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Study of Hydrogen Bonds of Hypophosphorous Acid by ^1H, ^2H, ^{31}P, and ^{15}N NMR Spectroscopy under Slow Exchange Conditions

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Abstract—The NMR spectra of solutions containing partially deuterated anhydrous hypophosphorous acid (H_2POOH) and its complexes with organic bases as proton acceptors were obtained in CD_2Cl_2 in the temperature range 183–253 K. Under these conditions, the state of slow exchange is achieved, as evidenced by the fine spin–spin and isotope (H/D) structure of the NMR signals. The formation and strengthening of the hydrogen bond by the OH group result in strong shielding of the ^{31}P nucleus and decrease the spin–spin coupling constants of nuclei in the PH_2 group. Saturation of these effects occurs in going from proton to base. Direct and long-range effects of H/D substitution in the OH and PH groups on the H, ^{31}P, and ^{15}N chemical shifts in complexes were measured. The signs of these effects were explained in terms of a simplified model of dynamic interaction of covalent and hydrogen bonds. The kinetics of the interconversion of a cyclic H_2POOH dimer and a zwitterionic complex with pyridine were studied by dynamic ^1H NMR, and thermodynamic and kinetic parameters of the process were measured. A hypothetical mechanism of the reaction with the transition state close to an open-chain dimer with one hydrogen bond was proposed.

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Acids containing POOH groups (in what follows, we call them phosphorus acids) are of great interest as partner molecules in hydrogen bonds. Both the OH and P=O groups in phosphorus acids are commonly stronger H-bond partners than the OH and C=O groups in carboxylic acids. This results in a very strong self-association of phosphorus acids both neat and in solutions. Thus, as shown in [1–3], the mean energy of the H bond in self-associated dialkyl- and diarylphosphinic acids R_2POOH can achieve 12–25 kcal mol^{-1}. The strong H bonds formed by ionized monoesters of phosphorus acids (substituted phosphate anions) often play not only structural, but also functional role in biochemical reactions. An example of such reactions is provided by the mutual transformation of dihydroxyacetone phosphate and *D*-glyceraldehyde 3-phosphate, catalyzed by triosephosphate isomerase [4]. Another well-known case is 3-ketosteroid isomerase that catalyzes exclusively fast transformation of Δ^5- to Δ^4-3-ketosteroids [5]. The H bonds formed by substituted phosphate groups of the provide stereoselective ferment–substrate bonding. Such H bonds play a significant role in bonding antibiotics with the phosphate backbone of viral RNA [6]. Detailed spectroscopic investigation of individual H bonds formed by POOH and POO$^-$ groups is reasonable to perform on a simple model molecule. In [7], multinuclear NMR spectroscopy under slow exchange conditions (at low temperatures) was used to study complexes and associates formed by Me_2POOH and $(MeO)_2POOH$ molecules, in particular, with the same molecules or corresponding anions. It was shown that in aprotic solvents at low temperatures (100–150 K) these acids prefer to exist as cyclic trimers and at higher temperatures, as cyclic dimers. The H bonds in such associates are largely cooperative, as evidenced, in particular, by significant effects of vicinal isotope substitution.

The main purpose of this work is analogous investigation of complexes and associates formed by hypophosphorous acid H_2POOH, the simplest phosphorus acid. This compound is advantageous in that it provides the possibility of using for structural considerations of an additional informative parameter: $^1J_{PH}$ spin–spin coupling constant. Moreover, the simplicity of this molecule allows its high-level quantum-chemical calculation.

Effect of hydrogen bonding on the NMR spectra of H_2POOH complexes. Hypophosphorous acid is exceptionally prone to self-association in solutions. Therefore, the NMR spectrum of H_2POOH in the

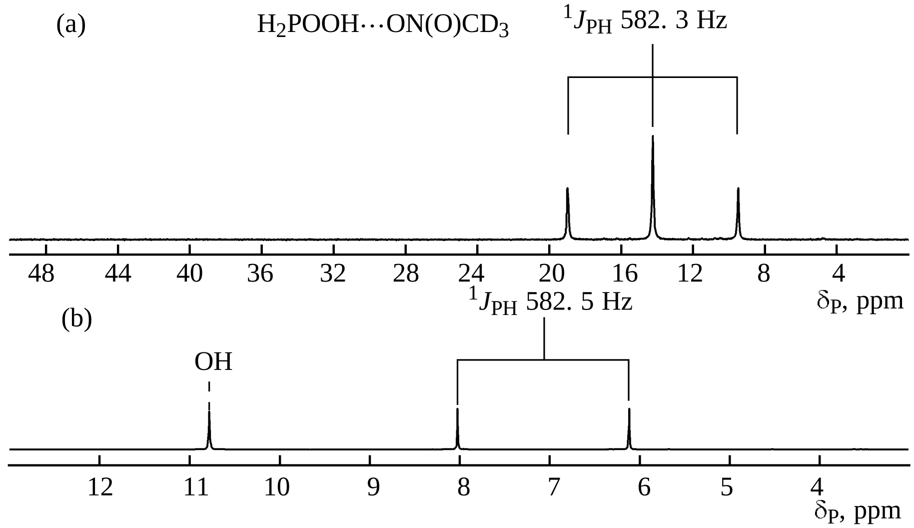


Fig. 1. (a) ^{31}P and (b) ^1H NMR spectra of a solution of anhydrous hypophosphorous acid (0.001 M) in nitromethane at 253 K. References internal TMS (^1H) and external 85% phosphoric acid (^{31}P).

monomeric form without H bonds is difficult to obtain. From the IR spectra it follows that in low-polarity aprotic solvents (chloroform, dichloromethane) the acid is dimerized almost completely even at a fairly low concentration (10^{-3} M) and high temperature. Even in the gas phase it exists mostly in the dimeric form, and attempts to achieve complete dissociation fail even at a fairly high temperature and low vapor density. This, the IR spectra of H_2POOH both in the gas phase and in solution show a broad ν(OH) band (effective width ~1000 cm^{-1}) of the dimer with an ABC structure typical of dimers of many R_2POOH acids [2, 3]. Heating of the acid vapor at a concentration of 10^{-4}–10^{-3} M to 350 K (temperature of active pyrolysis) at an optical layer thicknesses of 4–10 cm did not lead to appearance of even traces of the ν(OH) band of the monomer at 3670–3620 cm^{-1}. However, highly polar solvents should favor dissociation of such apolar cyclic dimers and formation of highly polar binary complexes. The NMR spectrum of a solution of the acid in nitromethane can be considered to approach to a certain extent the NMR spectrum of monomeric H_2POOH not very strongly perturbed by H bonding (Fig. 1). The phosphorus spectrum consists of a triplet with a large $^1J_{PH}$ constant, and the ^1H NMR spectrum contains the corresponding PH doublet and a singlet of the OH proton whose position is almost independent of concentration. This fact points to an extremely weak dimerization of the acid in this solvent. However, the chemical shift of the OH proton signal is still far from that calculated for the monomer (~5 ppm). The observed chemical shift should correspond to a solvated complex of H_2POOH with nitromethane. The NMR parameters of this complex (chemical shifts and coupling constants) are listed in Table 1 together with the spectral parameters of other complexes of this acid. With bases stronger than acetonitrile, complete dissociation of the dimer, as detected by the independence of δ(OH) on concentration, was already achieved at a certain excess of the base in a solution of the acid in methylene chloride).

Table 1. Proton [δ(OH)] and phosphorus [δ(P)] chemical shifts and proton–phosphorus spin–spin coupling constants ($^1J_{PH}$) of hypophosphorous acid complexes with proton acceptors[a]

Run no.	Proton acceptor	δ(OH), ppm	$^1J_{PH}$, Hz	δ(P), ppm	ΔH_H kcal mol^{-1}
1	CD_3NO_2	10.71	582.3	15.20	5.4
2	CD_3CN	10.88	577.7	14.51	5.6
3	$(CD_3)_2CO$	11.42	564.6	12.43	6.2
4	$(CD_3)_2NCDO$	11.94	548.0	12.12	6.8
5	H_2POOH	13.43	539.2	9.81	8.6
6	2,6-$(CH_3)_2$-γ-Pyrone	14.81	530.0	8.56	10.1
7	Pyridine	17.13[b]	526.1	5.16	12.8

[a] Line 5 relates to a cyclic dimer. The H-bond energies ΔH_H are estimated by the correlation equation in [10].

Figure 2 shows the ^1H and ^{15}N NMR spectra of the complex of hypophosphorous acid with pyridine enriched with ^{15}N, the strongest of the bases used. The downfield part of the ^1H spectrum contains a doublet with the $^1J_{NH}$ coupling constant of 88 Hz,

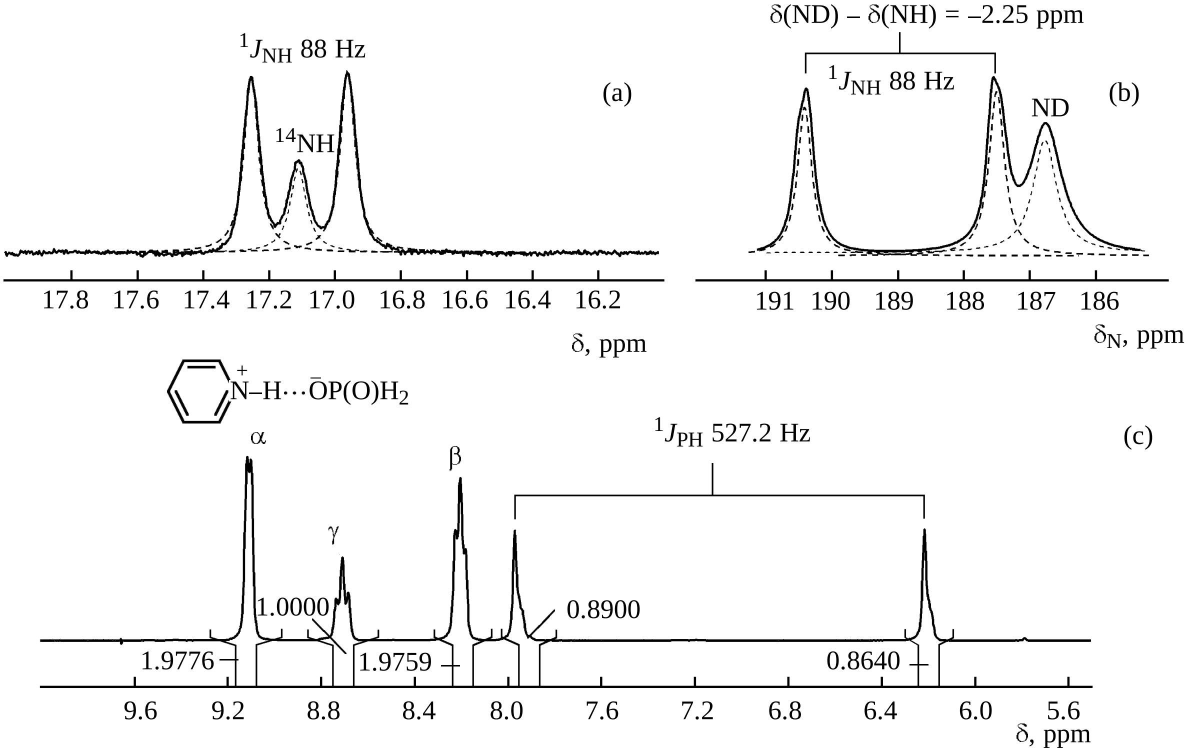


Fig. 2. (a, c) ^{1}H and (b) ^{15}N NMR spectra of a 1 : 1 complex of hypophosphorous acid (30% D) with pyridine (70% ^{15}N) in dichloromethane, concentration 0.05 M, temperature 188 K. Reference external nitromethane (^{15}N).

typical of the pyridinium ^{15}N ion. A spin doublet with the same (within experimental error) coupling constant is present in the ^{15}N NMR spectrum. This fact points to complete proton transfer, whereas the large proton chemical shift points to the fact that the pyridinium NH proton is involved in a strong H bond with the hypophospite counter ion. The upfield part of the proton spectrum contains a doublet from the PH_2 group with $^1J_{PH}$ 527 Hz, which is much lower than in the complex with nitromethane with a weak H bond.

As known, the energy of hydrogen bonds, as well as the average position of the proton in the hydrogen bridge, can be estimated from the chemical shift of the OH proton [8]. Judging from this criterion, the H-bond energy should rise monotonically in the series of the complexes listed in Table 1 from nitromethane to pyridine, in parallel with their proton-acceptor properties. Figure 3 shows the plots of the $^1J_{PH}$ and $δ_P$ values against the chemical shifts of the bridging proton. As δ(OH) increases and the OH···B hydrogen bond becomes stronger, the $δ_P$ and $^1J_{PH}$ (absolute value) of the PH_2 group decrease to achieve saturation upon proton transfer to the base (pyridine). These values are more convenient H-bond characteristics than proton chemical shifts, being unaffected by proton exchange in the OH group and can be used for estimating H-bond energies at high temperatures and in protic solvents, such as water and alcohols. The saturation of the decrease of $δ_P$ and $^1J_{PH}$ with increasing degree of proton transfer to base allows a number of functions to be used for approximation (fitting) several functions, of which the Boltzmann function (sigmoid) and the exponential decay function are the most convenient. Fitting with the Boltzmann function

$$y = A_2 + \frac{A_1 - A_2}{1 + \exp[(x - x_0)/dx]}$$

is shown in Fig. 3 (solid curve). The approximation parameters are as follows: A_1 and A_2 are two asymptotes; x_0, argument value in the curve inversion point; and dx, slope at the half height. This allows us to estimate spectroscopic parameters for monomeric H_2POOH ($^1J_{PH}$ 630 ± 8 Hz and $δ_P$ 4.0 ± 1 ppm) and hyphosphite anion ($^1J_{PH}$ = 525 ± 2 Hz and $δ_P$ = 20 ± 2 ppm). The chemical shift of the OH proton in monomeric H_2POOH ($δ_{OH}$ ~6.0 ± 0.4 ppm) was estimated by the approximate relation $-_1 \sim x_0 - 5dx$. Hence, H_2POOH dissolved in nitromethane is far from being free, and the H bond in the complex with nitromethane ($δ_{OH}$ 10.71 ppm) is fairly strong.

Fitting with the exponential decay function (dashed

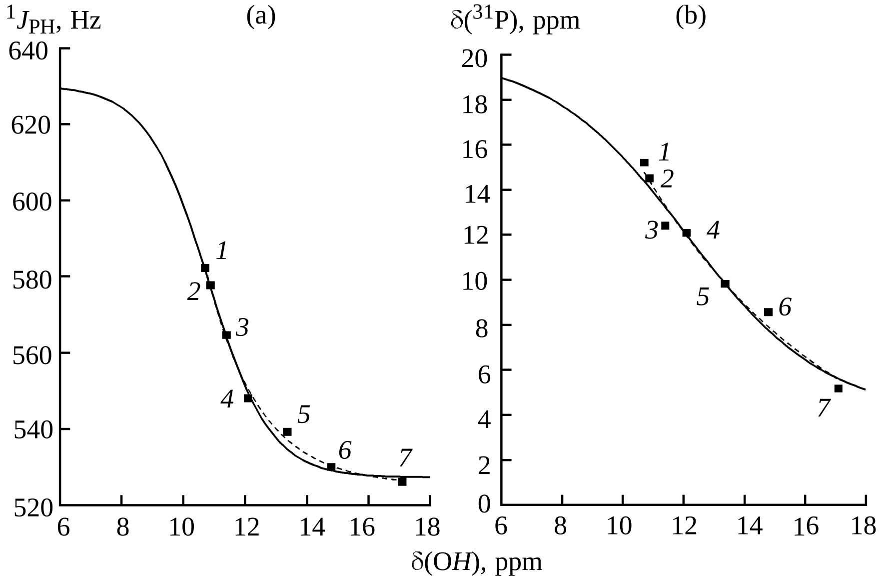


Fig. 3. Plots of the (a) ^1H and ^{31}P spin-spin coupling constants and (b) phosphorus chemical shifts in H_2POOH complexes with proton acceptors vs. chemical shifts of the bridging OH proton. The point numbers are the same as in Table 1. (Solid line) Boltzmann and (dashed line) exponential decay fits of experimental points.

$$y = y_0 + A\exp\frac{-(x - x_0)}{t}$$

curve in Fig. 3) leads, after taking logarithms, to linear correlations, which, together with the known correlation of proton chemical shift with H-bond energy [8] can be used for estimating the H-bond energies in hypophosphorous acid complexes. These estimations (Table 1) give the value of 5 kcal mol^{-1} for the H-bond energy in the complex of H_2POOH with nitromethane.

H/D isotope effects in the NMR spectra of H_2POOH complexes. Long-range isotope effects on chemical shifts and spin–spin coupling constants reflect dynamic interaction of vibrations of H bonds and covalent bonds in H-bonded complexes and can be used for determination of the sign and semiquantitative estimation of the strength of this interaction [9]. The primary effect of deuteron substitution for proton in an XH group is effective shortening of the X–H bond, caused by the anharmonicity of its stretching vibrations, and the corresponding shielding of the bridging deuteron compared to proton, as well as shielding of the heavy X nucleus. The dynamic interaction of the X–H bond vibration with other vibrations (that is, presence of other nondiagonal elements in the potential energy matrix in natural vibration coordinates) together with the anharmonic change in the X–H distance leads to secondary effects, namely, shortening or elongation of other bonds (in particular, the H bond [10, 11]). As a result, other nuclei of partner molecules exert shielding or deshielding, depending on the sign of the dynamic interaction constant and the form of the magnetic shielding function (as a rule, both covalently bonded nuclei exert deshielding with increasing interatomic distance). Thus, long-range isotope effects on chemical shift on deuteron substitution for proton in the neighboring group can be positive (shielding) or negative (deshielding). Simplified consideration in the framework of this model often allows one to predict the sign of the long-range isotope effect in the NMR spectra of molecules and complexes and to solve the reverse problem. Through-H-bond isotope effects that reflect interactions between covalent and hydrogen bonds in complexes are of special interest [12–14].

The isotope structure of the NMR signal of bridging nuclei is best resolved for the H_2POOH–pyridine complex with the strongest H bond (Figs. 2 and 4). The measured direct and long-range isotope effects are listed in Table 2. The resulting data can be qualitatively interpreted as follows. Judging from the $J_{H^{15}N}$ coupling constant (88 Hz) which relates to the pyridinium ion, the complex is an ion pair with complete proton transfer to the nitrogen atom. The primary effect of deuteron substitution for the bridging proton (NH) in such an ionic complex should reveal itself in a certain shortening of the covalent N–H bond and, as a result, in shielding and upfield shifting of the ^{2}H and ^{15}N signals. Furthermore, the negative dynamic interaction of vibrations of the covalent N–H bond and H···O bridge, which is common for unsymmetrical H bonds, leads to elongation and weakening of the H···O bond. In view of the correlation between the H-bond energy and the chemical shift of phosphorus, the latter nucleus exerts deshielding (positive isotope effect on chemical shift). Similarly, deuteron substitution for proton in the PH group results in shortening of the P–H bond. This leads to shielding of the ^{31}P nucleus with a certain decrease in the effective electron density on the oxygen atoms of the phosphinate anion and, as a sequence, to weakening of the H bond (negative dynamic interaction of the P–H and H···O bonds). The result is successive shielding of the bridging proton in the series PH_2–PHD–PD_2 and a negative sign of isotope effects through two covalent bonds and one H bond. (The relatively large width of the ^{15}N signals at low temperatures prevents resolution of their fine isotope structure and measurement of the isotope effect through three covalent bonds and one H bond).

Table 2. Isotope effects on the H, ^{31}P, and ^{15}N chemical shifts of the H_2POOH complexes with pyridine and DMF[a]

Pyridine		DMF	
parameter	δ, ppm	parameter	δ, ppm
$^0\Delta_{DH}\delta(H)$	–0.34	$^0\Delta_{DH}\delta(H)$	–0.41
$^1\Delta_{DH}\delta(N)$	–2.25		
$^1\Delta_{DH}\delta(P)$	–0.36	$^1\Delta_{DH}\delta(P)$	–0.36
$^{2h}\Delta_{DH}\delta(P)$	+0.06	$^2\Delta_{DH}\delta(P)$	+0.08
$^{3h}\Delta_{DH}\delta(H)$	–0.10	$^3\Delta_{DH}\delta(H)$	+0.09
$^2\Delta_{DH}\delta(H)$	–0.02	$^2\Delta_{DH}\delta(H)$	–0.02

[a] The prefix to Δ indicates the number of bonds that transmit the effect. The index *h* means that these bonds include one H bond.

In molecular complexes, unlike ionic, the covalent bond and H bond change places. As a result, successive deuteration of the PH_2 group in a molecular complex of H_2POOH with DMF leads to strengthening of the H bond and deshielding of the bridging (OHO) proton (Fig. 5 and Table 2). Deuteron substitution for the latter leads to shortening of the covalent O–H bond and to elongation and weakening of the H···O H-bond with the corresponding deshielding of the phosphorus nucleus, like with the above ionic complex. Note also the isotope effects on the chemical shift of one PH proton on deuteration of the other proton have the same sign for the two complexes. The

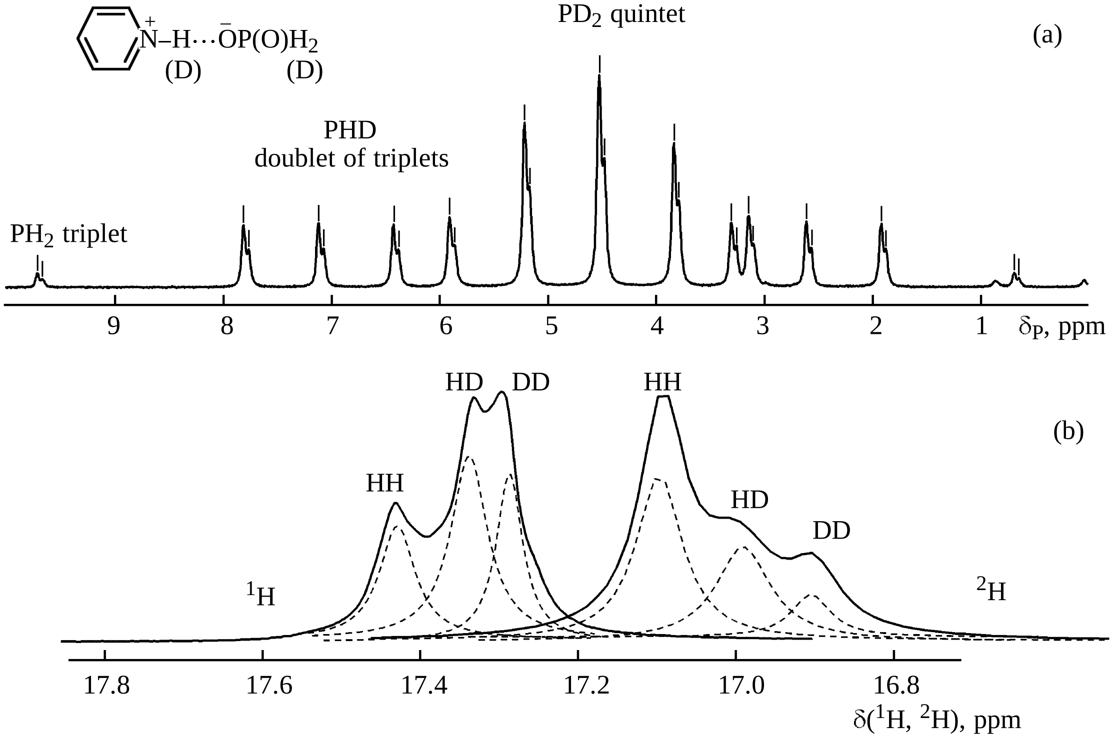


Fig. 4. Proton-decoupled ^{31}P NMR spectrum of a solution of the H_2POOH (90% D) complex with DMF in dichloromethane (*c* 0. 005 M) at 193 K. (a) ^{31}P (70% D) and (b) ^{1}H (60% D) and ^{2}H 36% D).

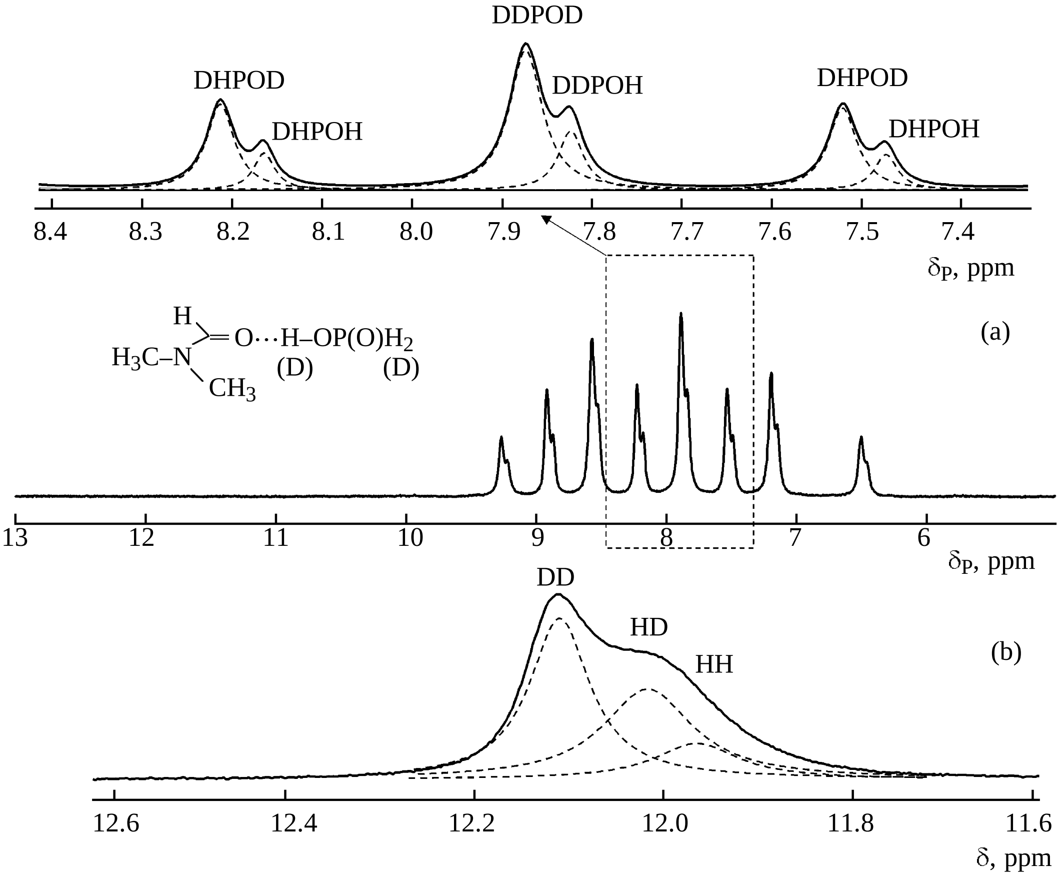


Fig. 5. (a) ^{31}P–{^{1}H} and (b) ^{1}H (75% D) of a solution of partially deuterated H_2POOH complexes with DMF in dichloromethane (*c* 0.04 M) at 193 K.

scheme of interaction of two covalent bonds in the PH_2 group does not depend on the position of the bridging proton and should remain the same in a free H_2POOH molecule.

As seen from the above consideration, the signs of direct and long-range isotope effects can be correctly described in the framework of a simplified scheme of dynamic interaction of vibrations. For quantitative evaluation of these effects, quantum-chemical calculations of the full anharmonic force field of the complex and magnetic shielding as a function of internal vibration coordinates are needed. Note that direct and long-range isotope effects are of the same order of magnitude.

Thermodynamics and kinetics of the cyclic dimmer–ionic complex equilibrium. In solutions in aprotic solvents containing one acid and two different bases or vice versa, an equilibrium between complexes of two sorts is established, and the rate of its establishment falls within the characteristic range of dynamic NMR at 140–250 K, depending on the H-bond strength [13]. This situation we used in [14, 15] to estimate the lifetimes of H bonds in solution and, from the lifetime–temperature dependences, the activation parameters of dissociation of complexes. Analysis of the resulting data allowed us to assume that the exchange of acid (or base) molecules between complexes occurs stepwise with intermediate formation of free partner molecules. For the molecular exchange between the cyclic dimer of formic acid and its complexes with pyridine or hexamethylphosphoramide, too, a step mechanism was proposed, involving cleavage of one of the H bonds in the cyclic dimer and formation of an open-chain dimer as the limiting step. In this work we attempted to perform an analogous study of the equilibrium between the cyclic dimer of hypophosphorous acid and its ionic complex with pyridine.

The ^{1}H NMR spectrum of a methylene chloride solution containing pyridine and a double excess of hypophosphorous acid, at 233 K shows a single labile proton (OH/NH) signal which broadens and splits into two signals with lowering temperature (Fig. 6). The upfield signal almost coincides in position with the signals of the cyclic H_2POOH dimer, and the downfield signal, with the signal of the complex of H_2POOH with pyridine. (This coincidence is not absolute, because the chemical shifts of labile protons depend on external conditions, mainly, on the total concentration.) Simulation of the spectra by the method of full contour shape analysis allows evaluation of the relative populations of exchanging states and their lifetimes as a function of temperature. From these data, equilibrium constants and direct and reverse reaction rate constants can be calculated. The pseudo monomolecular reaction rate constants (s^{-1}) were found as the reciprocal lifetimes of the dimer and complex, similarly to [14]. (Note that the pseudomonomolecular approximation is not quite correct, but it is necessary for comparison with the data in [14]). The constant of the equilibrium is calculated as follows:

$$K = \frac{[\text{com}]}{[\text{dim}]}\frac{[\text{com}]}{[\text{B}]^2} = \frac{[\text{com}]}{[\text{dim}]}\frac{[\text{B}]_0 - [\text{B}]}{([\text{B}])^2}$$

$$= \frac{[\text{com}]}{[\text{dim}]}\,\frac{1 - [\text{B}]/[\text{B}]_0}{[\text{B}]_0([\text{B}]/[\text{B}]_0)^2}.$$

Here B is the effective concentration of free base molecules; $[\text{B}]_0$, total (given) concentration of the base; and [com] and [dim], effective concentrations of the complex and dimer, respectively. The [com]/[dim] ratio was determined by simulation of OH(NH) signal contours. To determine the $[\text{B}]/[\text{B}_0]$ ratio requires simulation of base (pyridine) CH signal contours. However, the signals of free and bound pyridine molecules were unresolved in the temperature range used. Therefore, in practice the $[\text{B}]/[\text{B}_0]$ ratio was determined from the chemical shift of the average signal of the pyridine α-CH proton, which is the most sensitive to ionization:

$$[\text{B}]/[\text{B}]_0 = \frac{\delta_{\text{B(com)}} - \delta}{\delta_{\text{B(com)}} - \delta_{\text{B(free)}}},$$

where δ is the observed chemical shift.

Figure 7 depicts the log equilibrium and reaction rate constants of dissociation of the cyclic dimer and complex, plotted against reciprocal temperature (van't Hoff and Arrhenius plots, respectively). These plots are well approximated by straight lines, thus providing evidence for adequacy of the scheme used. The thermodynamic and kinetic equilibrium parameters are given in Table 3. As seen, the energetically preferable transformation of the dimer into complex leads to a significant entropy decrease. This most probably results not only from the decrease of the number of particles during reaction, but also from the much stronger solvation of the zwitterionic complex due to its high dipole moment.

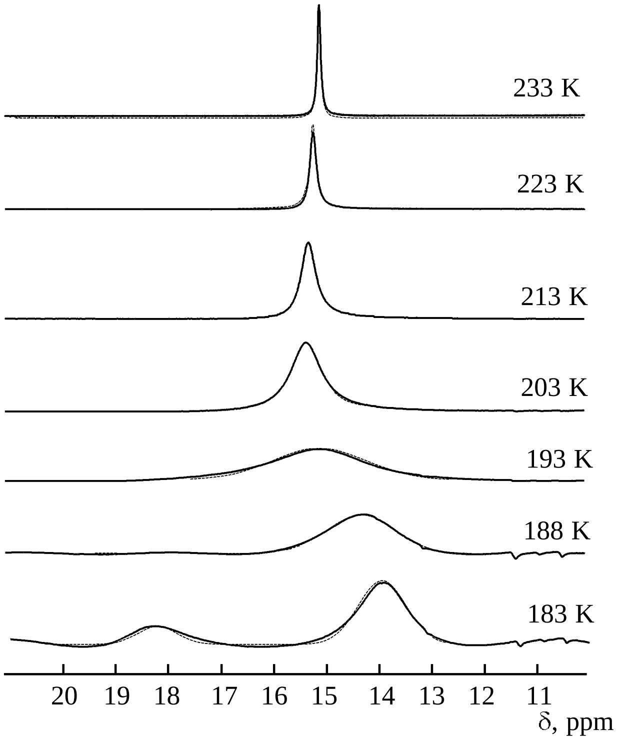


Fig. 6. (Solid line) Experimental and (dashed line) simulated ^1H NMR spectra of a solution containing a double excess of H_2POOH and pyridine-^{14}N in dichloromethane (*c* 0.005 M) in the range 183–233 K.

On interpreting kinetic data obtained by dynamic NMR, that is, for a system in the state of detailed equilibrium, one should bear in mind that the lifetimes of two positions (exchanging states) are defined exclusively by the relative free energy of these two stable and a single transition states [15]. The simplest possible mechanism of interconversion of the cyclic dimer of the acid into an ionic complex includes the steps of consecutive cleavage of two H bonds, interaction of the monomeric molecule with the base molecule, and proton transfer in the complex (Scheme 1). In this case, the highest point on the reaction path profile (on the potential energy–reaction coordinate scale) should be close to state **III**. However, the activation energy of the direct reaction (7.7 kcal mol^{-1}) was found to be much lower than the total energy of cleavage of two H bonds in the cyclic dimer. The real transition state (on the free energy–reaction coordinate scale) is most likely to be close to state **II** (open-chain dimer). Along with the nonzero dipole moment (zero for the cyclic dimer), form **II** possesses a strongly acidic OH group which is capable

Scheme 1.

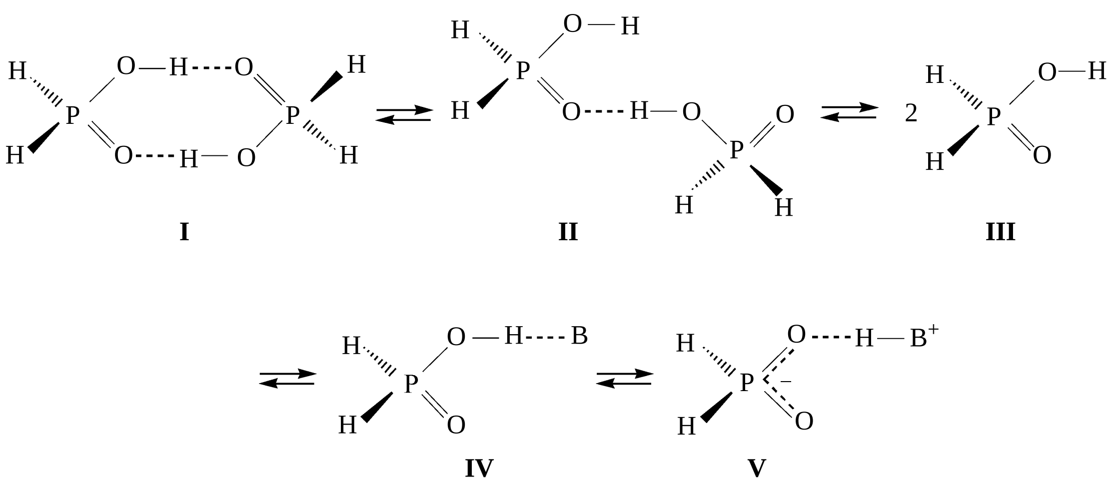


Table 3. Thermodynamic and kinetic parameters of interconversion of the cyclic dimer of hypophosphorous acid and its pyridine complex

Parameter	Direct reaction	Reverse reaction	Direct reaction for HCOOH
ΔH, kcal mol^{-1}	2.42 ± 0.06	–2.42 ± 0.06	–
ΔS, kcal mol^{-1} K^{-1}	–7.82 ± 0.1	7.82 ± 0.1	–
A, s^{-1}	1.1×10^{12}	1.37×10^{13}	4.6×10^{15}
$E^{\neq}$, kcal mol^{-1}	7.7 ± 0.2	8.5 ± 0.2	7.3 ± 0.6
ΔS^{-}, kcal mol^{-1} K^{-1}	–4.65	+0.2	+8.0

of H bonding with solvent (methylene chloride) molecules. Strong solvating of the open-chain dimer can lead to a substantial negative activation entropy of the direct reaction. Note that the activation entropy of the similar interconversion of the cyclic dimer of HCOOH, a much weaker acid than H_2POOH, is positive (Table 3, see [16]). The assumption that the open-chain dimer is a state close to the transition state of the reaction is consistent with the fact that the activation entropy of the reverse reaction is almost zero (Table 3). The complex–open-chain dimer transformation involves no change in the number of particles, and both states should be roughly equally solvated. The zwitterionic complex has a higher

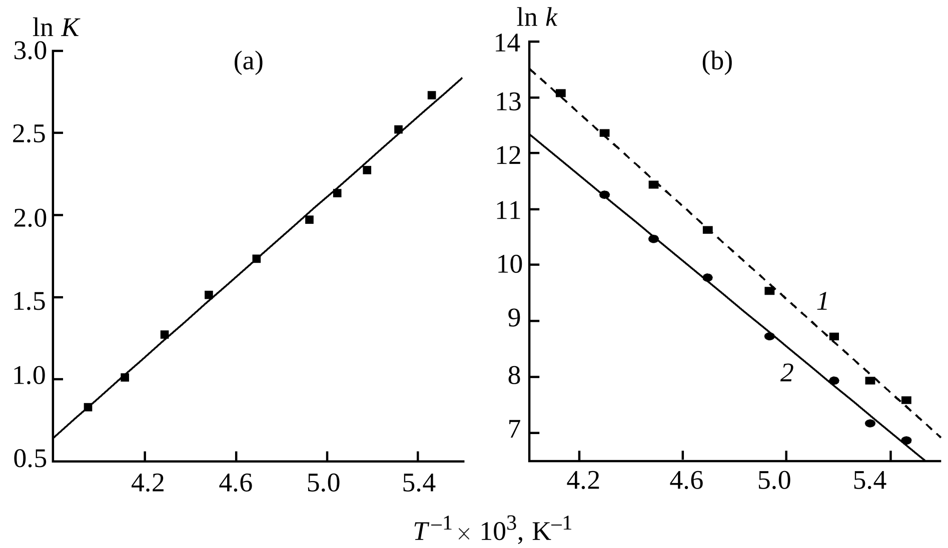
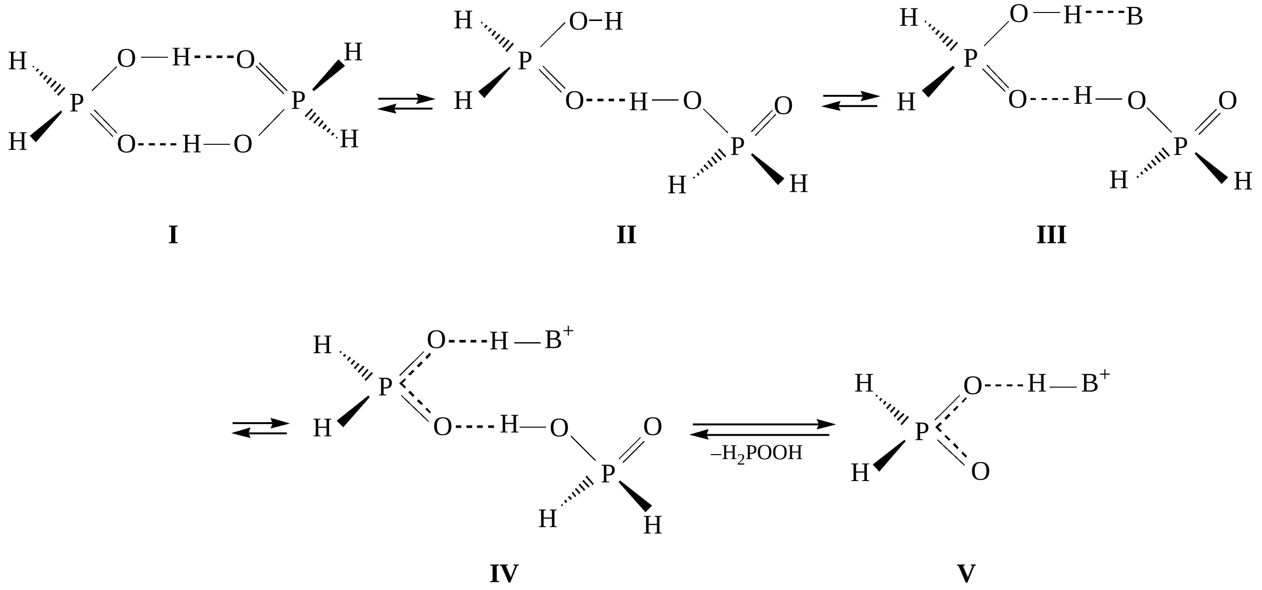


Fig. 7. Plots of the logarithms of the (a) equilibrium constants (van't Hoff straight line) and (b) rate constants of the direct and reverse reactions (Arrhenius straight lines) between the H_2POOH dimer and complex with pyridine vs. reciprocal temperature. Dissociation of the (*1*) complex and (*2*) dimer.

Scheme 2.



dipole moment, but the open-chain dimer contains a strongly acidic OH group.

The situation does not change if during the reaction the dimer does not dissociate completely to form monomeric H_2POOH molecules, and the open-chain dimer reacts with base (Scheme 2). In this case, too, the transition state can be close to open-chain dimer II, which leaves in force the interpretation of the kinetic parameters. It is also probable that the reaction mechanism changes from Scheme 1 to Scheme 2, depending on the initial acid-to-base ratio.

Note that the cyclic dimer of hypophosphorous acid proved to be much more stable in the kinetic aspect than the dimer of formic acid, but this stability is purely entropy (probably, solvation) in nature.

EXPERIMENTAL

The NMR spectra at 178–250K were registered in methylene-d_2 chloride and at 100–170 K, in a CDF_3 + CDF_2Cl mixture (1:3) on Bruker DPX-300 and AMX-500 instruments by the procedure described in [17]. Analysis of the contour shape of NMR signals under conditions of dynamic exchange was performed with the commercial DMDNMR program.

A 50% aqueous hypophosphorous acid (Aldrich) was used. The water was removed by multiple aseotropic distillation with methylene chloride at reduced pressure and low temperature. Distillation was continued until the acid crystallized. Final drying was performed in a high vacuum (~10^{-5} mbar).

Deuteration was performed by multiple addition of CH_3OD, followed by distilling off methanol in a vacuum and removing water traces by azeotropic distillation with methylene chloride. Note that prolonged (several minutes) contact of H_2POOH with deuterometanol results in that H/D isotope exchange occurs not only in hydroxy, but also in PH groups [18] to form a mixture of six isotopic modifications of the acid: H_2POOH, HDPOOH, D_2POOH, H_2POOD, HDPOOD, and D_2POOD. On the one hand, this much complicates the resulting spectra, but, on the other, provides additional nontrivial information on the direct and long-range isotopic effects on NMR parameters. Selective determination of deuterium content in the OH and PH groups was performed by deconvolution of low-temperature ^1H NMR spectra into signals of different isotopomers and their integration.

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