INFRARED SPECTRA AND STRUCTURES OF COMPLEXES FORMED BY DIBASIC CARBOXYLIC ACIDS WITH AMINES IN NONAQUEOUS SOLVENTS: MALONIC ACID

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Optical and NMR methods have repeatedly been applied [1-4] to the structures of complexes formed by monobasic carboxylic acids with amines and with nitrogen heterocyclics. The bond type is substantially affected by the interaction with the solvent, and sometimes there are two types of complex present together: molecular and ionic, with the latter formed by proton transfer along a OH···N hydrogen bond [1, 5, 6]. These systems show a tendency to produce complexes containing two or more acid molecules, particularly in inert nonpolar solvents. The second molecule of acid is attached to the oxygen atom in the carbonyl group in the acid–amine molecular complex, and this initiates a proton transition, so complexes of composition 2:1, 3:1, etc., have the form of ion pairs, with the anion attached to one, two, or more molecules of acid forming a hydrogen-bond chain [4, 7, 8].

It is thus realistic to consider the interaction mechanism for dibasic acids, in which there may be intramolecular OH···O hydrogen bonds that stabilize the monoanions. This has been suggested to explain the considerable differences in the first and second dissociation constants for dibasic acids in water and nonaqueous solvents [9-12]. The intramolecular hydrogen bond characteristics are determined by energy and entropy factors, and the specific features of dibasic acids should affect the first members of the series especially: malonic, succinic, and adipic acids [13]. Here we examine complexes formed by malonic acid with aliphatic amines in various solvents by reference to the IR spectra. The data indicate the interaction between the carboxyl groups, which affects the first and second dissociation constants in acid–base interaction.

Measurements have been made [14-20] on the vibrational spectra of malonic acid and malonates in relation to structure and hydrogen-bond effect, where aqueous solutions and solid materials have been used, but there are only a few papers on solutions in aprotonic solvents [20, 21]. Diffraction methods applied to the acid salts show that the monoanion of malonic acid forms strong intermolecular hydrogen bonds in the solid of symmetrical or unsymmetrical type [22-24]. The spectra of the acid salts in aqueous solution do not enable one to judge unambiguously whether there is an intramolecular hydrogen bond (views differ). A theoretical calculation on the free monoanion [25] shows that the most stable conformation corresponds to a structure with a symmetrical O···H···O intramolecular hydrogen bond (symmetry C_{2v}).

IR spectra have been recorded for solutions of malonic acid in the presence of secondary and tertiary amines using as solvents alcohols, dioxan, and $CHCl_3$, CH_3CN, $(CH_3)_2SO$ over the range 1500-1800 cm^{-1}, where the characteristic bands of the molecular and ionic forms occur.

Figure 1 shows spectra for solutions of malonic acid and dibutylamine of various compositions in CH_3OD. In the absence of the amine, there is a band with peaks at 1710 and 1740 cm^{-1} belonging to the ν (C=O) vibration. A doublet structure for this band is characteristic

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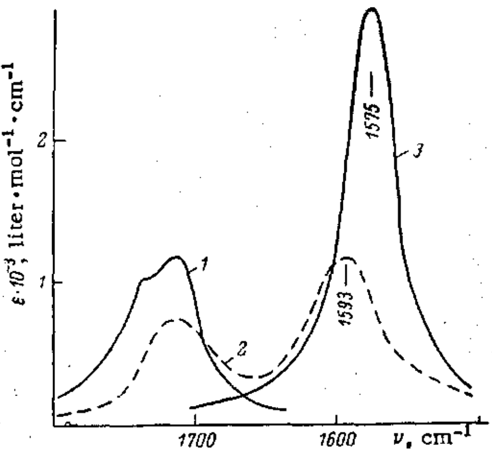
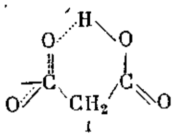


Fig. 1. Spectra of solutions of malonic acid and dibutylamine in CH_3OD, concentrations in mole/liter of acid 0.1 and amine: 1) 0; 2) 0.1; 3) 0.2.

also of alcoholic solutions of monobasic acids, and it is due to acid dimers and various complexes formed by the carboxyl group acting as dope proton donor and acceptor with alcohol molecules. It is not found that the acid ionizes under these conditions. On adding the amine, a band at 1593 cm^{-1} appears, which relates to the antisymmetric vibration of the acid anion ν_a (CO^-_2) , while at the same time the intensity of the ν (C=O) band decreases, particularly on account of the 1740 cm^{-1} component. With $c_a/c_m = 1$ (c_a and c_m are the concentrations of the amine and malonic acid in moles/liter), the ν (C=O) band becomes a singlet with its peak at 1710 cm^{-1}. Any further increase in amine concentration weakens not only the ν (C=O) 1710 cm^{-1} band but also ν_a (CO^-_2), and a new ν_a (CO^-_2) band appears at 1575 cm^{-1}, which remains the only one in this frequency range for $c_a/c_m = 2$. Similar changes on varying the acid–amine ratio are characteristic of aqueous solutions, as well as solutions of malonic acid containing other aliphatic amines. In nondeuterated solvents, the ν_a (CO^-_2) band is accompanied by a relatively weak δ (NH^+_2) one from the dibutyl ammonium cation at 1630 cm^{-1}.

The results have been interpreted on the assumption that there are singly-charged malonate anions having intramolecular hydrogen bonds (I):



I

which are formed in solution in water or alcohol under conditions where $c_a/c_m \leqq 1$; one of the oxygen atoms in the CO^-_2 group in this anion participates in a hydrogen bond to the unionized carboxy group of the malonic acid, while all the other oxygen atoms form hydrogen bonds to solvent molecules. Unsymmetrical perturbation means that the $C=O^-$ bonds in the anion become nonequivalent, and the ν_a (CO^-_2) band shifts to high frequencies by comparison with solutions of monobasic acids. The structure of (I) readily explains the picture in the ν (C=O) region for $c_a/c_m = 1$, where the number of possible types of hydrogen bond involving the carboxyl group is minimal and it is least likely that there will be acid dimers and various complexes with the solvent.

As the amine content increases, the intramolecular hydrogen bond in (I) is broken and the second carboxyl group ionizes, as is evident from the intensity reductions in the 1593 and 1710 cm^{-1} bands and the appearance of the 1575 cm^{-1} one. For $c_a/c_m = 2$, the acid becomes completely ionized. The persisting 1575 cm^{-1} band relates to ν_a (CO^-_2) in the doubly charged malonate anion having four equivalent $C=O^-$ bonds. Vibration interaction probably causes the integral absorption coefficient $A = 9.5 \cdot 10^4$ liters/(mole·cm^2) per CO^-_2 group and the halfwidth $\Delta\nu_{1/2}$ = 45-50 cm^{-1} of the ν_a (CO^-_2) band from the malonate ion in CH_3OD to exceed the corresponding quantities for the ν_a (CO^-_2) band for the singly charged anions of the monobasic carboxylic acids ($A = 7.5 \cdot 10^4$ liters/(mole·cm^2) and $\Delta\nu_{1/2}$ = 30 cm^{-1}).

Therefore, spectrophotometric titration of the acid with an amine indicates that the process occurs in two stages, which agrees with the ionization constants of malonic acid differing by three orders of magnitude (pK_1 2.86, pK_2 5.7). Unfortunately, malonic acid is only

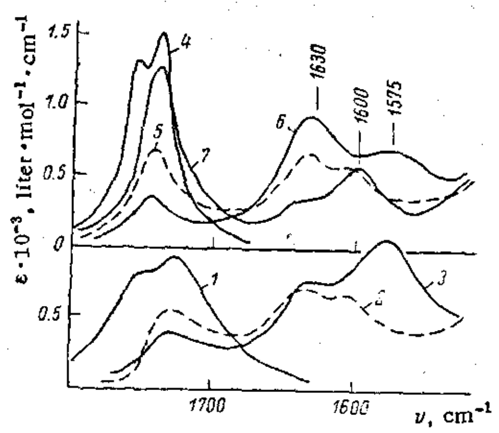
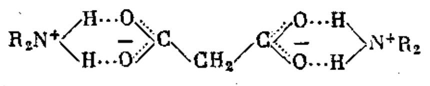


Fig. 2. Spectra of solutions of malonic acid in chloroform (1-3) and in dioxane (4-7) with the addition of dibutylamine (1-6) and tributylamine (7). Acid concentrations in moles/liter: 1) 0.01; 2, 3) 0.2; 4-7) 0.06; amine: 1, 4) 0; 2) 0.2; 3) 0.4; 5, 7) 0.06; 6) 0.12.

sparingly soluble in inert solvents, so one cannot record the spectra of the complexes with minimal environmental perturbation. Nevertheless, one can use solvents such as the proton-donor octanol and chloroform or dipolar acetonitrile and dimethylsulfoxyl (DMSO) or else the proton-acceptor nonpolar dioxane in order to establish the effects of the various interactions on the structure. Although the solvents differ in properties, the spectral signs of the interaction between malonic acid and amines are qualitatively similar for them. An exception is represented by DMSO, whose effects on the structure of the malonic acid—amine complexes is considered below.

Figure 2 shows that the ν (C=O) band of the acid occurs in the absence of the amine with its peak at 1715-1760 cm⁻¹; the ν (C=O) frequency is dependent on the solvent. With $C_8H_{17}\cdot OH$ and $CHCl_3$, where the carbonyl groups participate in forming dimers and molecular complexes with the proton-donor solvent molecules, the ν (C=O) band lies at about 1715-1730 cm⁻¹. In the cases of dioxane and acetonitrile, which are proton acceptors, the ν (C=O) band lies at higher frequencies; the interactions between the vibrations of the two carbonyl groups cause it to split into components at 1740 and 1758 cm⁻¹. Secondary amines (diethylamine or dibutylamine) weaken the ν (C=O) band and alter its shape, and for $c_a/c_m = 1$ the intensity of the ν (C=O) band is reduced by more than a factor 2. Solutions in dioxan and CH_3CN show the high-frequency component of the ν (C=O) band vanishing completely, while the 1740 cm⁻¹ component is observed against a background of a broad ν (C=O) band at 1720-1730 cm⁻¹. At the same time, bands at 1600-1610 and 1630 cm⁻¹ arise, which relate to ν_a (CO^-_2) and δ (NH^+_2) correspondingly. The high frequency of ν_a (CO^-_2) and the behavior of the ν (C=O) band indicate that at $c_a/c_m \leq 1$ one gets ion pairs with intramolecular $OH\cdots O^-$ hydrogen bonds and unsymmetrical $C\underline{\cdots}O^-$ bonds in the singly charged anion, which forms a hydrogen bond to the N^+H_2 group in the dialkylammonium cation. As the concentration of the secondary amine increases in accordance with $c_a/c_m > 1$, one gets further weakening in the ν (C=O) band and also a loss of intensity in the ν_a (CO^-_2) 1600-1610 cm⁻¹ one. With c_a/c_m of 2, the ν_a (CO^-_2) 1570-1580 cm⁻¹ band predominates, which belongs to the doubly charged malonate ion with equivalent $C\underline{\cdots}O^-$ bonds in the (II) complex:



II

The interaction of malonic acid with secondary amines in the solvents used here is not stoichiometric: there is an equilibrium between the free acid and structures I and II, which shifts toward the free form as the temperature increases or the concentration decreases. For example, dibutylamine—malonic acid mixtures in dioxan and CH_3CN show prominante ν (C=O) bands from complexes of malonic acid with the solvents, because the molecules of these compete with the amine to form hydrogen bonds with the acid. It has not proved possible to record molecular complexes with $COOH\cdots N$ hydrogen bonds evidently because the equilibrium between the molecular complex and the ion pair is heavily shifted toward the ionic form.

Malonic acid interacts with tertiry amines in chloroform, dioxan, and acetonitrile, but this does not go further than 1:1 complexes. Raising the amine concentration to a 30-fold excess over the acid does not influence the spectra: the intensities of the ν_a (CO^-_2) 1600 cm⁻¹ and ν (C=O) bands, whose frequencies are dependent on the solvent type, remain unchanged.

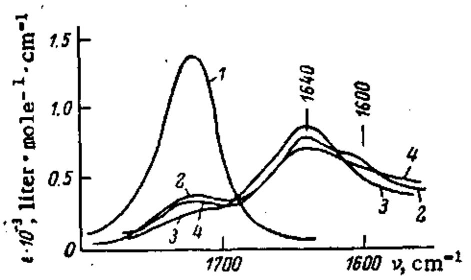
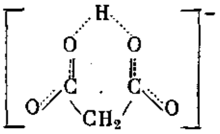


Fig. 3. Spectra of solutions of malonic acid and dibutylamine in dimethylsulfoxide, acid concentrations in moles/liter: 1) 0.2; 2) 0.43; 3, 4) 0.07; amine, moles/liter: 1) 0; 2) 0.6; 3, 4) 0.1; temperatures, °C: 1-3) 25; 4) 100.

The intensity of the ν (C=O) band indicates that about 80% of the carboxyl groups are in the molecular form. One assumes that structure I is also formed with tertiary amines, but the molecular complex-ion pair equilibrium is not so greatly shifted to the right as with the secondary amines, although it is so substantially more than when tertiary amines interact with aliphatic monobasic acids [14]. When excess tertiary amine is added to a solution of malonic acid in octanol, one can still produce the doubly charged malonate anion, evidently because of hydrogen bonds arising between the OH groups of the octanol and one of the oxygen atoms in the carboxyl groups of the monoanion.

Qualitatively different results are obtained with malonic acid and amines in DMSO. It is evident that there is a special mechanism in which interaction with the solvent affects the structure of the complexes. Figure 3 shows IR spectra of solutions in DMSO for malonic acid and mixtures of it with dibutylamine. The ν (C=O) acid band at 1720 cm^{-1} is due to complexes of the acid with DMSO via the strong hydrogen bonds. Adding an amine weakens this band, and for $c_a/c_m = 1$ the ν (C=O) band almost completely vanishes; the band at 1640 cm^{-1} dominates the 1500-1800 cm^{-1} region, although this band is not observed with other solvents and lies halfway between the ν (C=O) band of the molecular form of the acid at 1720 cm^{-1} and the ν_a (CO^-_2) band for the symmetrically perturbed malonate anion in an ion pair, which occurs at 1560 cm^{-1} in the amine–acid system with a ratio of 2:1. There is no doubt that the 1640 cm^{-1} band relates to vibrations of C=O bonds in the malonic acid anion. The intermediate frequency of this and the loss of the ν (C=O) band for $c_a/c_m = 1$ means that the acid interacts with a molecule of dibutylamine, where both carboxyl groups acquire a partially ionic character. This can occur only if a symmetrical singly charged malonate anion (III) is formed having an intramolecular hydrogen bond, which is provided by the central proton:



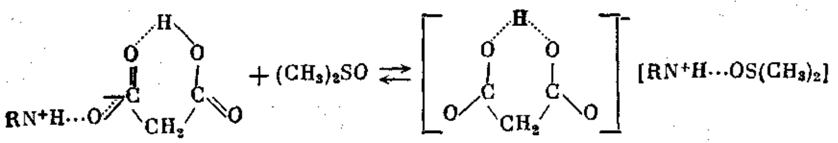
III

One assumes that the interaction between the malonate anion and the dialkylammonium cation is weakened in a solvent as polar as DMSO; an interesting point is that acetonitrile, which is only somewhat less polar than DMSO (ε of 36 and 42, μ of 3.4 and 3.9 D, respectively) does not give the symmetrical malonate anion. It seems that a necessary condition for the anion is capacity in the solvent molecules to form sufficiently strong hydrogen bonds to the cation, since the proton-acceptor capacity of DMSO is much higher than that of CH_3CN. It may be that the formation of comparatively strong $N^+H_2\cdots O{=}S$ bonds means that the δ (N^+H_2) vibration usually observed at 1620-1630 cm^{-1} does not contribute to the intensity of the 1640 cm^{-1} band, which does not alter when one uses deuterated malonic acid, where the δ (N^+H_2) band should be absent because of hydrogen exchange. A completely analogous picture is observed on adding a tertiary amine to malonic acid in DMSO, as the structure of (III) is independent of the amine. This indicates that a $N^+H\cdots O{=}S$ hydrogen bond is formed between the cation and the solvent.

When c_a/c_m for dibutylamine becomes greater than one, the spectral picture does not alter so it is unlikely that the doubly charged malonate anion is formed in DMSO. However, increasing the concentrations of the components with $c_a/c_m \geqq 1$ from the minimum possible, which is limited by the transparency of DMSO in the working region, leads to an increase in the intensity of the ν (C=O) 1720 cm^{-1} band and to the appearance of a shoulder at about 1600 cm^{-1} against the background of the strong 1640 cm^{-1} band. Similar changes occur on diluting the solution with carbon tetrachloride or adding small amounts of D_2O.

However, the reasons for the pattern changes are different. Increasing the concentration for reducing the polarity probably leads to contact ion pairs having noncentral intramolecular hydrogen bonds [structure (I)], while the water molecules form hydrogen bonds to one of the two free oxygen atoms in the malonate anion, which also leads to a structure similar to (I). Raising the temperature also has the same effect as increasing the concentration, i.e., it strengthens the 1720 cm^{-1} band, weakens 1640 cm^{-1}, and produces a low-frequency shoulder at about 1600 cm^{-1}.

Band intensity measurements for the complexes enable one to estimate the thermodynamic parameters in the hydrogen bonding of DMSO to alkylammonium cations, which is accompanied with the adoption of a symmetrical structure in the malonate ion (1):



(1)

The equilibrium constant for a tertiary amine takes the form

$$K = [A^-(B^+H\cdots S)]/[A^-HB^+]\cdot[S]$$

with obvious symbols. The 1720 cm^{-1} band serves to determine the $[A^-HB^+]$ concentration [structure (I)], since the number of acid molecules bound only to a solvent is negligible under our conditions, as is the number of acid—amine molecular complexes; the other concentrations are found from the conservation condition.

To determine K, we used malonic acid in DMSO containing dibutylamine or tributylamine with $c_a/c_m = 1.4$; the malonic acid concentrations were in the range 0.07-0.5 mole/liter. There were no differences in the spectra with the secondary or tertiary amine. The mean K at 25°C was 0.024 $liter^2/mole^2$ for dibutylamine or 0.27 liter/mole for tributylamine. The plot of ln K against 1/T gave the enthalpy change ΔH, and then we calculated the entropy change ΔS in (1). Correspondingly, $\Delta H = -(1.5 \pm 0.5)$ and $-(3.1 \pm 0.5)$ kcal/mole for dibutylamine and tributylamine, while ΔS is $-(13 \pm 2)$ eu for both. The heat of (1) is not too great, but there is a considerable reduction in the entropy, which is evidently related to the formation of the hydrogen bond between the cation and the DMSO.

The IR spectra were recorded with the UR-20 spectrophotometer with an NaCl prism (fourth slit program). Integral cells with fluoride windows were used, thicknesses of 49, 157, and 606 μm. The temperatures were measured to 1°C with a copper—Constantan thermocouple. The solvents were purified in the usual ways and were dried with the zeolite; the drying performance was checked from the spectra.

CONCLUSIONS

IR methods have shown that an intramolecular hydrogen bond is formed from the oxygen atom in the CO^-_2 group to the OH group and the other carboxyl group on the first ionization of malonic acid on interactin with aliphatic amines and alcohols, chloroform, dioxane, and acetylnitrile. In dimethylsulfoxide, a symmetrical intramolecular hydrogen bond is formed with a centrally placed proton.

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