cis−trans Formic Acid Dimer: Experimental Observation and Improved Stability against Proton Tunneling

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Formic acid dimer is a simple organic system which can form a variety of hydrogen-bonded structures. This offers a general model to study properties and reactions involving the C−H···O and O−H···O noncovalently bonded systems, which is of primary importance for many processes, including the science of life.[1] Formic acid (FA) can be found in two conformers shown in Figure 1a.[2] By vibrational excitation of the lower-energy *trans* form, *cis*-FA was prepared in an Ar matrix, and its IR absorption spectrum was studied.[3] *cis*-FA converts to *trans*-FA via a tunneling mechanism, which limits its lifetime.[4] In the gas phase, most FA molecules are in *trans−trans* cyclic dimers, which are theoretically the lowest-energy form.[5−7] Various *trans−trans* noncyclic dimers are higher in energy, and such structures were found in He droplets and Ar matrices.[8,9] Three *cis−trans* dimers were computationally predicted,[7] and they are relevant to a high-pressure FA phase.[10] In the present work, we report the first preparation of a *cis−trans* FA dimer in an Ar matrix. This higher-energy form converts to the *trans−trans* dimer, but its tunneling decay is much slower than the process for the FA monomer.

Figure 2a presents an IR absorption spectrum in the O−H and C=O stretching regions of an as-deposited FA/Ar matrix. Based on literature, the C=O stretching bands originate from the *trans*-FA monomer, *trans−trans* cyclic dimer,[6,7] and *trans−trans* noncyclic dimer shown in Figure 1b.[9] Additional bands in the spectrum belong to other dimers or higher multimers. Excitation at 3540.1 cm⁻¹ decreases absorptions of the *trans−trans* noncyclic dimer and promotes several new bands. Using the concept of resonant optical pumping,[11] the band at 3540.1 cm⁻¹ marked with an arrow in Figure 2b belongs to the free OH bond of the *trans−trans* noncyclic dimer. The bands rising upon the 3540.1 cm⁻¹ excitation are assigned to the *cis−trans* dimer shown on the right in Figure 1b. The *cis−trans* dimer is produced by light-induced rotation of the free OH bond of the *trans−trans* form. The *cis−trans* dimer converts in the dark back to the *trans−trans* form, which presumably occurs via a tunneling mechanism similarly to the FA monomer.[4] Several fundamental absorption bands of the *trans−trans* and *cis−trans* dimers were also identified in other spectral regions based on the optical pumping and dark decay experiments. Table 1 presents the obtained experimental and computational[12] data, and they are in good agreement with each other. For instance, a large dimerization-induced shift for the C=O stretching mode of the *cis−trans* form is found (−40 cm⁻¹ experimentally and −33 cm⁻¹ theoretically). Our results confirm the literature assignment of the bands at 1180 and 1131 cm⁻¹ to the *trans−trans* noncyclic dimer.[9]

The decay kinetics was measured using the intense deformation absorptions of *cis*-FA (1248.8 cm⁻¹) and *cis−trans* dimer (1259.0 cm⁻¹). Figure 3a presents the decay of the *cis*-FA monomer and *cis−trans* dimer at 8.5 K. A striking observation here is a clear difference (by a factor of ∼3) in decay rates of the monomer and dimer. Furthermore, the decay of the *cis*-FA monomer is enhanced at elevated temperatures (by ∼10 times at 30 K) as reported earlier.[4]
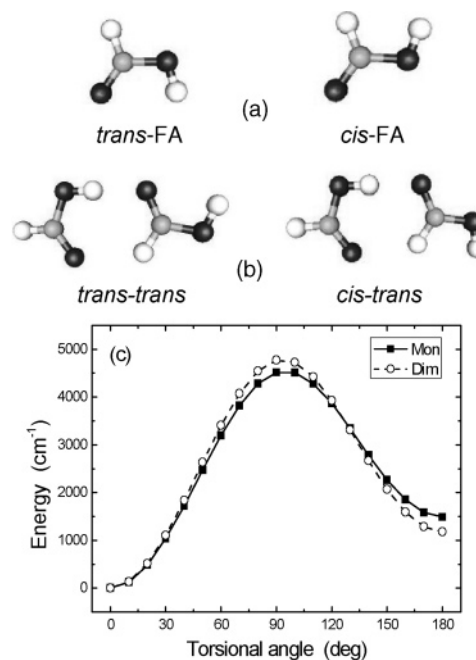

Figure 1. Conformers of formic acid (HCOOH): (a) *trans* and *cis* monomers; (b) *trans−trans* and *cis−trans* noncyclic dimers. (c) Torsional barrier for the FA monomer (squares) and noncyclic dimer (circles) at the MP2/6-311++G(2d,2p) level of theory. The conformational notation follows refs 2−4.

In sharp contrast, practically no increase of the decay rate was observed for the dimer in this temperature range, and at 30 K, the *cis−trans* dimer is ∼30 times more stable than the *cis* monomer. This is a surprising fact because the tunneling process mainly involves the free O−H bond of the *cis* conformer. In the following, we discuss these novel observations.

The computational torsional barrier for the conformational process is shown in Figure 1c. The *cis−trans* form is computationally stabilized by the 3432 cm⁻¹ barrier taking into account the zero point energy, which is quite higher than the stabilization barrier for the *cis*-FA monomer (2676 cm⁻¹). This difference in stabilization barriers can explain the slower tunneling-assisted decay of the dimer compared to that of the monomer at the lowest temperature in terms of barrier permeability. As a comparison, the *cis* acetic acid monomer has a computational stabilization barrier of 2310 cm⁻¹ that is ∼370 cm⁻¹ lower than the barrier for the FA monomer, and it decays in solid Ar at 8 K to the *trans* conformer ∼10 times faster than the FA monomer.[13] This is a good agreement taking into account such complicating reasons as different solvation effects and different vibrational state densities of these species.[4]

The negligible temperature dependence found for the *cis−trans* dimer decay deserves further discussion. The mechanism of the temperature dependence is contributed by various processes.[14] Due to the asymmetry of the torsional potential energy curve, tunneling
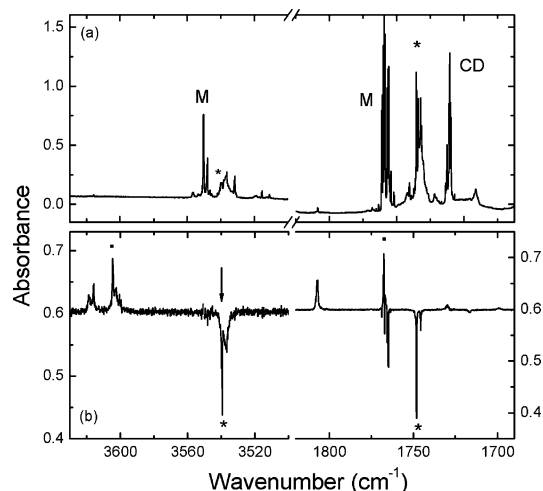
Figure 2. IR absorption spectra of FA in an Ar matrix at 8.5 K. (a) Spectrum after deposition. (b) Difference spectrum showing the result of excitation of the *trans−trans* dimer at 3540.1 cm^{-1} (marked with an arrow). Additional species are affected by nonresonant pumping to a smaller extent. The two parts of plot (b) are obtained in two experiments with different matrix thickness. Bands from *trans−trans* and *cis−trans* dimers are marked with asterisks and dots, and from monomers and cyclic dimers by M and CD, respectively. The FA/Ar (~1/500) gas mixture was deposited onto a CsI window at 25 K in an APD DE 202A cryostat. Vibrational excitation was done with pulsed narrowband IR radiation of an optical parametric oscillator (Continuum, Sunlite) with a pulse energy density of ~1 mJ/cm^2 and repetition rate of 10 Hz. The pumping wavelength was measured with a Burleigh WA-4500 wavemeter. The IR absorption spectra were recorded with a Nicolet 60 SX FTIR spectrometer.

Table 1. Experimental and Theoretical (in parentheses) IR Absorptions (in cm^{-1}) of FA Monomers and Dimers (see Figure 1). The Calculations Were Done at the MP2/6-311++G(2d,2p) Level

mode	trans-FA[a]	cis-FA[a]	trans–trans	cis–trans
ν(OH)	3550.5	3615.9	3540.1	3604.5
			3142.8	3115.4
			3101.4	3081.0
				3073.6
	(3783.9)	(3851.2)	(3776.2)	(3846.6)
			(3451.0)	(3420.4)
ν(CO)	1767.2	1806.9	1748.2	1766.6
	(1788.7)	(1829.0)	(1773.7)	(1796.2)
Def.		1248.8	1180.4	1259.0
	1103.2	1104.6	1131.8	1186.0
				1142.6
		(1287.1)	(1205.3)	(1300.8)
	(1123.3)	(1113.0)	(1155.9)	(1212.6)
				(1153.1)
τ(COH)	635.4	505.3	867.5	874.5
			658.1	550.2
	(676.6)	(536.6)	(936.1)	(945.7)
				(699.0)	(572.7)

[a] Data for site 2 of FA monomers following assignment of ref 11.

involves excited vibrational states of the *trans−trans* dimer as intermediates in the vibrational energy redistribution process. The energy mismatch between the *cis−trans* dimer ground state and the excited *trans−trans* dimer vibrational levels should be dissipated, and lattice phonons provide a temperature-dependent dissipation channel. The weak temperature dependence of the tunneling rate can be due to a decreased coupling of the accepting modes with the lattice phonons in the dimer. Indeed, the continuous energy spectrum of phonons is an important factor of the temperature dependence.[14] The temperature-independent tunneling rate can also originate from an increase of the energy mismatch on the Debye frequency scale (65 cm^{-1} for solid Ar). At least two mechanisms are operating here, which are different solvation of the monomers
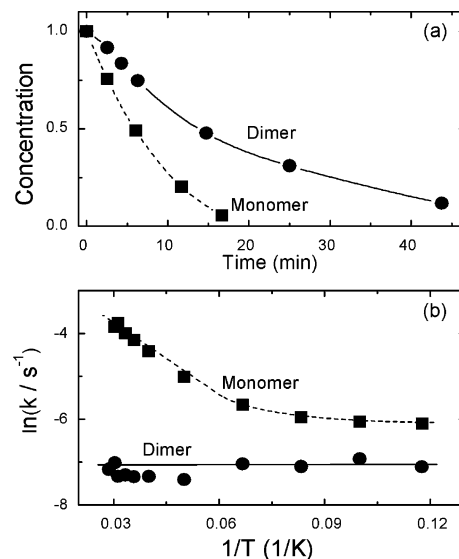

Figure 3. (a) Decay of the *cis−trans* dimer and *cis*-FA monomer in an Ar matrix at 8.5 K. (b) Decay rate as a function of 1/T. The rate constants were obtained by single exponential fit. A long-pass filter (<1800 cm^{-1}) suppressed the effect of glowbar radiation in the kinetics measurements.[11]

and dimers in solid Ar and the complexation-induced modification of the *trans−trans* vibrational manifold. These can also change the type of the accepting energy level.[4]

In conclusion, we report for the first time the vibrational spectrum of *cis−trans*-FA dimer. Its preparation was done by selective vibrational excitation of the *trans−trans* noncyclic dimer in an Ar matrix. It was found that the stability of the *cis−trans* dimer against proton tunneling is strongly improved compared to that of the monomer, especially at elevated temperatures (>30 K). This surprising phenomenon was explained by differences in energetic and vibrational properties of the dimer and monomer. The obtained results show that the proton tunneling reactions can be strongly modified in the hydrogen-bonded solid network compared to the monomers.

Supporting Information Available: Full citation for ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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