Double proton migrations in the associates of formic acid with nitrous, nitric, orthophosphoric, and sulfuric acids

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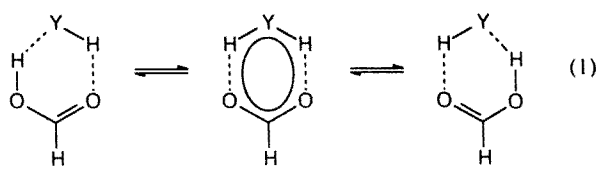
Mechanisms of the proton transfer in dimeric associates of formic acid with nitrous, nitric, orthophosphoric, and sulfuric acids were studied by the *ab initio* (HF/6-31G**) method. The mechanism of the cooperative (concerted or one-step) proton transfer was shown to occur in all cases. The calculated activation barriers of the proton transfer reactions for the associates investigated are equal to 19.9, 14.2, 13.3, and 10.7 kcal mol^{-1}, respectively.

Key words: formic acid, nitrous, nitric, orthophosphoric, and sulfuric acids, associates; double proton shift; potential energy surface; reaction pathway.

The carboxylic group (or the carboxylate ion $-COO^-$) is known to be one of the main binding components of the active centers of enzymatic systems.[1–4] The processes of the interaction between this group and different substrates serve as the basis for recognition of the enzyme and enzyme fixation, and transmission of the signal along the whole length of a protein molecule. Donation (or acceptance) of a proton by these groups initiates the chain of enzymatic transformations. Mutually transforming associates of formic acid with various organic and inorganic compounds are the simplest systems for simulating the interactions between a carboxylic group and a substrate molecule.[5–7]

Several works[8,9] have been dedicated to investigations of intermolecular cooperative proton migrations in associates (**1**) of formic acid with methane (Y = Me), ammonia (Y = NH_2), water (Y = OH), and hydrogen fluoride (Y = F) by the *ab initio* (HF/STO-3G)[10] method.



(1)

1a **2** **1b**

Y = Me, NH_2, OH, F

It has been established that significant lowering of the activation barrier to the cooperative 1,3-transfer of a proton occurs in the sequence Y = Me, NH_2, OH, F. This is determined by changing in proton affinity of the YH group as well as by an increase in both the electronegativity of the central atom and the acidity of the Y—H bond. Thus, according to calculations, the mediator molecule YH provides the cooperative 1,3-transfer of the proton in the associates **1**.

It was of interest to investigate analogous systems in which inorganic oxygen-containing acids of elements of the second and third periods act as the mediator molecule YH. The aim of the present work was to study the mechanisms of intermolecular proton transfer (reaction (1)) in associates **1** of formic acid with nitrous (Y = ONO), nitric (Y = ONO_2), orthophosphoric (Y = $O_2P(OH)_2$), and sulfuric (Y = O_3SOH) acids by the *ab initio* HF/6-31G** method and to elucidate the dependence of the activation barrier to this reaction on the nature of the mediator molecule.

Procedures of the Calculations

The *ab initio* calculations were carried out by the restricted Hartree—Fock (HF) method[6,10] using the GAUSSIAN-94 program[11] on a RISC-6000 workstation. The valence-split STO-6-31G(d,p) basis set (a synonym of the 6-31G** basis set),[10] which includes polarization d-atomic orbitals on the second period elements and p-atomic orbitals on hydrogen atoms, was used. Full optimization of the geometry of the molecular structures corresponding to the saddle points (λ = 1; hereinafter λ is the number of negative eigenvalues of the Hesse matrix at a given critical point[6,12]) and to the energy minima (λ = 0) on the potential energy surface (PES) was carried out up to the gradient magnitude of 10^{-5} Hartree B^{-1}. The force constants matrix was calculated using a program incorporated into the GAUSSIAN-94 complex.

The structures corresponding to the energy minima on the PES were found by the method of steepest descent (movement along the gradient line) from the saddle point (transition state) to the neighboring critical point (a saddle point or a minimum). This method correctly determines the gradient reaction pathway[12] connecting the minima to the corresponding saddle points. The initial direction of the gradient line was specified

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by minor displacement along the direction of the transition vector of the corresponding transition structure. Optimization of the structures in the vicinity of stationary points was performed using the Newton—Raphson method according to the Berny scheme. In order to correctly evaluate the energy of the hydrogen bonds in associates **1**, the structures of nitrous, nitric, phosphoric, and sulfuric acid monomers were found by optimization of their geometry. The starting geometry of those monomers was taken from their conformations in the corresponding associates **1**.

The superposition error in the calculations of the stabilization energy of associates with respect to the individual molecules was not taken into account since generally the intraassociate reaction pathways were studied rather than the dissociation limits, for which the inclusion of this error is of particular importance. It is also known[10] that the superposition error is negligible for the STO-6-31G** basis set. Graphic images of the molecular structures were obtained using the PC MODEL[13] program (the PLUTO mode) for which Cartesian atomic coordinates (taken from the *ab initio* calculations) served as input parameters.

Results and Discussion

Mechanisms of the double proton transfer

Associate of formic and nitrous acids 1a (Y = ONO). The calculations show that **1a** corresponds to the energy minimum (λ = 0) while cyclic structure **2** (Y = ONO) with C_{2v} symmetry corresponds to the saddle point (λ = 1) on the PES. The calculated energetic and geometric parameters of structures **1** and **2** for Y = ONO are presented in Table 1 and in Fig. 1.

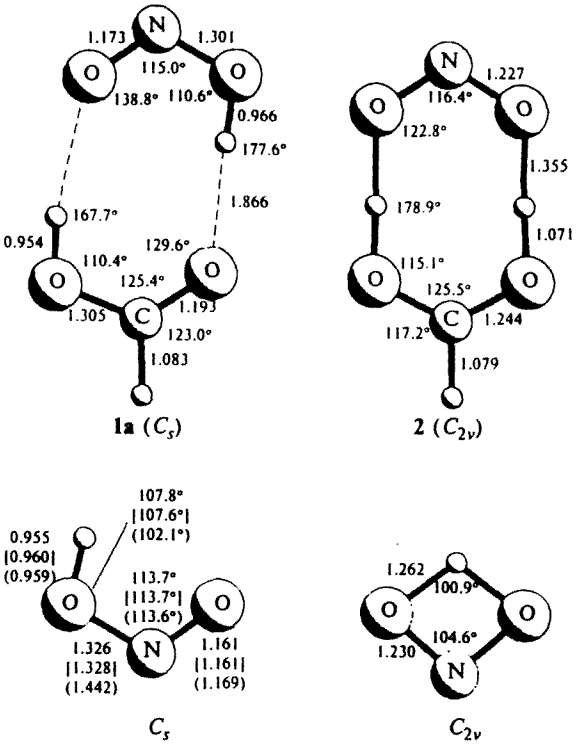


Fig. 1. The structures of associate **1a** (Y = ONO), of the nitrous acid monomer (with C_s symmetry), and of the transition states of intermolecular (**2**) and intramolecular proton transfer calculated by the HF/6-31G** method. Bond lengths (in Å) and bond angles are indicated; the results of calculations[20] by the MP2/6-31G** method and the experimental data[19] are given in brackets and in parentheses, respectively.

Table 1. The total (E_{tot}) and the relative (ΔE) energies, the number of negative eigenvalues of the Hessian (λ), and the two minimum (ν_1, ν_2) or imaginary (iν) frequencies for associates **1**, structures **2**, and for individual molecules (obtained by the HF/6-31G** method)

Structure	Symmetry	$-E_{tot}$ /au	ΔE [a] /kcal mol^{-1}	λ	iν (ν_1, ν_2) /cm^{-1}
1 (Y =ONO)	C_s	393.43298	0	0	(63, 135)
1 (Y =ONO_2)	C_s	468.24345	0	0	(49, 80)
1 (Y =$O_2P(OH)_2$)	C_1	830.83986	0	0	(55, 110)
1 (Y =O_3SOH)	C_1	886.84702	0	0	(35, 55)
2 (Y =ONO)	C_{2v}	393.40124	19.92	1	i863.5
2 (Y =ONO_2)	C_{2v}	468.22074	14.25	1	i330.3
2 (Y =$O_2P(OH)_2$)	C_{2v}	830.81637	14.74	2	i1565.6, i221.6
2 (Y =$O_2P(OH)_2$)	C_2	830.81872	13.26	1	i1246.8
2 (Y =O_3SOH)	C_s	886.82997	10.70	1	i144.9
HC(O)OH	C_s	188.77057	—	0	(692, 712)
ONOH	C_s	204.64616	10.20[b]	0	(741, 784)
ONOH	C_{2v}	204.57707	43.35[c]	1	i2456.2
O_2NOH	C_s	279.45075	13.89[b]	0	(944, 685)
O_2NOH	C_{2v}	279.38549	40.95[c]	1	i2370.9
$OP(OH)_3$	C_1	642.03913	18.93[b]	0	(141, 208)
$OP(OH)_3$	C_3	642.04058	—	0	(172(e))
$OP(OH)_3$	C_2	641.96419	47.93[c]	1	i2219.5
$O_2S(OH)_2$	C_1	698.05026	16.43[b]	0	(944, 685)
$O_2S(OH)_2$	C_2	698.05280	—	0	(263, 332)

[a] 1 au = 627.5095 kcal mol^{-1}. [b] The relative energies of the states with individual molecules of monomers (with no allowance for the superposition error). [c] The activation barrier to the intramolecular 1,3-H transfer.

The associate of formic and nitrous acids **1a** is stabilized by two hydrogen bridges with an energy of 10.2 kcal mol^{-1}. It is interesting to note that the H atoms of formic and nitrous acids participating in the formation of hydrogen bonds in structure **1a** are aligned very nearly along the axes of the sp^2-hybrid orbitals of the corresponding O atoms containing unshared electron pairs. This is in agreement with the general structural properties of hydrogen bonds in various associates.[14,15] The geometric parameters of formic acid molecules change slightly upon formation of the H-bonded complex while the bond lengths and bond angles in the nitrous acid molecules increase substantially. To the best of our knowledge no experimental data on associates of formic and nitrous acids in the gas phase are available; at the same time, the high dimerization energy allows one to assume a high probability of their formation.

Nitrous acid is extremely unstable in solution.[16] It has only been observed and identified spectroscopically in the gas phase when mixed with NO, NO_2, H_2O, N_2O_4, N_2O_3, and HNO_3.[17–19] Experimental geometric parameters (in parentheses)[19] and data obtained by the MP2/6-31G** method (in brackets)[20] for the nitrous acid monomer in the gas phase are presented in Fig. 1. They agree fairly well with the values calculated in the present work.

According to nonempirical calculations, the planar cyclic structure **2** (Y = ONO) with C_{2v} symmetry corresponds to the saddle point (λ = 1) and to the transition state of reaction (1). This points to the fact that the double proton transfer (1) proceeds cooperatively by a one-channel pathway **1a** ⇌ **2** ⇌ **1b**. The calculated activation barrier is equal to 19.9 kcal mol^{-1}, *i.e.*, it is significantly lower than that for intramolecular 1,3-transfer of a proton in the formic and nitrous acid monomers.[21–23] According to nonempirical calculations, the activation barrier in the latter case is equal to 43.3 kcal mol^{-1} (see Table 1), which is close to the value of 44.6 kcal mol^{-1} obtained previously[23] by the HF/4-31G method. Analogously, the nonempirical calculations of the 1,3-H shift in the molecules of formic acid[21–23] also predict an activation barrier value over 40 kcal mol^{-1}.

Associate of formic and nitric acids 1a (Y = ONO_2). The calculations show that **1a** corresponds to the energy minimum (λ = 0) while cyclic structure **2** (Y = ONO_2) with C_{2v} symmetry corresponds to the saddle point (λ = 1) on the PES. The calculated energetic and geometric parameters of structures **1** and **2** for Y = ONO_2 are presented in Table 1 and in Fig. 2.

The associate of formic and nitric acids is stabilized by two hydrogen bridges that are shorter than those in the associate of formic and nitrous acids. The calculated dimerization energy equals 15.2 kcal mol^{-1} and is close to the experimentally obtained value of the dimerization energy of formic acid (14.8 kcal mol^{-1}).[24,26] As can be seen in Fig. 1, the geometric characteristics of nitric acid change significantly when it forms an associate with

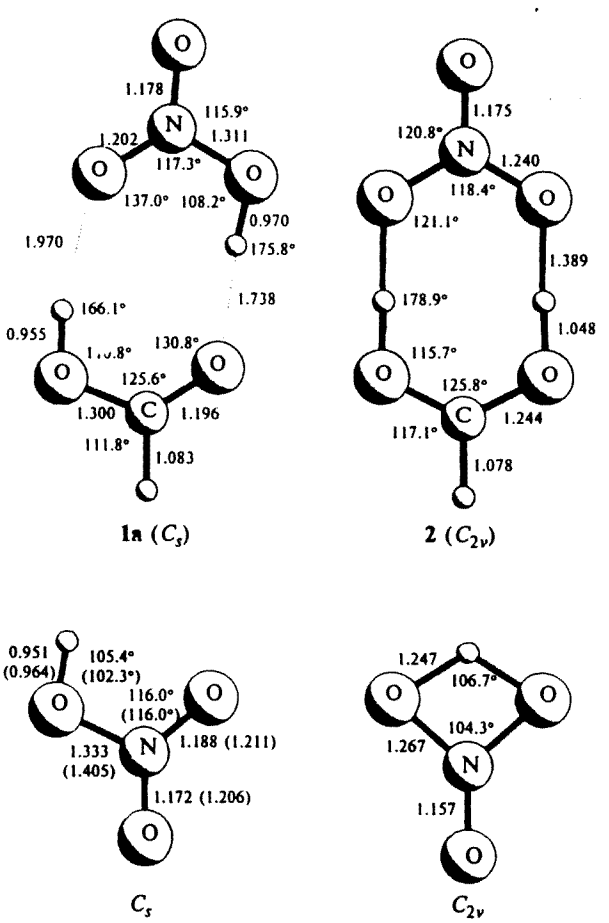
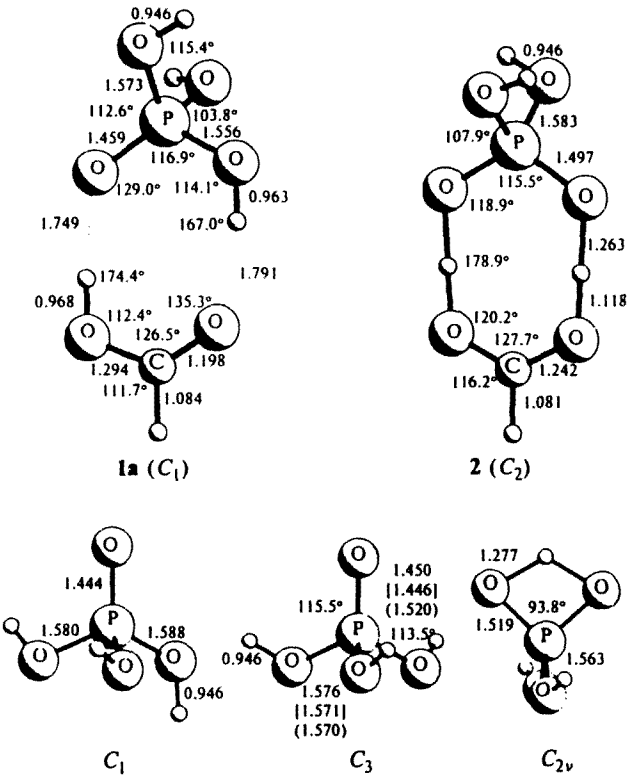


Fig. 2. The structures of associate **1a** (Y = ONO_2), of the nitric acid monomer (C_s), and of the transition states of intermolecular (**2**) and intramolecular (C_{2v}) proton transfer calculated by the HF/6-31G** method. Bond lengths (in Å) and bond angles are indicated; experimental data[25] are given in parentheses.

formic acid: the N=O and the O—H bond lengths and bond angles increase while the N—O bond becomes shorter.

According to nonempirical calculations, the planar cyclic structure **2** (Y = ONO_2) with C_{2v} symmetry corresponds to the saddle point (λ = 1) and is the transition structure in reaction (1) with an activation barrier of 16.6 kcal mol^{-1}, which is close to the corresponding experimental values (~14—18 kcal mol^{-1}) for double proton transfer in the formic acid dimer.[27,28] The activation barrier calculated for intramolecular 1,3-H transfer in the nitric acid molecule (40.9 kcal mol^{-1}) is substantially higher than that for intermolecular 1,3-H transfer (see Table 1). Thus, the intermolecular double proton transfer **1a** ⇌ **2** ⇌ **1b** (Y = ONO_2) proceeds cooperatively, overcoming a significantly lower activation barrier than in the case of intramolecular 1,3-H transfer in formic and nitric acid monomers.



1a (C_1) **2** (C_2)

C_1 C_3 C_{2v}

Fig. 3. The structures of associate **1a** (Y = $O_2P(OH)_2$), of the orthophosphoric acid monomers (with C_1 and C_3 symmetry), and of the transition states of the intermolecular (**2**) and intramolecular (C_{2v}) proton transfer calculated by the HF/6-31G** method. Bond lengths (in Å) and bond angles are indicated; the results of calculations[31] by the HF/6-311++G** method and the experimental data[29] are given in brackets and in parentheses, respectively.

Associate of formic and orthophosphoric acids 1a (Y = $O_2P(OH)_2$). The calculations show that **1a** corresponds to the energy minimum ($\lambda = 0$), cyclic structure **2** (Y = $O_2P(OH)_2$) with C_{2v} symmetry corresponds to the stationary point with index two ($\lambda = 2$), and conformer **2** (Y = $O_2P(OH)_2$) with C_2 symmetry corresponds to the saddle point ($\lambda = 1$). The calculated energetic and geometric parameters of structures **1** and **2** for Y = $O_2P(OH)_2$ are presented in Table 1 and in Fig. 3.

The associate of formic and phosphoric acids **1a** is stabilized by two hydrogen bridges whose energy of formation is 10.2 kcal mol^{-1}; it is nonplanar and has C_1 symmetry. The geometric characteristics of the hydrogen bridges OH...O in this associate are fairly close to those in the formic acid dimer.[26] The P=O and O—H bond lengths are slightly longer, the P—O bond is shorter, and the bond angles P—O—H and O—P—O are smaller in the associate. Unfortunately, experimental data on the existence of similar associates of formic and phosphoric acids in the gas phase or in solutions are not available, though the orthophosphoric acid monomer has been investigated experimentally[29] and theoretically[30,31] in detail.

The X-ray (in parentheses[29]) and recent theoretical (in brackets[31]) data for the phosphoric acid monomer, which agree fairly well with the corresponding values calculated in the present work, are presented in Fig. 3. It is interesting to note that when phosphoric acid binds with formic acid to give associate **1**, it adopts a conformation with C_1 symmetry. At the same time, the most stable conformer of the phosphoric acid monomer is the conformer with C_3 symmetry (not with C_{3v} symmetry as was predicted previously[31]) which is 0.9 kcal mol^{-1} more stable thermodynamically than the first conformer. The conformer with C_1 symmetry (0.7 kcal mol^{-1} less stable than the conformer with C_{3v} symmetry) was described recently.[31]

The cyclic C_2 structure **2** (Y = $O_2P(OH)_2$), differing from the C_{2v} conformer by the rotation of the O—H bonds and the formation of two intramolecular hydrogen bonds, corresponds (according to nonempirical calculations) to the saddle point ($\lambda = 1$) and to the transition state of the reaction **1a** ⇌ **2** ⇌ **1b** of cooperative proton transfer with an activation barrier of 13.3 kcal mol^{-1}. The energetic difference of 1.5 kcal mol^{-1} between the C_2 and C_{2v} conformers can be considered as the energy of formation of the two intramolecular hydrogen bonds in the transition C_2 structure **2**. It is interesting to note that reaction (1) of the double proton transfer proceeds with inversion of the tetrahedral configuration at the phosphorus center. Nonempirical calculations of the activation barrier to intramolecular 1,3-H transfer in the phosphoric acid molecule gives the value of 40.9 kcal mol^{-1}, which is much higher than that for intermolecular hydride transfer.

Associate of formic and sulfuric acids 1a (Y = O_3SOH). The calculations show that **1a** with C_1 symmetry corresponds to the energy minimum ($\lambda = 0$) while structure **2** (Y = O_3SOH) with C_s symmetry corresponds to the saddle point ($\lambda = 1$) on the PES. The calculated energetic and geometric parameters of structures **1** and **2** for Y = O_3SOH are presented in Table 1 and in Fig. 4.

The associate of formic and sulfuric acids **1a** is stabilized by two hydrogen bridges whose calculated energy of formation is equal to 16.4 kcal mol^{-1}. The geometric parameters of the hydrogen bridges OH...O in this associate are fairly close to those in the formic acid dimer.[26] The S=O and O—H bond lengths are slightly longer, the S—O bond is shorter, and the bond angles S—O—H and O—S—O are smaller in the H-bonded complex.

No experimental data on the existence of similar associates of formic and sulfuric acids in the gas phase or in solutions are available. At the same time, the sulfuric acid monomer has been studied both experimentally[19,25,29,32] and theoretically[33–35] in detail. Experimental data (in parentheses[32]) for two conformations of the sulfuric acid monomer, the structure with C_1 sym-

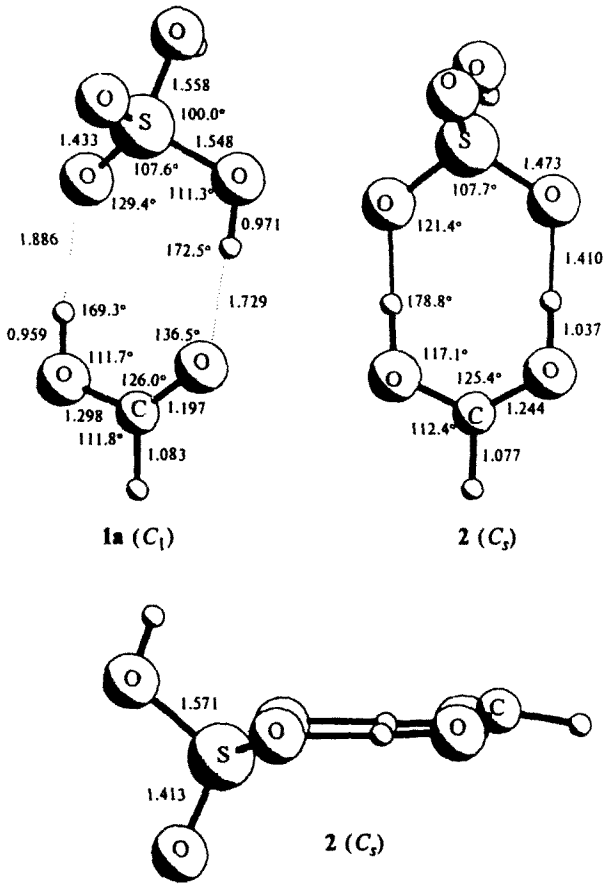


Fig. 4. The structures of associate **1a** (Y = O_3SOH) and of the transition state **2** (two projections) of the intermolecular proton transfer calculated by the HF/6-31G** method. Bond lengths (in Å) and bond angles are indicated.

metry (bound to formic acid) and the most stable C_2 form, are presented in Fig. 5.

As calculations have shown, the symmetric C_2 structure of sulfuric acid is 1.6 kcal mol^{-1} more thermodynamically stable than the conformation with C_1 symmetry. The calculated geometric parameters of the C_2 conformer are in fairly good agreement with the corresponding experimentally measured values (see the numbers in parentheses[32] in Fig. 5). Data obtained by the MP2/6-311+G(d,p) method[34] are also presented in Fig. 5 (see the numbers in brackets).

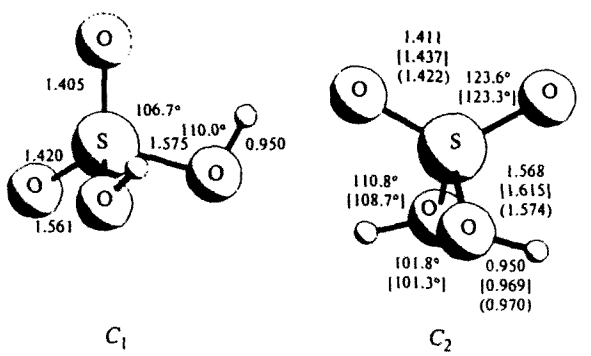


Fig. 5. Stable structures of the sulfuric acid molecule (with C_1 and C_2 symmetry) calculated by the HF/6-31G** method. Bond lengths (in Å) and bond angles are indicated; the results of calculations[32] by the MP2/6-311+G** method and the experimental data[34] are given in brackets and in parentheses, respectively.

According to nonempirical calculations, the chair-shaped cyclic structure **2** (Y = O_3SOH) with C_s symmetry corresponds to the saddle point (λ = 1) and to the transition state of the reaction **1a** ⇌ **2** ⇌ **1b** of cooperative proton transfer. Attention is drawn to the fairly large deviations (~13°) of the O—S—O and O—C—O fragments from the plane in which the four O atoms are located and to the pyramidalization of the carbonyl C atom, which is evidence for violation of the aromatic character of the cycle. All the attempts to find a transition structure of intramolecular 1,3-H transfer in the sulfuric acid monomer failed because of its dissociation into O_2 + SO + H_2O fragments with a substantial increase (>60 kcal mol^{-1}) in the total energy on the assumed reaction pathway.

Stereochemical conditions of a cooperative reaction

The inorganic acid molecule in associates **1a** (Y = ONO, ONO_2, $O_2P(OH)_2$, O_3SOH) is a bifunctional (acid-base) catalyst acting as both a proton donor and a proton acceptor, *i.e.*, cooperatively (concertedly or in one step) transferring two protons along the two hydrogen bridges. The transfer of a proton from one atom to another proceeds presumably *via* a linear transition state;[5,14] however, both calculated[5,8,9,14] and experimental[36] data point to the fact that the energy of the hydrogen bridges is not very sensitive to angular deformations within ±20°. At the same time, the activation barrier to the proton shift strongly depends on the distance between the heavy atoms in the hydrogen bridge.[13]

The activation barriers to cooperative proton transfer in associates **1a** predicted by calculations decrease monotonically in the sequence Y = ONO, ONO_2, $O_2P(OH)_2$, O_3SOH (19.9, 14.2, 13.3, and 10.7 kcal mol^{-1}, respectively). They correlate with a decrease in the distance between the covalently nonbonded H and O atoms in the hydrogen bridge as well as with increasing acidity of the O—H bond. Thus, the longest distances between oxygen atoms in the O—H...O bridges are observed in associate **1a** with nitrous acid (the weakest among YH acids under study). Correspondingly, calculations give the highest (among structures investigated) value of the activation barrier for this associate.

The lowest activation barrier to the proton shift is overcome in the associate of formic acid with the strongest acid, sulfuric acid, which is characterized by fairly short bonds in the hydrogen bridge. It should be noted that in transition state **2** the displacement of both migrating protons to the O atoms of formic acid (see

Figs. 1—4) increases as the strength of the acid (pK_a) increases. Thus, the calculations performed have shown that the principle of stereochemical correspondance[8,9] must be obeyed in order for low-barrier cooperative (concerted or one-step) reactions of double proton transfer to be proceeded.

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