the pyridine value for K using the 1574 cm^{-1} band for the free pyridine and 1591 cm^{-1} band for pyridine bound to the acid; spectra in this region were recorded with 0.5 M pyridine in C_2Cl_4, the acid concentration varying from 0.2 to 1.0 M. The bands were separated graphically, and their integral intensities were used to calculate c^b and c^{ab}; K was calculated from

$$K = \frac{c^{ab}}{\alpha (c_0^a - c^{ab})c^b}.$$

Here $\alpha(c_0^a - c^{ab})$ is the concentration of monomer molecules of the acid. We calculated the degree of dissociation α for the acid dimers via data of [9]. Table 1 also gives the K for 20 and 100°C; the K for 20° were measured via the band for the acid monomer and independently via pyridine bands; the values coincided, which shows that the method is reliable and free from substantial systematic errors, because the concentrations in these two series of experiments were very different. The value of K for pyridine coincided with the 220 liter/mole recorded [16] for pyridine with acetic acid, which has a proton-donor capacity similar to that of isobutyric acid.

The points fit closely to straight lines in plots of log K against 1/T, including the point K = 18 liter / mole, which was measured via the pyridine band at 100°C. From the line slope we determined the hydrogen-bond energy for dioxan as 4.6 ± 0.3 kcal/mole, while for pyridine we found 7.5 ± 0.4 kcal/mole. The latter agrees well with the 7.6 found calorimetrically for solutions of acetic acid in pyridine [18].

These results may be compared with ones for hydrogen bonds of type OH...B, which are formed by these acceptors with alcohols and phenols. The accuracy of many results is low, and there are many discrepancies between results in different papers but all the same there is a tendency for the strength of the hydrogen bonds to increase for the given acceptor in the sequence alcohol-phenol-acid, which is quite clear. For pyridine, the values for aliphatic alcohols are 3.5-4 kcal per mole [1, 19]; phenols 5.5-7 [1, 22], and with isobutyric acid 7.5 (our result). For dioxan, the energies are 2.8-3.2 for alcohols [1], 4.0-4.2 for phenols [20, 21], and 4.6 kcal/mole for isobutyric acid, in accordance with the proton-donor capacity.

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