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Hydrogen Bonding between Formic Acid and Water: Complete Stabilization of the Intrinsically Unstable Conformer

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We studied hydrogen bonding between formic acid (FA) and water in solid argon and identified the first water complex with the higher-energy conformer *cis*-FA. In sharp contrast to *cis*-FA monomer, *cis*-FA interacting with water is very stable at low temperatures, which was explained by strong O−H···O hydrogen bonding. These benchmark results show that hydrogen bonding can terminate proton tunneling reactions and efficiently stabilize intrinsically unstable conformational structures in complex asymmetrical hydrogen-bonded networks. This general effect occurs when the energy difference between conformers is smaller than the hydrogen bond interaction energy, which opens perspectives in chemistry on intrinsically unstable conformers.

Hydrogen bonding, proton tunneling, and molecular conformation are central concepts in many branches of science. The C−H···O and O−H···O noncovalently bonded systems determine many condensed-phase physical properties as well as chemical and biological reactions.[1,2] Molecular conformation and molecular charge distribution play a crucial role in the selectivity and function of biologically active molecules.[2] Formic acid (HCOOH, FA) is a simple organic molecule that can form a variety of such hydrogen-bonded structures, and water is a generally important interaction counterpart, particularly in environmental research. Formic acid can be found in two conformers that differ by orientation of the OH group.[3] By vibrational excitation of the lower-energy *trans*-FA monomer, the higher-energy cis form was prepared in solid argon and its IR spectrum was studied.[4] *cis*-FA converts to *trans*-FA by proton tunneling, which limits its lifetime to several minutes.[5] Hydrogen bonding in the *cis*−*trans*-FA dimer stabilizes to some extent the cis conformer against tunneling of the "free" hydrogen atom.[6] The FA−water complex has been studied theoretically and experimentally, the experiments being limited to the low-energy *trans*-FA conformer.[7−11] In the present work, we report on the first complex of the higher-energy conformer *cis*-FA with water in solid argon. In sharp contrast to *cis*-FA monomer, no decay of *cis*-FA interacting with water is observed at low temperatures, which is due to strong O−H···O hydrogen bonding.

In our experiments, the FA/H_2O/Ar gas mixture was deposited onto a CsI window in an APD DE 202A cryostat. Vibrational excitation was done with pulsed narrowband IR radiation of an optical parametric oscillator (OPO, Continuum, Sunlite) with repetition rate of 10 Hz. The pumping wavelength was measured with a Burleigh WA-4500 wavemeter. The IR spectra were recorded with a Nicolet 60 SX FTIR spectrometer (resolution 1 cm^{-1}).

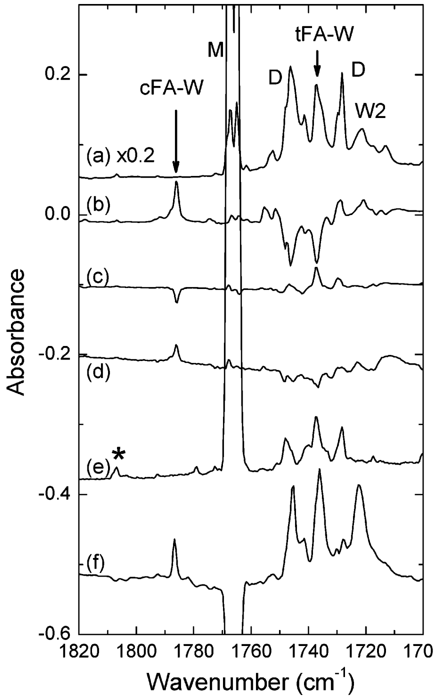

Figure 1. IR spectra of the FA−water system in the C═O stretching region in an Ar matrix at 9 K. (a) Spectrum after deposition at 28 K (notice the multiplying factor). (b) Difference spectrum showing the result of 10 h OPO irradiation of this sample at ~6200 cm^{-1} with pulse energy density ~1 mJ/cm^2. (c) Difference spectrum showing the result of the next 2 h irradiation around 6600 cm^{-1} of the same sample. (d) Difference spectrum showing the result of the globar irradiation for 250 h of as-deposited sample with FA−water complexes. (e) Spectrum after deposition at 12 K. The small band of *cis*-FA monomer is marked with an asterisk. (f) Difference spectrum showing the result of simultaneous OPO irradiation at 6935 cm^{-1} and annealing at 25 K of this sample.

Figure 1a presents the IR spectrum of an as-deposited FA/H_2O/Ar matrix in the characteristic C═O stretching region at 9 K. The relatively high deposition temperature (28 K) and matrix ratio (~1/1000 for FA and water) lead to the formation of

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TABLE 1: Frequencies and Complexation-Induced Shifts from the Monomeric Values (cm^{-1}) for Complexes between FA and Water

	trans-FA···H_2O (tFA−W)			*cis*-FA···H_2O (cFA−W)		
mode	freq exp[a]	shift exp[b]	shift calc[c]	freq exp	shift exp[b]	shift calc[c]
OH stretch	3692	−42	−34	3722	−12	−9
(water)	3537	−103	−134	3634	−4	−7
O−H stretch	3212	−339	−357	3386	−230	−236
C−H stretch	2944	−9	−3	2882	−14	−5
C═O stretch	1737	−30	−44	1786	−21	−21
deformation	1172	+69	+86	1342	+93	+90
				1139	+34	+54
torsion	829	+194	+291	785	+280	

[a] The frequencies of tFA−W for water and OH stretching, C═O stretching, and deformation modes of FA agree with ref 10. [b] Data for water monomer from ref 18 and for FA monomer (site 2) from ref 17. [c] From ref 11.

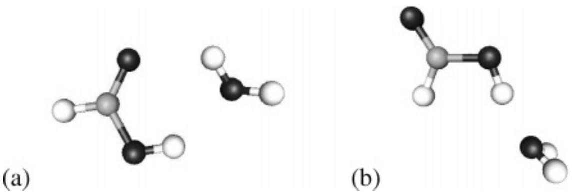

Figure 2. Complexes of trans and cis conformers of FA with water: (a) tFA−W; (b) cFA−W. The geometries are from ref 11. Our nomenclature of the FA conformers follows refs 3 and 4.

complexes. The complex between *trans*-FA and a water molecule (tFA−W) is evidenced by the C═O stretching absorption at 1737 cm^{-1},[10] and the other absorption bands of this complex are given in Table 1. The complexation-induced shifts are in good agreement with the theoretical data of Zhou et al., and the complex structure is shown in Figure 2a.[11] This is the lowest-energy complex with BSSE-corrected interaction energy of −32.9 kJ/mol [CCSD(T)/MP2].[11] This configuration was observed in the gas phase, the experimental structural data being very close to the computational results.[8] The other bands in our IR spectrum are from *trans*-FA monomer (M, 1767 cm^{-1}),[4] various *trans*-FA dimers (D, 1748 and 1728 cm^{-1}),[6,12] and a complex of *trans*-FA and two water molecules (W2, 1722 cm^{-1}).[10]

Figure 1b shows the result of OPO irradiation at about 6200 cm^{-1}. This irradiation bleaches the absorption bands of the tFA−W complex and promotes a number of new absorptions, in particular, a well-defined band at 1786 cm^{-1}. A set of bands correlating with the 1786 cm^{-1} band is presented in Table 1. These absorption bands appear only in samples containing both FA and water; hence, they belong to some complexes between FA and water. We assign these bands to the complex structure presented in Figure 2b (cFA−W). It is computationally the lowest-energy complex between *cis*-FA and a water molecule (BSSE-corrected energy −29.6 kJ/mol),[11] and the agreement with the theoretical spectrum is very good for all characteristic bands. Due to the known matrix effect and limitations of the harmonic theory, the structural identification is done most reliably using the complexation-induced shifts rather than the absolute computed frequencies. The participation of *cis*-FA in the complex is particularly evidenced by two fingerprint bands at 1342 and 1139 cm^{-1} in the deformation region and the 1786 cm^{-1} C═O stretching band that is at a higher energy from the *trans*-FA monomer band. This is the first time when a hydrogen-bonded complex between the higher-energy *cis*-FA conformer and water has been prepared. Figure 2 makes clear that the tFA−W → cFA−W process needs not only the trans to cis conformational change but also a more extensive rearrangement of the system, especially taking into account the solid argon surrounding. In agreement, the efficiency of the light-induced tFA−W → cFA−W conversion is several orders of magnitude lower than the trans to cis process for FA monomers. The reverse cFA−W → tFA−W process was also achieved by infrared pumping with the OPO, and the result is presented in Figure 1c: the decrease of the cFA−W concentration correlates with an increase of the tFA−W concentration, which strongly supports our assignment. In particular, the complex of FA with two water molecules is unchanged upon this OPO excitation, confirming the 1:1 complex structure. The action spectra of the obtained light-induced processes show quite broad bands, which is specific for absorption of hydrogen-bonded systems[13] and limits the pumping selectivity. It was found that the globar light gradually produces cFA−W from tFA−W even when the sample is kept at 30 K, which is practically the maximal isolation temperature in solid argon. The result of globar irradiation for 10 days at 9 K is shown in Figure 1d, and it is similar to the OPO pumping effect.

The value of the present experimental observation of the cFA−W complex evidently exceeds the simple spectroscopic curiosity. Most importantly, the cFA−W bands are stable in dark at 9 K on a day scale within our experimental accuracy limited by the signal-to-noise ratio (∼1%), which strongly differs from the situation with *cis*-FA monomer that has a lifetime of ∼10 min at this cryogenic temperature.[5,6] Thus, the stabilization of *cis*-FA upon interaction with water is at least 4−5 orders of magnitude; i.e., the lifetime is at least several months. We believe that the lifetime of the cFA−W complex is practically *infinite* at the low temperatures (longer than several months); i.e., proton tunneling to the *trans*-FA configuration is efficiently terminated. In addition to the experimental results, this conclusion is based on the calculated energetics of the complex between *cis*-FA and water shown in Figure 2b. Tunneling of *cis*-FA in the cFA−W complex to *trans*-FA would suddenly destroy the hydrogen bonding, the tunneling proton would become surrounded by argon matrix atoms, and the positions of other atoms would be unchanged during the tunneling time. The interaction energy of the cFA−W complex is −29.6 kJ/mol,[11] the *trans*-FA monomer is lower in energy than the *cis*-FA monomer by 16.7 kJ/mol,[3] and the interaction between *trans*-FA and argon atoms is very weak.[14] This suggests that the energy of the configuration after proton tunneling should be substantially higher than the initial energy. It follows that proton tunneling from the cFA−W configuration is suppressed in adiabatic approximation according to the Fermi golden rule.[15,16] The final tunneling state at the initial energy simply does not exist in this case! Thus, the strong asymmetry of hydrogen bonding in favor of the cis conformation can stop proton tunneling at low temperatures. It seems also that similar stabilization of the cFA−W configuration might take place in the gas phase. In general, it is known that hydrogen-bonded interactions can influence conformation of flexible molecules.[2] However, most considerations of small molecules like formic acid concentrate on the lowest-energy conformers.

The next experiment emphasizes the stability of cFA−W in solid argon and suggests an efficient synthesis procedure. The FA/water/Ar matrix deposited at 12 K is rather monomeric with respect to FA as seen in Figure 1e. Annealing of this sample at 25−30 K in the dark leads to the formation of complexes, and the resulting spectrum is similar to curve a. The result changes drastically if the sample is irradiated *during annealing* with light producing *cis*-FA monomer. In this situation, the light-produced *cis*-FA monomers can form complexes with vicinal water molecules, in other words, annealing “freezes” the unstable conformer by interaction with water. Indeed, the most prominent set of bands formed upon simultaneous annealing and optical pumping belongs to the cFA−W complex (see Figure 1f). For instance, this synthesis can be done by exciting the first OH-stretching overtone of *trans*-FA monomer at 6935 cm^{-1}.[17] It should be emphasized that both optical pumping and annealing are required for the cFA−W formation. The different synthesis method changes the cFA−W absorption energies; for instance, the OH-stretching mode changes from previous 3386 to 3363 cm^{-1}, the deformation mode changes from 1342 to 1338 cm^{-1}, and the C═O stretching band narrows and shifts slightly upward. These spectral modifications are from different organizations of local matrix morphology perturbing the complex structure (matrix-site effect). The described synthesis method can be successfully applied to photochemical preparation of complexes of desired (unstable) conformers.

In conclusion, we reported the preparation and identification of the first complex of the higher-energy conformer *cis*-FA with water in solid argon. It is found that the lifetime of *cis*-FA interacting with water is practically unlimited (longer than several months at 9 K), which is drastically longer than the lifetime of *cis*-FA monomer (∼10 min). The observed stabilization effect is explained by the strong O−H···O hydrogen bonding between formic acid and water. In general, the present study demonstrates that intrinsically unstable conformational structures can be thermodynamically stable in asymmetrical hydrogen-bonded networks. This effect occurs when the energy difference between conformers is smaller than the hydrogen bond interaction energy, which allows chemistry on unstable conformers to be studied.

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