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The infrared spectra and enthalpies of strongly bound dimers of phosphinic acids in the gas phase. $(CH_2Cl)_2POOH$ and $(C_6H_5)_2POOH$

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Abstract

Infrared spectra of phosphinic acids R_2POOH ($R = CH_2Cl$, C_6H_5 and CH_3) have been recorded in the gas phase. The equilibrium between monomers and dimers of R_2POOH is studied in the temperature range of 400–650 K. The broad absorption band in the region 3600–900 cm^{-1} is assigned to the ν(OH) stretching vibration of the very strongly bound cyclic dimer. The characteristic ABC structure of the ν(OH) band, typical for the spectra of strongly hydrogen-bonded complexes in the solid phase, is observed in the gas phase spectra of dimers. Unlike the case of solid-phase spectra, the intensity of components decreases in the sequence A, B, C. The ν(OH) bands of free R_2POOH molecules (effective half-width is about 35 cm^{-1}) appear in the range 3660–3630 cm^{-1} at temperatures 420–500 K. The dimerization constants, the spectral moments of monomer and dimer bands, and their intensities have been determined. The H-bond energies are estimated from the temperature dependence of equilibrium constants of dimerization. The values obtained for phosphinic acids are found to be equal to 25–50 kcal mol^{-1} per dimer. The spectral and energetic features of phosphinic acid dimers are typical for very strong hydrogen bonds with a partial covalent character.

Keywords: IR spectra; Hydrogen bond; Phosphinic acids; Dimerization enthalpy

1. Introduction

The hydrogen bonds involving the POOH group of phosphinic acids R_2POOH belong to the strongest intermolecular bonds formed by neutral molecules. In the crystalline phase, these molecules form infinite chains or, more rarely, cyclic dimers due to OH···O=P bonds, in which the O···O separation in the POHOP fragment lies, according to the data of X-ray and neutron scattering analysis, in the interval 2.40–2.55 Å [1–7]. According to the classification [8], such distances are characteristic for the strongest bonds of the OHO type in homoconjugated ions. In some cases [1,5], the separations in adjacent PO groups are equal or so close to each other that the proton position in the hydrogen bridge can be considered symmetric or almost symmetric. These bonds are the most typical examples of a three-center four-electron bond A–H···:B; i.e. their nature is essentially covalent [8,9]. In spite of the fundamental importance of such interactions for the theory of chemical bonding and intermolecular interactions and the key role played by hydrogen bonds involving the phosphate group in biological processes [10–12], their

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energetics, dynamics, and spectral manifestations are virtually unstudied. The authors of Ref. [13] were able to observe the monomer–dimer equilibrium for dimethylphosphinic acid $(CH_3)_2POOH$ by studying the gas-phase IR spectra with the use of a special technique for performing measurements at temperatures up to 700 K. The obtained energy and spectral characteristics of dimers are in satisfactory agreement with the results of high-level quantum-mechanical calculations [14]. The purpose of our work is to record the IR spectra of two phosphinic acids R_2POOH: diphenylphosphinic acid ($R = C_6H_5$) (PA1) and bis-(chloromethyl)-phosphinic acid ($R = CH_2Cl$) (PA2) and to determine the enthalpy of their dimerization in the gas phase, to compare the spectra of dimers in the gas and condensed phases at low temperatures, to examine the correlation between the spectral and energy characteristics of dimers. In addition, a number of experiments were performed with the dimethylphosphinic acid $(CH_3)_2POOH$ (PA3).

2. Experimental

The diphenylphosphinic acid (PA1) 99% was purchased from Aldrich; the dimethylphosphinic acid (PA3) 97% was purchased from Acros; the bis-(chloromethyl)-phosphinic acid (PA2) was synthesized and kindly provided by Prof. M.A. Pudovik, Kazan University; all compounds were used without further purification.

The IR spectra were recorded in the temperature range 300–650 K in gas cells of three types (with cell lengths 5–8 cm): I—glass cells (volume $V = 15$–$20\ cm^3$) with welded sapphire windows and a low-frequency transmission limit at $1550\ cm^{-1}$; II—a quartz cell ($V = 60\ cm^3$) with quartz windows and a low-frequency transmission limit at $2350\ cm^{-1}$ (the similar quartz cells were used by Maltsev [15]); III—glass cells ($V = 6$–$8\ cm^3$) with MgF_2 windows fixed on a ceramic ring and a low-frequency transmission limit at $1050\ cm^{-1}$. Most experiments were performed by using cells of the I type, in which the loss of a substance during temperature measurements was small, but the ν(OH) band of dimers are not recorded over the entire frequency range. The measurements of the absorption band intensities are most accurate with the use of the II cell, because, due to its large volume, the concentration of a sample is determined with the highest accuracy, although, in this case, only the higher-frequency part of the broad dimer band is recorded. A cell of the III type allows almost the whole band of dimers to be recorded, but in such a cell, the temperature range of measurements is the narrowest because of the onset of sample decomposition on the ceramic already at relatively low temperature. Consideration of the results obtained in these cells allows us to achieve an optimum combination of an accurate recording of the entire band shape of dimers and the measurement of its intensity as a function of temperature.

In all the experiments, an amount of the substance studied was placed in a cell, the cell was pumped out down to pressures about 10^{-2} Torr (defined by vapor pressure above the solid sample at 300 K) and sealed. The optimal measurements were carried out at concentrations of $(0.6–3.0) \times 10^{-3}\ mol\ l^{-1}$, which corresponds to a solid sample mass of 3–15 mg. The cells were placed in a copper heater with KBr external windows, whose design guarantees the temporal stability of temperature and its spatial homogeneity, with the temperature gradient in the cell being within 2–4 K. The temperature in the range 300–700 K was measured with an accuracy of 1–4 K. The temperature interval of measurements is governed, on the one hand, by the vapor pressure of acids, at which the spectra are reliably recorded (370–400 K for PA2 and PA3 and 450–470 K for PA1) and, on the other hand, by the chemical stability of the sample (650–700 K for PA1 and PA3 and 520–530 K for PA2).

The spectra of solid films of phosphinic acids in the 80–300 K interval were recorded in the standard cryostat with KBr windows. The films were deposited on a CsI window, cooled down to 80 K by liquid nitrogen, from an ampoule with the substance placed in the cryostat and heated up to 440–480 K. The layer thickness was controlled by the spectra recorded during deposition. The films were annealed at 250–300 K, the spectra of annealed films are totally reversible on temperature variation in the interval 80–300 K. At 300 K, these spectra practically coincide with the solid-phase spectra of acids in KBr pellets and in Nujole emulsion [16].

The spectra were recorded with the Fourier spectrometer Bruker IFS-28 with the resolution of 2–5 cm^{-1}

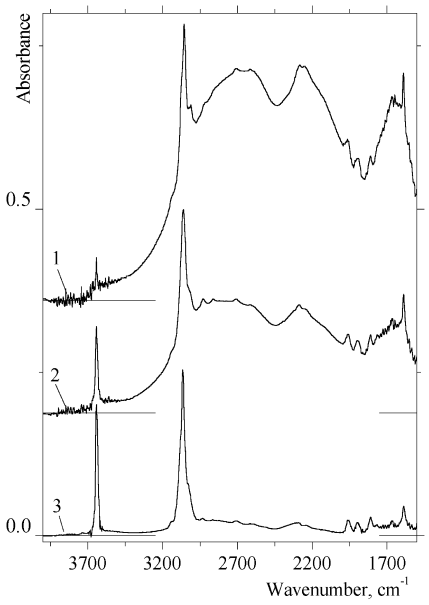

Fig. 1. The absorption spectra of diphenylphosphinic acid in the gas phase at different temperatures. 1: 475 K; 2: 515 K; and 3: 555 K. The spectra were recorded in the cell with sapphire windows, $C_0 = 0.8 \times 10^{-3}$ mol l^{-1}, $\ell = 8$ cm.

for the gas-phase spectra and 1 cm^{-1} for the solid-phase spectra.

3. Results

3.1. The shape of dimer bands

At 300 K, all the acids studied are in the solid phase. On increasing the temperature up to 400–470 K and increasing the vapor pressure above the solid sample, it becomes possible to record a broad ν(OH) absorption band of dimers ranging from 3500 to 1000 cm^{-1}. As an example, Fig. 1 displays the spectra of PA1 recorded in a cell with sapphire windows in the range 4000–1500 cm^{-1}. The broad absorption ν(OH) band of dimers is superimposed by relatively narrow bands of stretching (in the region of 3050 cm^{-1}) and bending (near 1700 cm^{-1} and at lower frequencies) modes of the C–H groups of phenol rings. At temperatures 470–490 K, the ν(OH) absorption band of a monomer appears near 3645 cm^{-1} (see Fig. 1, spectrum 1) and on increasing the temperature, its intensity increases. The intensity of the dimer band also increases until a certain temperature, which depends on the initial concentration of the acid, and then its intensity decreases (Fig. 1, spectrum 2). At temperatures 515–540 K, the intensity of the monomer band reaches its maximum (Fig. 1, spectrum 3), and only the CH modes and very weak bands of dimers are observed in the region 3500–1500 cm^{-1}. Finally, on increasing the temperature up to 600–650 K, the intensity of the ν(OH) monomer band begins to decrease, and the absorption bands associated with products of pyrolysis of acids appear in the spectra.

For all the acids studied, the absorption spectra in the region 4000–1000 cm^{-1} have a similar structure (see also Fig. 2) and behave similarly as temperature varies. The changes in the relative intensity of monomer and dimer bands are reversible up to temperatures of pyrolysis. The maximum of the ν(OH) absorption band of monomers is observed at frequencies 3640, 3645, and 3650 cm^{-1} for PA2, PA1, and PA3, respectively. The band shape of the PA3 monomer is governed by the rotational motion and

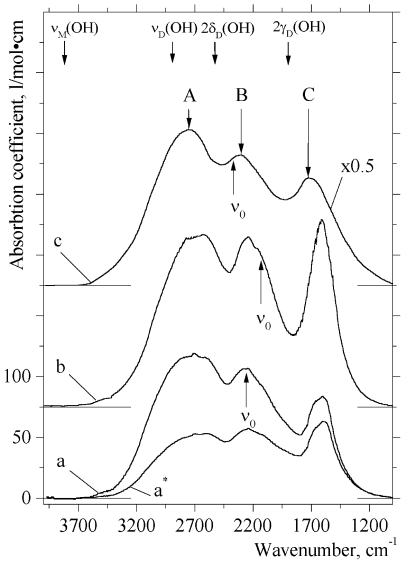

Fig. 2. The ν(OH) dimer band of phosphinic acids: a, diphenylphosphinic acid (PA1); b, bis-(chloromethyl)-phosphinic acid (PA2); and c, dimethylphosphinic acid (PA3) scaled by factor 0.5. a^* is the spectral function $S(\nu)$ of PA1 dimer (in relative units). The arrows denote: the center of gravity ν_0 of the dimer band; the calculated frequencies of PA3 [14], where indices M and D indicate the monomer and dimer frequencies; and the frequencies of ABC components.

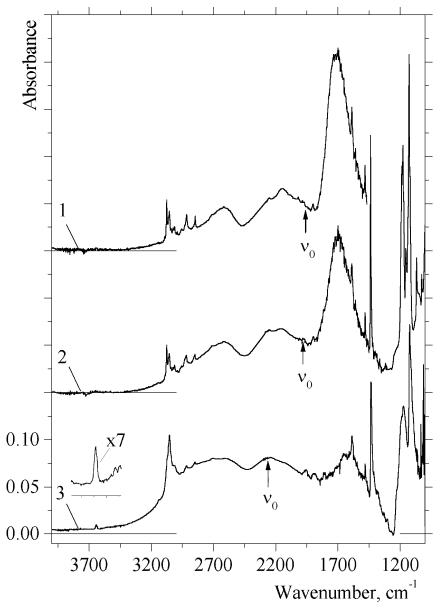

Fig. 3. The absorption spectra of diphenylphosphinic acid. 1: 80 K (solid state); 2: 300 K (solid state); and 3: 510 K (gas phase). The arrows denote the center of gravity ν_0 of the dimer band. The monomer band at 510 K scaled by factor 7 is presented also.

consists of three strongly overlapping P, Q, and R components with an effective halfwidth of about 35 cm^{-1}. On passing from PA3 to PA2 and further to PA1, when the moment of inertia increases, the monomer band becomes structureless with a halfwidth of about 25 cm^{-1}. The total concentration of acids at each temperature can be estimated from the intensity of absorption bands of CH modes. Note here that from the calculation [14] it follows that the intensity of CH absorption bands somewhat increases on formation of the PA3 dimer. By using the spectra recorded at high temperatures, it is possible to separate the bands in the region 3700–1200 cm^{-1} and obtain the ν(OH) band shape for dimers of all the acids studied, which are presented in Fig. 2.

One can see from Fig. 2 that, in all the systems under study, very broad absorption bands ν(OH) of dimers are observed which have the structure typical for strong hydrogen bonding and includes the so-called A, B, and C components. Such an ABC structure is usually observed in the case of systems with strong hydrogen bonding in solutions and solid samples and is accounted for by Fermi resonance between the ν(OH) mode and the overtones of low-frequency vibrations of the hydroxyl group (2γ(OH) and 2δ(OH)) of a dimer [17,18]. Fig. 2 also presents the values of vibrational frequencies of the PA3 dimer, in particular, frequencies of the 2γ(OH) and 2δ(OH) modes, calculated in Ref. [14], which are in satisfactory agreement with the 'transparency windows' of the dimer band. It should be noted that the dimer bands of the phosphinic acids in question are, in general, similar. For PA1 and PA2, the frequencies of A, B, and C components are almost the same. The maximum of the A component lies near 2800 cm^{-1} for PA3 (at 530 K), 2630 cm^{-1} for PA2 (at 435 K), and 2660 cm^{-1} for PA1 (at 475 K), the maximum of the B component lies near 2400, 2240, and 2260 cm^{-1}, and the maximum of the C components lies near 1700, 1610, and 1610 cm^{-1}, respectively. As temperature increases, the position of B and C components practically does not change, and the maximum of the A component shifts toward higher frequencies in the spectra of the three acids. In the region 450–550 K, the temperature coefficients of shifting is about 2.5 cm^{-1} K^{-1} for PA1 and about 1 cm^{-1} K^{-1} for PA2 and PA3.

It follows from Figs. 3 and 4, where the spectra of

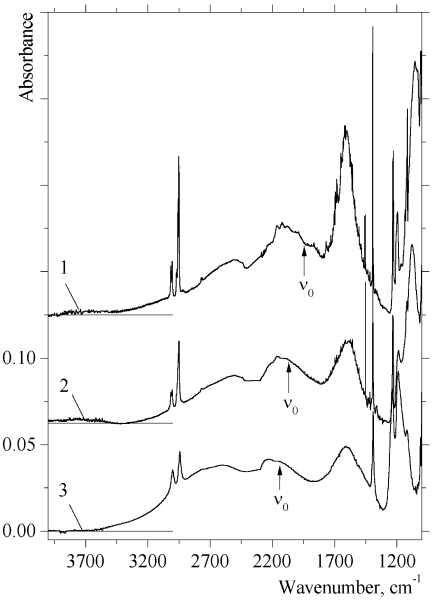

Fig. 4. The absorption spectra of bis-(chloromethyl)-phosphinic acid. 1: 80 K (solid state); 2: 300 K (solid state); and 3: at 455 K (gas phase). The arrows denote the center of gravity ν_0 of the dimer band.

Table 1
The center of gravity ν_0 and the effective half width $\nu_{1/2}$ (cm^{-1}) of the ν(OH) band of the phosphinic acid dimers in the gas and solid phase

Acid		T (K)	ν_0	$\nu_{1/2}$
$(CH_3)_2POOH$	Gas	460	2350	1060
		525	2400	1050
	Solid	80	1945	870
		300	2070	930
$(CH_2Cl)_2POOH$	Gas	435	2130	1020
		475	2150	1060
	Solid	80	1920	830
		300	1980	870
$(?_6?_5)_2POOH$	Gas	515	2270	1050
		575	2310	1100

PA1 and PA2 condensed on a window at 80 K are presented, that the band shape of dimers does not change significantly on passing to solid samples. One can observe only an intensity redistribution between the A, B, and C components, which makes the C component the most intense in the spectrum. A relative increase in the intensity of C component also takes place with increasing temperature. A similar situation is observed also for PA3.

In considering complicated and broad bands of molecular complexes, it is advisable to determine and analyze the set of normalized spectral moments. In experiments at different temperatures, we obtained the following spectral moments: the zero spectral moment $M_0 = \int S(\nu)\mathrm{d}\nu$ (the integral intensity of a band), the first spectral moment $M_1^* = M_0^{-1} \int S(\nu)\nu\,\mathrm{d}\nu \equiv \nu_0$ (the center of gravity of the band related to the fundamental transition ν(OH) of a dimer), and the second spectral moment $M_2^* = M_0^{-1} \int S(\nu)(\nu - \nu_0)^2\,\mathrm{d}\nu$, the effective half width $\nu_{1/2}$ of a complicated band is $\nu_{1/2} = 2\sqrt{M_2^*}$. Here, $S(\nu) = D(\nu)/[\nu(1 - \exp(-\nu/T))]$ is the spectral function, $D(\nu)$ is the absorbance, and T is the temperature in cm^{-1}. The spectral function describes the distribution of transition probability eliminating the frequency dependence and the induced emission from an observed absorption spectrum. As an example, Fig. 2 presents the spectral function of the ν(OH) band of a PA1 dimer. As expected, in the low-frequency region, the relative magnitude of the spectral function is larger than that of the absorption function. The values of ν_0 and $\nu_{1/2}$ of the dimer bands of phosphinic acids are presented in Table 1. The spectral moments were evaluated over the range 4000–900 cm^{-1}, with the band wings at $\nu < 1100\ cm^{-1}$ and $\nu > 3500\ cm^{-1}$ approximated by exponential functions. It follows from the Table 1 that all the dimers are characterized by an extremely large low-frequency shift of the center of gravity relatively monomer frequencies ($\Delta\nu \sim 1250$–$1500\ cm^{-1}$) and a significant half width of a band ($\nu_{1/2} \sim 1000\ cm^{-1}$). The position of the center of gravity and the half width of the band only insignificantly change with temperature.

3.2. Intensities of monomer and dimer bands

The integral absorption coefficients of ν(OH) band of monomers ξ_M and dimers ξ_D were obtained from the integral intensities of corresponding bands $B_i = C_i \ell \xi_i$, where ℓ is the path length and C_i is the concentration (i = M or D). In system containing monomers and dimers, the total concentration of an acid is $C_0 = C_M + 2C_D$, and it follows the relationship

$$\frac{B_M}{\xi_M C_0 \ell} + 2\frac{B_D}{\xi_D C_0 \ell} = 1 \quad (1)$$

that, if the value of C_0 and ξ_i does not change during experiments at different temperatures, the experimental values of $B_M/C_0\ell$ and $2B_D/C_0\ell$ at each temperature should lie on a straight line which intersects the coordinate axes at points ξ_D and ξ_M, respectively. Our measurements showed that for PA1, PA2, and PA3, the experimental points at different C_0 satisfactorily lie on a straight line, which indicates both the absence of complicated complexes in a gas and the absence of a significant dependence of ξ_D and ξ_M on temperature. The magnitude of C_0, which can be obtained from weighting the acid, varied within the interval $(0.6\text{–}3.0) \times 10^{-3}\ mol\ l^{-1}$ for the acids studied. The values of integral absorption coefficients are presented in Table 2.

Table 2
The dimerization enthalpy, ΔH (kcal mol^{-1}) and integral absorption coefficients of monomers ξ_M and dimers ξ_D ($10^4\ l\ mol^{-1}\ cm^{-2}$) of the phosphinic acids

Acid	ΔH	ξ_M	ξ_D
$(CH_3)_2POOH$	24 ± 6	0.3 ± 0.1	35 ± 9
$(CH_2Cl)_2POOH$	35 ± 5	0.19 ± 0.05	20 ± 7
$(C_6H_5)_2POOH$	50 ± 8	0.16 ± 0.05	16 ± 4

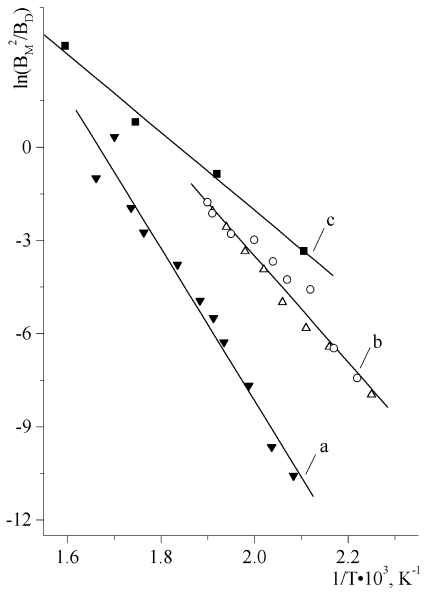

Fig. 5. The dependence of $\ln(B_M^2/B_D)$ vs. $1/T$ for phosphinic acids in the gas phase: a, diphenylphosphinic acid; b, bis-(chloromethyl)-phosphinic acid; and c, dimethylphosphinic acid.

3.3. Hydrogen bonding energies of the acid dimers

The dimerization enthalpy ΔH of phosphinic acids can be found from the temperature dependence of the equilibrium constant $K_D = C_M^2/C_D = K_0 \exp(-\Delta H/kT)$ of the dimer formation $2ROH \rightleftharpoons (ROH)_2$, that follows:

$$\ln(K_D(T)) = -\Delta H/kT + \ln K_0$$

$$= \ln\left(\frac{B_M^2(T)}{B_D(T)}\right) + \ln\left(\frac{\xi_D}{\mathcal{L}\xi_M^2}\right) \quad (2)$$

Assuming that the quantities ξ_D, ξ_M, and C_0 are independent of temperature, we obtain:

$$\ln\left(\frac{B_M^2(T)}{B_D(T)}\right) = -\Delta H/kT + \text{const.} \quad (3)$$

It is important that expression (3) does not depend on C_0, i.e. to determine the dimerization enthalpy ΔH, it is possible to use the experimental values of intensities of the monomer and dimer bands measured during the evaporation process when $C_0 \neq$ const. Since the measurements of ΔH were carried out in a cell I with sapphire windows, only a part of the dimer band limited by the low-frequency transmittance boundary ($\sim$1600 cm^{-1}) could be recorded in experiments at different temperatures. To determine the dimer band intensity, it is possible to use a simple relation $B_D = \kappa B_D^*$, where B_D^* is the integral intensity of a part of the dimer absorption band, lying within the frequency interval 4000–1700 cm^{-1}, of a spectrum recorded in a cell I. The value of κ can be obtained from the experiments carried out using a cell III with MgF_2 windows. Additional experiments showed that κ can be assumed to be constant to within 10% over a wide temperature range.

Fig. 5 displays the dependencies of $\ln(B_M^2/B_D)$ on $1/T$ for all the acids studied. One can see that the deviation of experimental points from the straight lines obtained by the least-squares method is small. The enthalpies of dimerization of phosphinic acids derived from Eq. (3) are presented in Table 2.

4. Discussion

For the first time, the gas-phase spectra of the dimers and monomers of acids with the dimerization energies of 20–50 kcal mol^{-1} were recorded. Since, at room temperature, the equilibrium is strongly shifted toward dimers and the vapor density of these substances is very low, it is possible to record in the gas phase the monomer and the dimer spectra only at high temperatures. Solution of this problem required the development of a special technique and procedure for performing the experiment.

An extremely broad and intense ν(OH) band with the structure typical for strong OH$\cdots$O bonds is characteristic for the dimers of the phosphinic acids studied in the gas phase. It should be noted that despite the sufficiently large distinction in the dimerization energies (Table 2) the shape of this band is virtually the same for all the three phosphinic acids. It is interesting that the ν(OH) absorption band shape of a strong cyclic complex with hydrogen bonds remains in general unchanged on transition from the gas to solid phase as well. The effective halfwidth of these bands is also practically unchanged. The individual specific features of intensity distribution within the broad band are governed by an interaction with low-frequency modes of a particular acid, rather than by the dimerization energy of the dimer. In the

analogous series of carboxylic acids (the acetic acid, its halogen derivatives, and benzoic acid), the ν(OH) band shape of a cyclic dimer is the same, and the dimerization energy practically does not change, being of the order of 11–14 kcal mol^{-1} [19–22]. The last fact is explained by the opposite influence of substituents on the proton-donor and proton-acceptor ability of the carboxyl group and by mutual compensation of their effects upon dimerization.

The decrease in the integral intensity of the ν(OH) band of dimers in the series of phosphinic acids with increasing dimerization energy (Table 2) revealed in this work is surprising. The experimental data obtained disagree with the known regularities which are obeyed the spectral characteristics of complexes with moderately strong hydrogen bonds—an increase in the low-frequency shift, width, and integral intensity of the ν(XH) band as the hydrogen bond energy increases [23,24]. The empirical correlation regularities relating the hydrogen bond strength and the spectral characteristics of a complex, established mainly for solutions, were often used to estimate its energy. However, these relationships were obtained for complexes whose energies do not exceed 12–15 kcal mol^{-1}; therefore, it can be assumed that the breakdown of these relationships in the case of stronger complexes is indicative of a change in the interaction mechanism and, conceivably, a significant increase in the covalent contribution to the energy of a hydrogen bond. It should be mentioned here that the deviation from such correlation regularities in the gas phase was observed earlier for weaker bonds, for example, for the OH···N system in a mixture of fluorinated alcohols and tertiary amines [25].

Finally, it would be useful to compare the contribution of a cooperative interaction to the energy of dimers of carboxylic and phosphinic acids because it could provide an insight into the mechanism of transfer of the electronic influence via the phosphorous atom of a phosphoryl group. The direct method consists in measuring the energy of an open dimer with a single hydrogen bond. The experimental possibilities for such a measurement are extremely scarce due to a short lifetime of an open dimer. The study of dissociation kinetics of carboxylic acids in the gas phase by the method of a laser temperature jump allowed the authors of Ref. [26] to suggest that, for the acetic and trifluoroacetic acids, the magnitude of the cooperative effect is smaller than the experimental inaccuracy. The theoretical consideration [27] showed that the energy of a cyclic dimer of acetic acid is larger than twice the energy of an open dimer by 2–3 kcal mol^{-1}. Almost the same value was obtained in Ref. [14] for phosphinic acids, so that at present it is impossible to make even preliminary comparative estimates of the magnitude of cooperative effects in carboxylic and phosphinic acids.

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