Isomerization of Matrix-Isolated Formamide: IR-Spectroscopic Detection of Formimidic Acid

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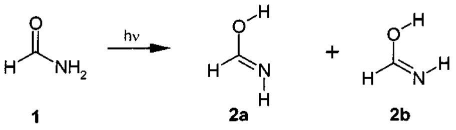
Ultraviolet irradiation of matrix-isolated formamide (**1**) in solid argon with light of wavelength 248 nm leads to the formation of formimidic acid (**2**). Comparison of the experimental IR spectrum of the photoproduct with the calculated IR spectrum of **2** shows clearly that two rotamers **2a** and **2b** are formed.

Introduction

The prototype imidic acid, formimidic acid (**2**), which is tautomeric with formamide (**1**), was generated in the gas phase by one-electron reduction of the corresponding radical cation by Terlouw and co-workers in 1994.[1] Räsänen and co-workers studied the behavior of formamide (**1**) upon irradiation with light of wavelength 193 nm (ArF excimer laser) in solid argon.[2] They reported the formation of hydrogen-bonded, carbon- and oxygen-attached complexes between ammonia and carbon monoxide (NH_3–CO and NH_3–OC). Isomerization of **1** to formimidic acid **2** was not observed under these conditions. As described below, **2** is the main product when **1** is irradiated in argon matrices at 10 K with light of wavelength 248 nm (KrF excimer laser).

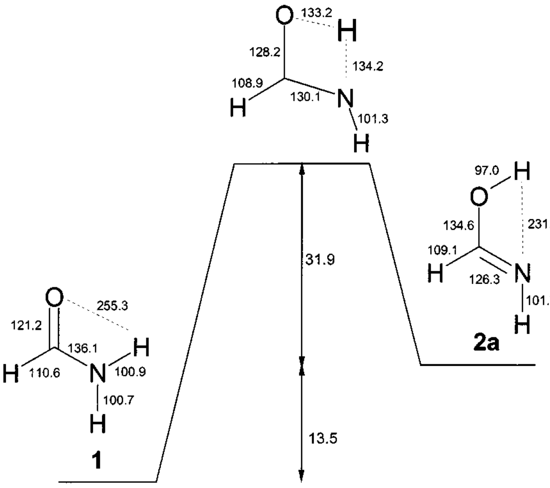


Calculations

The relationship between formimidic acid (**2**) and its tautomer formamide (**1**) has been the subject of several ab initio molecular orbital calculations.[3,4] The imidic acid **2** is found to lie 12.1 kcal mol^{-1} above **1**.[3] The calculations also predict that the barrier for the tautomerization **1** → **2** is relatively high (48.9 kcal mol^{-1} above **1**).[3]

Because our structural elucidation is based on the comparison of experimental matrix IR spectra with calculated IR spectra, we have performed additional calculations[5] using the hybrid DFT/HF method B3LYP with a standard 6-311+G(d,p) basis set.

Four rotamers of formimidic acid (**2**) have to be taken into account, with the (*s-Z*)-(*E*) form **2a** (the first notation indicates the rotation around the C–O bond, the second describes the configuration at the C=N double bond) being the most stable conformer lying 3.6 kcal mol^{-1} below the (*s-Z*)-(*Z*) isomer **2b** (Figure 1).



Scheme 1. Calculated reaction energies (in kcal mol^{-1}) for the intermolecular 1,3-hydrogen shift of formamide (**1**); bond lengths are given in pm

The calculated transition state for the isomerization **1** → **2a** lies 31.9 kcal mol^{-1} above **2** and has a planar structure (Scheme 1). This value, which is in good agreement with the previously published results,[3] indicates that it should be possible to trap **2** in a matrix at 10 K.

Matrix Photolysis of Formamide (1)

Upon irradiation of **1** with a KrF excimer laser (λ = 248 nm) the intensities of the bands of **1** decrease very fast and two new absorptions – as well as some other bands – arise at $\tilde{\nu}$ = 1665.3 and 577.7 cm^{-1} and reach their maximum intensity after ca. 1.5 h. In the experimental difference spectrum of this photoreaction the bands of the new species are in good agreement with the calculated IR spectrum of the most stable rotamer **2a** of formimidic acid (Table 1, Figure 1).

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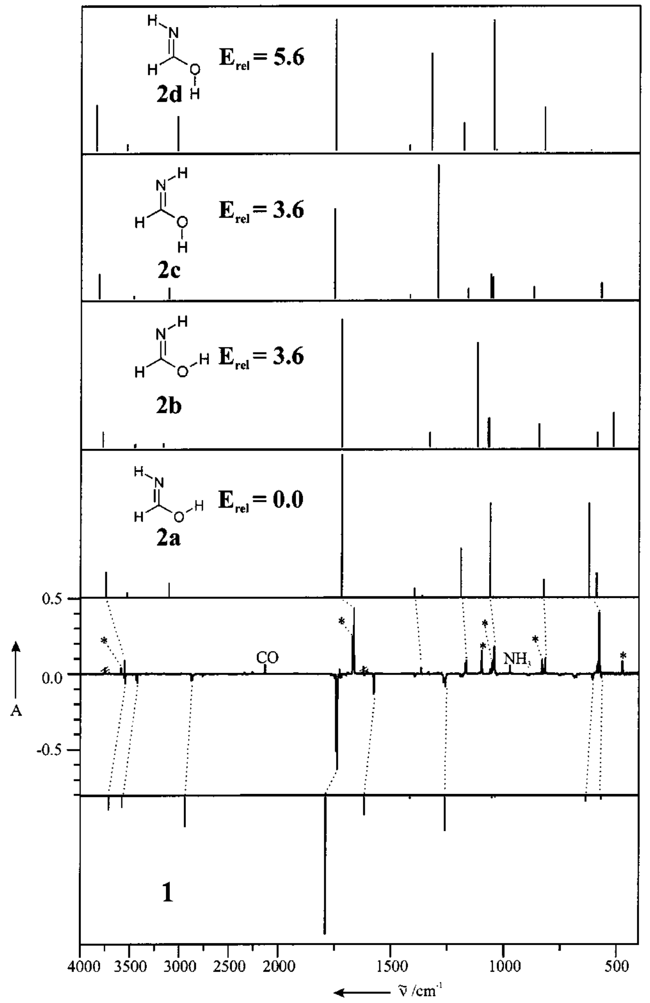

Figure 1. Comparison of the experimental spectrum (4000–400 cm^{-1}) observed after irradiation of formamide (**1**) with a KrF excimer laser (λ = 248 nm, argon, 10 K) with the calculated infrared spectra of the tautomers **2a**–**2d** of formimidic acid; the positive bands in the experimental difference spectrum increased and the negative bands disappeared upon irradiation; relative energies of the four tautomers are given in kcal mol^{-1}; signals marked with an asterisk belong to **2b**

Table 1. Comparison of the calculated infrared spectrum for the (*s*-*Z*)-(*E*) form **2a** of formimidic acid with the experimental (argon, 10 K) infrared spectrum after irradiation of formamide (**1**) with λ = 248 nm

	Sym.		$\tilde{\nu}_{exp}$/cm^{-1} (I_{exp})[a]	$\tilde{\nu}_{alcd}$/cm^{-1} (I_{calcd})
ν_1	A′	ν_{OH}	3557.1 (w)	3740.6 (0.18)
ν_2	A′	ν_{NH}	–	3530.5 (0.03)
ν_3	A′	ν_{CH}	–	3106.8 (0.10)
ν_4	A′	ν_{CN}	1665.3 (vs)	1718.4 (1.00)[b]
ν_5	A′	$\delta_{CH/NH}$ (i.p.)	1368.2 (w)	1397.2 (0.06)
ν_6	A′	$\delta_{OH/CH}$ (i.p.)	–	1362.9 (0.01)
ν_7	A′	$\delta_{CH/OH}$ (i.p.)	1168.4 (m)	1191.2 (0.34)
ν_8	A′	δ_{NH} (i.p.)	1044.5 (m)	1061.6 (0.66)
ν_{10}	A"	δ_{OH} (o.o.p.)	–	1048.6 (0.00)
ν_{11}	A"	δ_{NH} (o.o.p.)	816.3 (m)	823.3 (0.12)
ν_{12}	A"	δ_{CH} (o.o.p.)	577.7 (s)	622.7 (0.66)
ν_9	A′	δ_{OCN}	–	589.1 (0.17)

[a] vs = very strong, s = strong, m = medium, w = weak. – [b] Calculated absolute intensity: 299.2 km mol^{-1}.

In addition five bands at ṽ = 3592.9, 1670.5, 1099.0, 831.7, and 475.4 cm^{-1}, which are not reproduced by the calculated IR spectrum of **2a**, can be detected in the spectrum of the photoproduct. They may belong to one of the other three conceivable stereoisomers.

The best fit is reached by comparison with the calculated IR spectrum of diastereomer **2b** (Figure 1, Table 2). In other words, the photochemically induced tautomerization of formamide (**1**) with light of wavelength 248 nm does not only lead to the (*s*-*Z*)-(*E*) form **2a** of lowest energy but also to the (*s*-*Z*)-(*Z*) isomer **2b** of formimidic acid. Compound **2b** is probably formed via a second photochemical step from **2a**. Since we have a photoequilibrium the relative ratios are independent of the calculated relative energies.

Table 2. Comparison of the calculated infrared spectrum for the (*s*-*Z*)-(*Z*) form **2b** of formimidic acid with the experimental (argon, 10 K) infrared spectrum after irradiation of formamide (**1**) with λ = 248 nm

	Sym.		$\tilde{\nu}_{exp}$/cm^{-1} (I_{exp})	$\tilde{\nu}_{calcd}$/cm^{-1} (I_{calcd})
ν_1	A′	ν_{OH}	3592.9 (w)	3776.1 (0.12)
ν_2	A′	ν_{NH}	–	3448.4 (0.03)
ν_3	A′	ν_{CH}	–	3164.0 (0.03)
ν_4	A′	ν_{CN}	1670.5 (s)	1720.2 (1.00)[a]
ν_5	A′	δ_{CH} (i.p.)	–	1410.3 (0.00)
ν_6	A′	$\delta_{OH/NH}$ (i.p.)	–	1330.9 (0.12)
ν_7	A′	$\delta_{OH/CH/NH}$ (i.p.)	1099.0 (s)	1119.7 (0.82)
ν_{10}	A"	$\delta_{CH/NH}$ (o.o.p.)	1053.2 (m)	1071.7 (0.23)
ν_8	A′	δ_{NH} (i.p.)	1048.9 (m)	1068.5 (0.23)
ν_{11}	A"	δ_{NH} (o.o.p.)	831.7 (m)	845.5 (0.18)
ν_9	A′	δ_{OCN}	581.7 (w)	585.9 (0.12)
ν_{12}	A"	δ_{OH} (o.o.p.)	475.4 (m)	514.9 (0.27)

[a] Calculated absolute intensity: 305.8 km mol^{-1}.

Experimental Section

Cryostat: Displex closed-cycle refrigeration system HC-2 from APD. Spectrometers: IR: FT-IR spectrometer IFS 55 from Bruker, resolution 0.7 cm^{-1}. Light sources: Excimer laser LPX 105 from Lambda Physics.

Formamide (1): Commercially available **1** was dried over molecular sieves (4 Å). Matrix-isolated samples were prepared by sublimation of **1** at –25 °C and deposited on a CsI window at 10 K together with a large excess of argon (molar ratio ca. 1:1000).

Acknowledgments

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