Four-proton migrations in associates of two molecules of formic acid with two molecules of water or hydrogen fluoride

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The mechanisms of proton transfer in associates of two molecules of formic acid with two molecules of water or hydrogen fluoride were studied using *ab initio* (SCF/6-31G**) method. Cooperative (concerted, or one-step) four-proton transfer occurs in the associates studied. The structures of the transition states are in complete agreement with the previously proposed concept of stereochemical correspondence for cooperative reactions. The calculated energy barriers to cooperative proton transfer in the associates investigated are 32.9 and 24.2 kcal mol^{-1}, respectively.

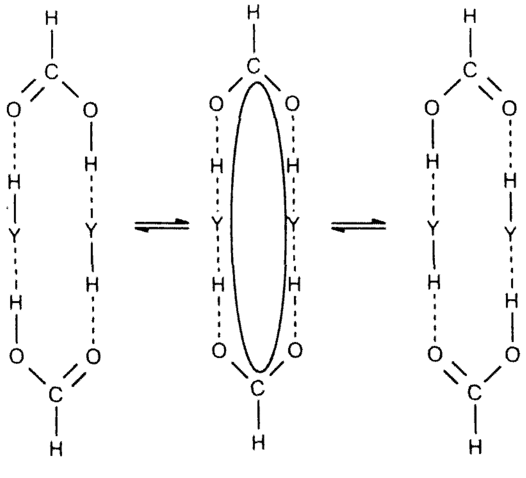
Key words: formic acid, associate; concerted four-proton transfer; potential energy surface, *ab initio* calculations.

Cooperative transfers of two or several groups (or atoms) with no valent bondings along the reaction chain of a molecular system play a fundamental role in many chemical and biochemical processes.[1—5] The cooperative transfer of two, three, and a larger number of protons in organic compounds or in their associates have been studied experimentally as well as theoretically with great intensity.[6—23] The data obtained show that in almost all dimers,[5, 6, 24—30] dimeric molecular associates,[8—10] or dimeric contact complexes,[20—23] where suitable stereochemical conditions are realized, proton transfer occurs concertedly (as a one-step cooperative reaction).

At the same time, it is known that one-step proton transfers occur in the hydrogen-bonded chains of water molecules when the associates consist of a small number of molecules (~3—5).[15] Stepwise transfer of protons occurs in long H-bonded chains (when the number of water molecules >5). It was shown in Refs. 18, 19 that double proton transfer occurs in the dimer of 1,2-imidazole, whereas in the trimer and tetramer the stepwise mechanism is realized. Thus, the mechanism of proton transfer depends not only on the stereochemical correspondence of the monomers to each other in the structure of the associate, but also on the length of the H-bonded system in which it occurs.

According to *ab initio* calculations and experimental data, proton transfer occurs cooperatively in all of the dimers of carboxylic acids investigated.[5—11]

It is important to elucidate whether the mechanism and energetics of cyclic proton transfer change when the H-bonded system is lengthened through the incorporation of two additional molecules of solvent (for instance, water or hydrogen fluoride) into the hydrogen bridge between two molecules of formic acid, *i.e.*, on going to associates of type **1**. The aim of this work was to study the effect of the length of an H-bonded system on the mechanism and energetic characteristics of intermolecular proton transfer (1) in associates **1** formed by two molecules of formic acid and two molecules of water (Y = OH) or hydrogen fluoride (Y = F), using *ab initio* RHF/6-31G** method. The calculation procedure used in this work is analogous to a procedure described previously.[31]



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

Mechanisms of double proton transfer

The associate of two molecules of formic acid and two water molecules (**1a**, Y = OH), according to calculations, corresponds to the energy minimum (λ = 0;

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Table 1. Total (E/a.u.) and relative (ΔE/kcal mol^{-1}) energies, the number of negative eigenvalues of the Hessian (λ), and two minimum (ν_1, ν_2/cm^{-1}) or imaginary ($i\nu$/cm^{-1}) frequencies predicted by the *ab initio* (RHF/6-31G**) method

Structure	$-E^a$	ΔE	λ	$\nu_1, \nu_2/i\nu$
1 (C_1), Y = OH	526.64315	0	0	32; 38
1 (C_2), Y = OH	529.64305	1.7	1	i34.9
2 (C_{2v}), Y = OH	529.59077	32.9	1	i953.5
1 (C_2), Y = F	577.62140	0	0	30; 38
2 (C_{2v}), Y = F	577.49057	24.2	1	i1524.5
HC(O)OH (C_s)	188.77057	—	0	692; 712
H_2O (C_{2v})	76.02361	34.4^b	0	1770; 4146
HF ($C_{\infty v}$)	100.01169	35.7^b	0	4492

^{a} 1 a.u. = 627.5095 kcal mol^{-1}. ^{b} Relative energies of four isolated molecules.

hereinafter λ denotes the number of negative eigenvalues of the Hesse matrix at a given critical point[32]), while cyclic structure **2** with C_{2v} symmetry corresponds to the saddle point (λ = 1) on the potential energy surface (PES). The calculated energetic and geometric characteristics of structures **1** and **2** are presented in Table 1 and in Figs. 1, 2.

Associate **1a** is stabilized by four hydrogen bridges with a fairly high value of the formation energy (34.4 kcal mol^{-1}) and has an unusually asymmetric structure (all of the similar geometric parameters in the monomeric fragments differ significantly). High H-bond energies are observed in cationic associates containing several hydrogen bonds or in polyesters.[33] It is of interest to note that the hydrogen atoms of both the formic acid and the water molecules participating in the formation of hydrogen bonds in structure **1a** are aligned very nearly along the sp^2- or sp^3-hybrid orbitals of the corresponding oxygen atoms containing unshared electron pairs. This agrees with the general structural properties of hydrogen bonds in various associates,[11,34–36] hydrates, and polymorphic structures of ice.[34–36]

The distance between the oxygen atoms of two water molecules in associate **1** is 2.929 Å, which is very close to that experimentally measured (2.98(0) Å) in the water dimer in the vapor phase,[7,37] whereas in polymorphic forms of ice[35,36] it lies in the range from 2.74 to 2.87 Å, which is significantly shorter than in **1**. In spite of the high values of the formation energy of the H-bonds, the geometric characteristics of isolated molecules of both formic acid and water change insignificantly in the course of the formation of the H-bonded complex **1**. There are no experimental data on the formation of type **1** associates in the gas phase; at the same time, the high value of the association energy points to a high probability of their existence in the gas phase.

According to *ab initio* calculations, cyclic structure **2**, with C_{2v} symmetry (see Fig. 2), corresponds to the saddle point (λ = 1) and transition state of reaction (1). This indicates that proton transfer (1) for Y = OH occurs concertedly with the simultaneous transfer of

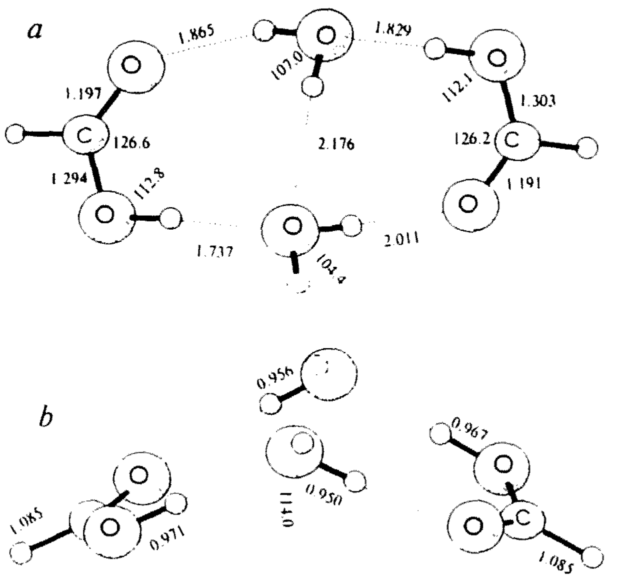


Fig. 1. Geometric characteristics of associate **1** (Y = OH) with C_1 symmetry calculated by the *ab initio* (RHF/6-31G**) method: *a*, the top view from the plane passing through four oxygen atoms of formic acid; *b*, the side view. The bond lengths (*d*) are given in Å, the bond angles (ω) are given in degrees.

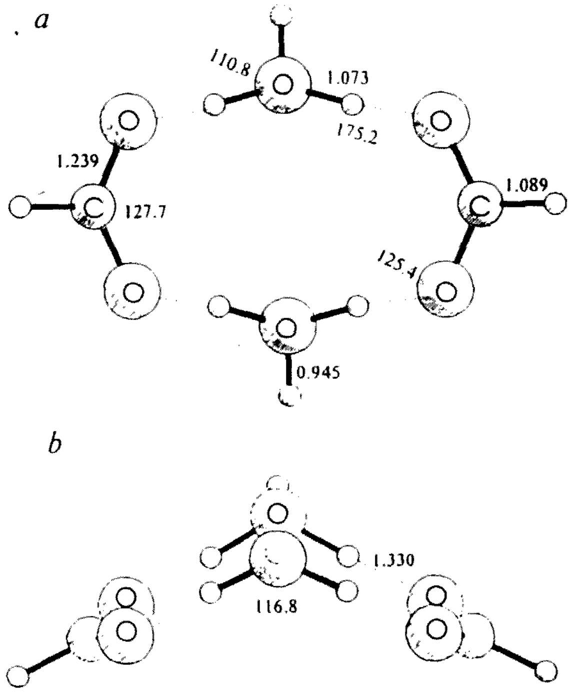
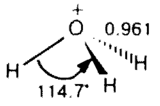


Fig. 2. Geometric characteristics of transiton state **2** (Y = OH) with C_{2v} symmetry calculated by the *ab initio* (RHF/6-31G**) method: *a*, the top view from the plane passing through four oxygen atoms of formic acid; *b*, the side view (*d*/Å; ω/deg).

four protons. The calculated energy barrier to the reaction is 32.9 kcal mol^{-1}, which is significantly higher than in the case of the double proton transfer in the formic acid dimer (14—15.5 kcal mol^{-1} and 14—16 kcal mol^{-1} according to *ab initio* calculations[24—27] and experimental data,[38,39] respectively). The structure of the OH_3 fragment in associate **2** is very close to that of the oxonium cation OH_3^+ (**4**) (RHF/6-31G** calculations).



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It is significant that the gradient reaction pathway,[32] issuing out of the saddle point (corresponding to complex **2**) on the PES at a direction tangent to the transition vector, does not enter minima **1a** or **1b**, but the adjacent saddle point (λ = 1) corresponding to the transition structure **5** (Fig. 3), which reflects the asymmetrization of all the geometric parameters:

$\mathbf{1a} \rightleftharpoons \mathbf{5} \rightleftharpoons \mathbf{1a'}$ (**1a'** and **1a** are enantiomers).

The associate of two molecules of formic acid and two molecules of hydrogen fluoride (1a, Y = F), according to calculations, corresponds to the energy minimum (λ = 0), while the cyclic structure **2** (Y = F) with C_{2v} symmetry corresponds to the saddle point (λ = 1) on the PES. The calculated energetic and geometric characteristics of structures **1**, **2** (Y = F) are presented in Table 1 and in Figs. 4, 5.

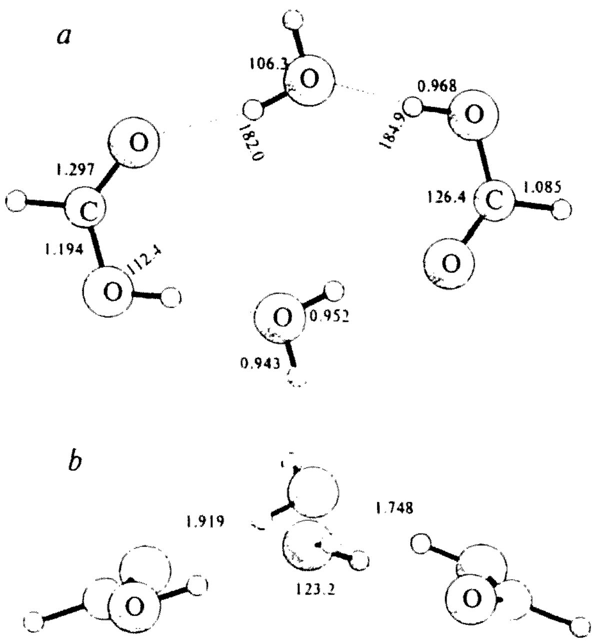


Fig. 3. Geometric characteristics of transiton state **5** (Y = OH) with C_2 symmetry calculated by the *ab initio* (RHF/6-31G**) method: *a*, the top view from the plane passing through four oxygen atoms of formic acid; *b*, the side view (*d*/Å; ω/deg).

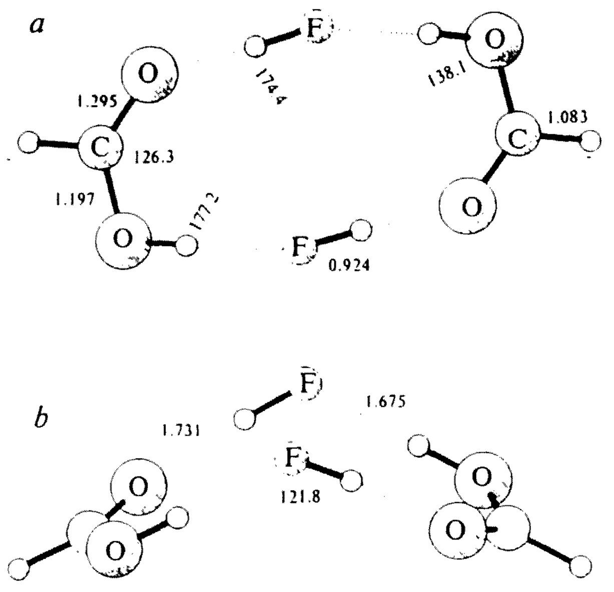
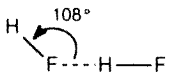


Fig. 4. Geometric characteristics of associate **1** (Y = F) with C_2 symmetry calculated by the *ab initio* (RHF/6-31G**) method: *a*, the top view from the plane passing through four oxygen atoms of formic acid; *b*, the side view (*d*/Å; ω/deg).

Associate **1a** (Y = F) is stabilized by four hydrogen bridges that are significantly shorter than those in the case of water molecules. The calculated value of the energy of association is 35.6 kcal mol^{-1}, which is somewhat higher than that for associate **1a** (Y = OH). As can be seen from Fig. 4, the geometric characteristics of the monomeric fragments do not change significantly in the course of formation of complex **1a**. Associate **1a** (Y = F) has a boat structure. The angle between the planes in which the formic acid molecules are located is 121.8°. This angle is larger than that found by the microwave method for associates of hydrogen fluoride **6** in the gas phase,[40] but it is close to the similar angle in solid HF (**7**) (neutron diffraction studies of DF at 85 K)[35] and is somewhat smaller than that in the structure of KH_2F_3 (**8**) (X-ray studies).[35]



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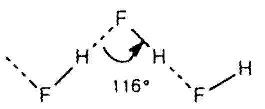

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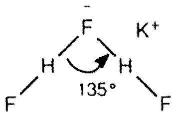

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According to *ab initio* calculations, cyclic structure **2** (Y = F) with C_2 symmetry corresponds to the saddle point (λ = 1) and is a transition structure in reaction (1) with an energy barrier of 24.2 kcal mol^{-1}, which is significantly lower than the barrier to the four-proton transfer in the studied associate of formic acid with water. It is important to note that in transition state **2** when Y = OH the transferring protons are shifted to-

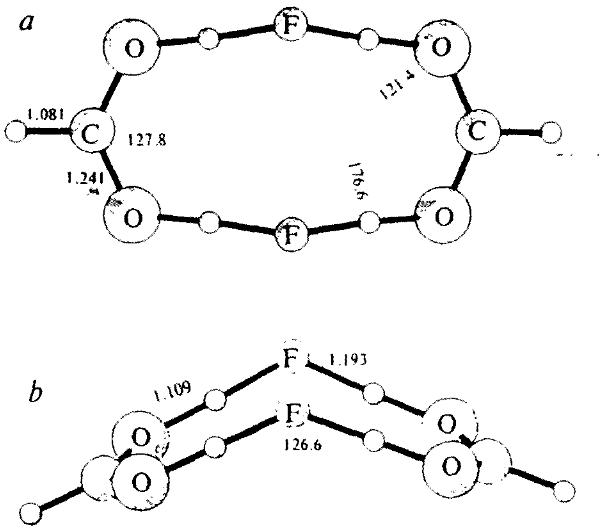

Fig. 5. Geometric characteristics of transition state **2** (Y = F) with C_{2v} symmetry calculated by the *ab initio* (RHF/6-31G**) method: *a*, the top view from the plane passing through four oxygen atoms of formic acid; *b*, the side view (d/Å; ω/deg).

wards the central oxygen atoms, whereas when Y = F they are shifted to a greater degree in opposite direction, to the oxygen atoms of formic acid (see Fig. 5). This structural discrepancy can be explained by the fact that the proton affinity of hydrogen fluoride (131.4–138.4 kcal mol^{-1})[41] is lower than that of water (153.6–164.6 kcal mol^{-1}).[41]

Stereochemical conditions of the cooperative reaction. Summing up the hypotheses proposed previously,[6,8,9,11,42] one can state the general stereochemical conditions necessary for a low-barrier cooperative reaction to proceed: (a) stereochemical similarity of the structures of the transition state **2** and the pre-reaction complex **1**, and (b) stereochemical correspondence of the bond configurations around each atom in the ring in the transition form **2** and in the transition states of all "elementary" bimolecular reactions.

Comparing structures **1** and **2**, presented in Figs. 1–5, one can draw the conclusion that they are sufficiently similar both structurally (values of geometric parameters) and topologically (they have an equal number of chemical bonds distributed around each atom, with the unshared electron pair considered as a ghost-ligand for both atoms located on either side of it). This points to the fulfillment of the first stereochemical condition. Analogously, comparing the structures of the oxonium cation or HFH^+ and those of the corresponding nodes in form **2**, and taking into account the linearity of the hydrogen bridges in the latter, one can conclude that the second stereochemical condition is also fulfilled. The extent of fulfillment of both stereochemical conditions increases on going from Y = OH to Y = F (the lengths of the H-bonds and the proton affinity decrease on going from H_2O to HF), which explains the decrease in the energy barriers to cooperative proton transfer in this series predicted by the calculations (32.9 and 24.2 kcal mol^{-1}).

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