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Conformation-Dependent Chemical Reaction of Formic Acid with an Oxygen Atom

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Conformation dictates many physical and chemical properties of molecules. The importance of conformation in the selectivity and function of biologically active molecules is widely accepted. However, clear examples of conformation-dependent bimolecular chemical reactions are lacking. Here we consider a case of formic acid (HCOOH) that is a valuable model system containing the −COOH carboxyl functional group, similar to many biomolecules including the standard amino acids. We have found a strong case of conformation-dependent reaction between formic acid and atomic oxygen obtained in cryogenic matrices. The reaction surprisingly leads to peroxyformic acid only from the ground-state trans conformer of formic acid, and it results in the hydrogen-bonded complex for the higher-energy cis conformer.

Conformation dictates many physical properties of molecules including absorption and emission of light.[1] Conformation-dependent dynamics in the excited state influences the photodissociation channels.[2,3] The importance of conformation in the selectivity and function of biologically active molecules is widely accepted.[4] However, clear examples of conformation-dependent *bimolecular* reactions with understandable detailed mechanisms are obviously lacking. Here we report a strong case of conformation-dependent reaction between formic acid (FA, HCOOH) and atomic oxygen in cryogenic matrices. Formic acid may be considered as a valuable model system containing the −COOH carboxyl functional group, similarly to the biologically important standard amino acids. The FA + O reaction surprisingly leads to peroxyformic acid (HCOOOH) only from the ground-state *trans*-FA conformer, and it results in the hydrogen-bonded FA···O complex for the higher-energy *cis*-FA conformer. The *cis*-FA···O complex can be reacted to peroxyformic acid by IR-light excitation. These two reaction channels are strongly supported by IR absorption spectroscopy and quantum chemical calculations; both experimental and theoretical data completely agree on the reaction products. The theoretical explanation of the observed reaction routes requires an assumption that the singlet O(^{1}D) atoms, formed upon photolysis of the N_2O precursor, are responsible for the reactive interaction with *trans*-FA whereas the experimental observations are better consistent with an assumption of the ground-state O(^{3}P) atoms.

The FA/N_2O/Ng (~1/1/1000, Ng = Kr and Xe) matrices were studied in a closed-cycle helium cryostat (APD, DE 202A) at temperatures down to 8 K. The matrices were photolyzed by a 193 nm excimer laser (MPB, MSX-250). The IR spectra were measured with a Nicolet 60 SX FTIR spectrometer in the 4000−400 cm^{-1} range with the 0.25−1 cm^{-1} resolution. The matrices were also irradiated by IR light from an optical parametric oscillator with an IR extension (Sunlite, Continuum) to promote the *trans*-to-*cis* FA conformational change.[5] The quantum chemical calculations of the equilibrium geometry configurations and harmonic frequencies were performed using the MP2/aug-cc-pVTZ approximation for the singlet states of formic and peroxyformic acids and the CASSCF(16/11)/aug-cc-pVDZ approximation for the FA···O complexes and for scanning potential energy surfaces of the FA + O reaction. The energies reported below were computed in the CASSCF approximation since the equilibrium structures and transition states should be simulated at the same level of theory. The PC GAMESS package,[6] which is a version of the GAMESS(US) program,[7] was used in the calculations. Traditional scaling of the computed vibrational frequencies was performed to make comparison to the experimental band positions in solid matrices.

Most of the present experiments were performed in Kr matrices. After deposition of a matrix, formic acid is mainly in the more stable trans conformer and 193 nm photolysis produces no cis conformer either (Figure 1, spectrum 1).[5,8] The 193 nm photolysis of N_2O in matrices produces N_2 molecules and O atoms isolated in the matrix.[9] Partial decomposition of formic acid is also observed leading to the $CO\cdots H_2O$ complex as the main product and $CO_2\cdots H_2$.[10] Thermal annealing at 25 K activates extensive mobility of O atoms in solid krypton, and they can participate in diffusion-controlled reactions as discussed elsewhere.[11]

The first important observation of the present work is that thermally mobilized O atoms chemically react with *trans*-formic acid, which leads to the formation of two absorbers marked by I and II in spectrum 2 in Figure 1. In addition, the $CO_2\cdots H_2O$ complex is formed from the $CO\cdots H_2O$ + O reaction as well

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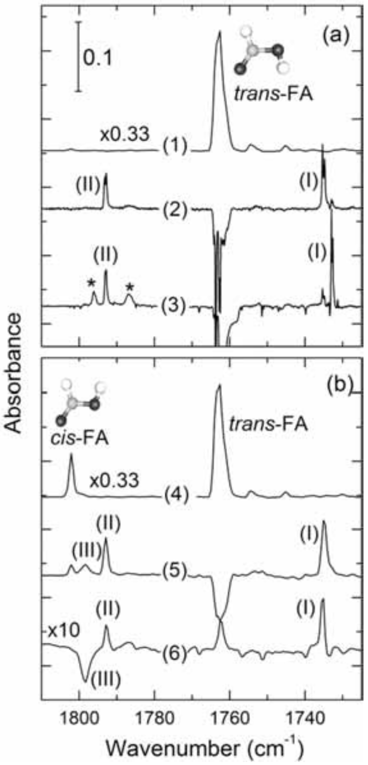

Figure 1. FTIR spectra in the C=O stretching region showing thermal reactions between O atoms and FA in solid krypton. (a) Spectra obtained from *trans*-FA: (1) spectrum after 193 nm photolysis for *trans*-HCOOH (multiplied by 0.33); (2) and (3) spectra after annealing at 25 K for *trans*-HCOOH and *trans*-HCOOD. (b) Spectra obtained from matrices containing *cis*-FA: (4) spectrum of a matrix after 193 nm photolysis and IR-induced conversion to *cis*-HCOOH (multiplied by 0.33); (5) spectrum after annealing of this matrix at 25 K; (6) difference spectrum of the same matrix after prolonged exposure to broadband IR light (multiplied by 10). Absorbers I, II, and III are assigned to *cis*-HCOOOH, *trans*-HCOOOH, and the *cis*-HCOOH···O complex, respectively. The bands marked with asterisks belong to *cis*-HCOOD. The FA/N_2O/Kr matrices are first irradiated at 193 nm and then annealed. The spectra were measured at 8 K.

as a minor amount of ozone, confirming global mobility of O atoms at this temperature. Absorbers I and II are formed synchronously during annealing featuring diffusion-controlled reaction of O atoms. Fortunately, these two absorbers have different stability when exposed to 193 nm light (II more stable than I), which allows separation of other bands belonging to them (see Table 1).

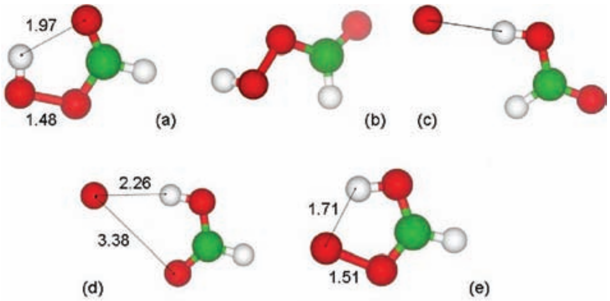

Figure 2. Computational geometries obtained in the FA + O reaction: (a) *cis*-peroxyformic acid; (b) *trans*-peroxyformic acid with a nonplanar structure (3.9 kcal mol^{-1} higher in energy); (c) *cis*-FA···O complex with the O···H distance of 2.29 and 2.11 Å for O(^{3}P) and O(^{1}D), respectively; (d) and (e) stages of the reaction between O(^{1}D) and *trans*-FA leading to peroxyformic acid. The trans and cis conformers of peroxyformic acid are named following ref 24.

The assignment of absorber I is straightforward. On the basis of literature data,[12,13] this species is the most stable (cis) conformer of peroxyformic acid shown in Figure 2a, and our computations produce supporting results (see Table 1). The observed vibrational frequencies exhibit typical matrix shifts. This assignment is fully confirmed by the experiments with deuterated formic acid (*trans*-HCOOD). In particular, the C=O stretching mode of the deuterated species (I) shifts down in energy in a krypton matrix by ca. −2.5 cm^{-1} as seen in spectrum 3 in Figure 1 (computationally by −4 cm^{-1}). We have found most of the fundamental modes of this molecule in agreement with the literature data.[12,13]

Absorber II has not been previously reported in the literature to our knowledge. We assign it to the higher-energy (trans) conformer of peroxyformic acid shown in Figure 2b. The calculated spectrum supports this assignment (see Table 1). For example, the C=O stretching modes of absorbers I and II differ by ca. 58 cm^{-1} experimentally and by 43 cm^{-1} computationally, which should be considered as a good agreement. The OH stretching mode of *trans*-HCOOOH is shifted from the cis conformer by +257 cm^{-1} experimentally and by +228 cm^{-1} computationally. The experimental C=O stretching band of this absorber shifts only marginally (by ca. 0.1 cm^{-1}) upon deuteration (OD), which is in perfect agreement with our computations predicting a negligible shift of 0.2 cm^{-1}.

Panel b in Figure 1 describes the experiment with matrices containing *cis*-FA, which is produced by vibrational excitation of *trans*-FA.[5] It is known that *cis*-HCOOH decays back to ground-state *trans*-HCOOH via quantum tunneling of hydrogen,[14,15]

TABLE 1: Characteristic IR Absorption Bands (in cm^{-1}) of *cis*-HCOOOH, *trans*-HCOOOH, and *cis*-HCOOH···O Complex[a]

	cis-HCOOOH (I)			*trans*-HCOOOH (II)		*cis*-HCOOH···O (III)	
mode	in Kr	in Ar[b]	theory[c]	in Kr	theory[c]	in Kr	theory[c,d]
νOH	3301.0	3334.0	3336	3558	3564	–	3598
	(2445.6)	(2467.9)	(2464)	(2630.3)	(2636)	(2659.1)	(2646)
νC=O	1735.4	1737.3	1739	1793.1	1782	1798.3	1778
	1734.7			1792.8			
	(1733.0)	(1736.8)	(1735)	(1793.2)	(1782)	(1787.0)	(1785)
	(1732.6)			(1792.8)			
def	1119.9	1113.9	1145	1095	1091	1264.8	1275
	(1123.1)	(1124.5)[e]	(1147)	(–)	(1124)	(1174)	(1194)
	(1089.8)	(1115.5)[e]	(1087)			(930.2)	(944)
	(1091.0)	(1091)					

[a] The data for the OD species are presented in parentheses. [b] From ref 13. These matrix-isolation data agree with the gas-phase data reported in ref 12. [c] Our calculated values were scaled by factors obtained by comparing the calculations and the experimental data in a Kr matrix for the same modes of formic acid. [d] Data for O(^{3}P); data for O(^{1}D) do not differ substantially. [e] Fermi resonance between ν_5 and ($\nu_8 + \nu_9$).[13]

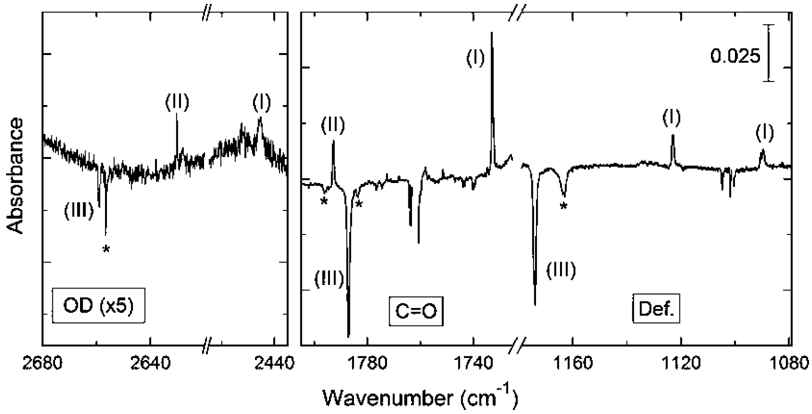

Figure 3. FTIR spectra in the OD stretching, C=O stretching, and deformation regions showing products of thermal reactions between O atoms and FA in solid krypton. The difference spectrum is obtained after prolonged exposure to broadband IR light for a matrix containing *cis*-HCOOD and preliminarily photolyzed at 193 nm and annealed at 25 K (similarly to trace 6 in Figure 1). Absorbers I, II, and III are assigned to *cis*-HCOOOD, *trans*-HCOOOD, and the *cis*-HCOOD···O complex, respectively. The bands marked with asterisks belong to *cis*-HCOOD. The spectra were measured at 8 K.

practically limiting the achievable amount of *cis*-HCOOH (see spectrum 4 in Figure 1). Nevertheless, the effect of annealing at 25 K in solid krypton becomes clearly different from the previous case of *trans*-HCOOH because an additional absorber III appears in spectrum 5, and this is the second important observation of the present work. This new absorber forms during annealing quite synchronously with absorbers I and II coming from residual *trans*-HCOOH; hence, it is presumably formed via the diffusion-controlled reaction of *cis*-HCOOH with mobile O atoms. The spectrum of absorber III is typical for *cis*-FA participating in hydrogen bonding.[16,17] In particular, the C=O stretching vibration (1798.3 cm^{-1}) shifts down in energy as compared to the *cis*-HCOOH monomer (1802 cm^{-1}). The deformation mode of absorber III is at 1264.8 cm^{-1}, i.e., substantially blue-shifted from that of the *cis*-HCOOH monomer (1248 cm^{-1}). We did not observe the OH stretching band in this case, but it probably overlaps with the same mode of *cis*-HCOOH monomer or is broadened.

On the basis of these data, we assign absorber III to the *cis*-FA···O complex (see Figure 2c) in accordance with the computational data (see Table 1). Hydrogen tunneling in the *cis*-HCOOH···O complex should be effectively suppressed as found previously for the *cis*-HCOOH···H_2O complex,[17] and accordingly, we did not observe any significant decay of absorber III on the time scale of hours; thus, hydrogen bonding with O atoms stabilizes the intrinsically unstable *cis*-FA against hydrogen tunneling. However, this stabilization takes place only in the dark. If the sample is exposed to the broadband IR light of the globar source, the *cis*-FA···O complex slowly decomposes, producing both conformers of peroxyformic acid (see spectrum 6 in Figure 1). This is a natural process of the IR-induced cis-to-trans conversion of formic acid followed by the in-cage reaction of *trans*-FA with the O atom, which strongly supports our assignments.

Better spectra of absorber III were obtained from the reaction of deuterated formic acid HCOOD with O atoms because much higher relative amounts of the cis conformer could be obtained in this case due to much slower back-tunneling of deuterium.[14,15] These results fully agree with the previous discussion. For the deuterated species, we could find the OD stretching band of the *cis*-HCOOD···O complex at 2659 cm^{-1}, which is close to the *cis*-HCOOD monomer absorption at 2656.7 cm^{-1}. The C=O stretching and deformation absorptions are at proper positions of 1787 and 1174 cm^{-1}, respectively, and an additional band at 930.2 cm^{-1} appears in agreement with theory. Upon IR light, *cis*-HCOOD···O converts to both conformers of HCOOOD (see Figure 3) similarly to the case of HCOOH.

We also performed similar experiments in Xe matrices, and the results were essentially the same as in Kr matrices. The annealing-induced spectral bands exhibit normal matrix shifts; for instance, the C=O stretching modes of *cis*- and *trans*-HCOOOH are seen at 1730.3 and 1786.5 cm^{-1}, and the shifts from the bands of monomeric formic acid are basically preserved. The experiments in xenon matrices confirm that the observed reactions originate from thermally activated mobility of O atoms because the reaction temperature characteristically increased to 30−35 K.[18,19]

Thus, according to the experimental evidence, the following processes occur:

$$\textit{trans}\text{-HCOOH} + \text{O}\,(\Delta T) \rightarrow \textit{trans}\text{-HCOOOH and } \textit{cis}\text{-HCOOOH} \quad (1)$$

$$\textit{cis}\text{-HCOOH} + \text{O}\,(\Delta T) \rightarrow \textit{cis}\text{-HCOOH}\cdots\text{O} \quad (2)$$

where ΔT denotes thermal annealing activating O atom mobility in a solid matrix. These results are interesting in two respects. First, it is somewhat surprising that an organic species can chemically react by the carboxylic functional group with an oxygen atom at such a low temperature, evidencing low activation energy (reaction 1). The experiment suggests that the reaction barrier is not higher than the barrier for O atom mobility in solid krypton (1.6 kcal mol^{-1}).[11] Reaction 1 can be computationally reproduced in terms of O(^{1}D) atoms, which are energetically possible in the experiments (see later). According to the CASSCF(16/11)/aug-cc-pVDZ calculations, this reaction proceeds as follows. First, a local minimum on the potential energy surface corresponding to the *trans*-FA···O(^{1}D) complex is formed (Figure 2d). When the O(^{1}D) atom approaches the carbonyl oxygen of FA, a very low activation barrier (<1 kcal mol^{-1}) is required to reach another local minimum with the new O−O bond (see Figure 2e). Finally, the proton from the O−H group is easily (activation barrier <1 kcal mol^{-1}) transferred to the terminal oxygen of the O−O bond, forming one of the peroxyformic acid conformers (Figure 2a). A higher-energy conformer of peroxyformic acid (Figure 2b) may be obtained by rearrangement of the structure shown in Figure 2a, and the required energy is obviously available in the reaction. The direct insertion of O(^{1}D) into the O−H bond of formic acid is not attainable because of enormous energy expenses.

The second and even more remarkable result is that the products of the FA + O reaction are different for *trans*- and *cis*-FA (reactions 1 and 2), which is probably the first observation of a conformation-dependent bimolecular reaction of small species. While *trans*-FA chemically reacts with an oxygen atom producing peroxyformic acid, the higher-energy cis conformer does not chemically react and produces only a hydrogen-bonded *cis*-FA···O complex. In calculations, a path for the *cis*-FA + O(^{1}D) productive reaction was not found, supporting the experimental conclusions. The reason for that is clear by viewing the structure of the hydrogen bonded *cis*-FA···O complex shown in Figure 2c: this arrangement prevents an attack of the oxygen atom on the carbonyl oxygen of *cis*-FA, which is an essential step in the reaction of *trans*-FA.

A possibility to stabilize singlet oxygen atoms in solid matrices should be finally discussed. The 193 nm photolysis can energetically produce O(^{1}D) atoms from N_2O. However, this excited atom has a relatively short lifetime (in the gas phase ca. 110 s).[20] The annealing step is separated from the photolysis step by a long time (up to hours), which seems to be sufficient for the O(^{1}D) decay. In principle, the solid host can stabilize the excited species; however, no experimental evidence for the hypothetical stabilization of O(^{1}D) in solid matrices is available. In our previous experiments in Kr matrices, the oxygen atoms similarly obtained from N_2O formed a stable complex with water upon thermal diffusion whereas O(^{1}D) could react with water.[11] The O(^{3}P) + H_2O interaction could be made reactive, leading to a stable singlet-state product H_2O_2 only upon electronic excitation of the system and the spin flip.[11] In the present work, we prepared analogous experiments with the $CH_4/N_2O/Kr$ mixtures, photolyzed the matrices at 193 nm, and annealed them at 25−30 K. As a result, we found no indication of reaction between methane and O atoms producing CH_3OH or any other product that could feature singlet oxygen atoms.[21] These experimental facts suggest that reactions 1 and 2 probably occur with triplet oxygen atoms. However, this experimental model has no theoretical explanation. We attempted to find reaction routes leading to the peroxyformic acid starting from the ground-state triplet oxygen atom O(^{3}P) and the ground singlet state of FA. The CASSCF(16/11)/aug-cc-pVDZ approach was used to scan fractions of the triplet-state potential energy surface FA + O(^{3}P). We could locate weakly bound complexes similar to those shown in Figure 2c,d. Upon approaching the species FA and O(^{3}P) along the perspective reaction coordinates on the triplet-state potential surface, we observed only a growth of energy inconsistent with the low-temperature matrix conditions ($>$25 kcal mol^{-1}). However, our computations are performed for species in a vacuum and the polarizable medium may produce some catalytic effect on the reaction barriers. The cases of species in a vacuum and in a solid medium are obviously different, which makes a strong challenge for computational chemistry. It should be mentioned that numerous gas-phase reactions are known between the triplet-state oxygen atoms and small organic molecules leading to radicals as reaction products.[22,23]

In conclusion, we have found a conformation-dependent reaction between formic acid (FA, HCOOH) and atomic oxygen in cryogenic matrices. The FA + O reaction leads to peroxyformic acid (HCOOOH) only from the ground-state *trans*-FA conformer whereas it results in the hydrogen-bonded FA···O complex for the higher-energy *cis*-FA conformer. These two reaction channels are strongly supported by IR absorption spectroscopy and quantum chemical calculations; both experimental and theoretical data completely agree on the reaction products. However, the reaction mechanism is not fully understood, which creates challenges for future work.

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