

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/8944253>

Rotational Isomerism in Acetic Acid: The First Experimental Observation of the High-Energy Conformer

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JANUARY 2004

Impact Factor: 12.11 · DOI: 10.1021/ja038341a · Source: PubMed

CITATIONS

52

READS

112

5 AUTHORS, INCLUDING:



Ermelinda Maçôas

University of Lisbon

39 PUBLICATIONS 772 CITATIONS

SEE PROFILE



Rui Fausto

University of Coimbra

330 PUBLICATIONS 4,496 CITATIONS

SEE PROFILE



Markku Rasanen

University of Helsinki

267 PUBLICATIONS 7,017 CITATIONS

SEE PROFILE

Rotational Isomerism in Acetic Acid: The First Experimental Observation of the High-Energy Conformer

Ermelinda M. S. Maçôas,^{*,†,‡} Leonid Khriachtchev,[†] Mika Pettersson,^{†,§} Rui Fausto,[‡] and Markku Räsänen[†]

Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland, and Department of Chemistry-CQC, University of Coimbra, P-3004-535, Coimbra, Portugal

Received September 4, 2003; E-mail: emacoas@qui.uc.pt

Conformational studies of simple carboxylic acids and amines aid to understand the reactivity of biologically relevant molecular systems, where the conformational properties of these functional groups play an important role.^{1–3} Recently, conformation-selective photochemistry has been recognized as a new approach to laser control of chemical reactions.⁴ Different conformers can exhibit quite different photochemistry as it was shown, for example, in the case of UV photolysis of *cis*- and *trans*-formic acid (HCOOH).⁵

Acetic acid (CH₃COOH, AA) is a molecule of considerable interest from the point of view of conformation-selective photochemistry. This molecule can theoretically adopt two stable structures (see Figure 1). Both conformers belong to the *C_s* symmetry group and have the in-plane hydrogen of the methyl group eclipsed with the carbonyl bond. The lowest energy conformer is characterized by the *trans* arrangement around the C–O bond with respect to the relative orientation of the O–H and C–C bonds. The other conformer, which is predicted to be 1882.7 cm^{–1} higher in energy,⁶ exhibits the *cis* arrangement of these two bonds around the C–O bond. Despite the reliable theoretical predictions, no experimental evidence of the existence of the *cis* conformer has been found so far.^{6–11} In this work, we report the first experimental observation of *cis*-AA. We show that *cis*-AA can be produced in an Ar matrix by vibrational excitation of the conformational ground state and that it decays back to *trans* in dark, even at 8 K, via tunneling. The tunneling mechanism for the *cis* → *trans* dark reaction is supported by studies on the CH₃COOD isotopologue showing a very strong effect of deuteration on the reaction rate.

In the experiments, acetic acid (Sigma-Aldrich, >99%) was mixed with argon (AGA 99.9999%) in a bulb with the ratio AA/Ar = 1/1000. The samples were deposited on a CsI window held at 15 K in a cryostat (APD DE 202 A). After deposition, the samples were cooled to 8 K. The IR pumping was carried out with pulsed (~5 ns) narrowband IR radiation of an optical parametric oscillator (Sunlite with an IR extension, Continuum, FWHM ~0.1 cm^{–1}, repetition rate = 10 Hz, and pulse energy density ~0.5 mJ/cm²) as described elsewhere.^{12–14} The IR absorption spectra were measured with a FTIR spectrometer (Nicolet 60 SX) with a resolution of 1 or 0.25 cm^{–1}. The experimental setup was arranged in such a way that IR absorption spectra could be recorded during irradiation. The Gaussian 98 program package was used for the ab initio calculations.¹⁵

After deposition, the AA monomer is present in the matrix only in the *trans* geometry, and our IR absorption spectrum agrees well with the literature data.¹⁰ To excite the *trans*-AA monomer at energies above the internal rotation barrier, we used the OH

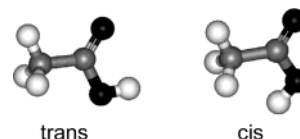


Figure 1. *Cis* and *trans* conformers of acetic acid (CH₃COOH).

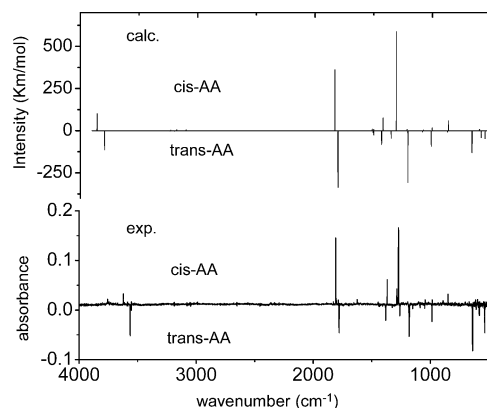


Figure 2. Theoretical and experimental vibrational spectra of *cis*- and *trans*-acetic acid. The lower trace is the experimental difference spectrum showing the result of vibrational excitation of the *trans* conformer in the Ar matrix at 8 K. In the upper trace, the difference spectrum is simulated based on MP2/6-311G++(2d,2p) calculations. The bands of the *cis* conformer point upward, while the bands due to the *trans* conformer point downward.

stretching overtone (2νOH at 6957.9 cm^{–1}). Resonant excitation of this mode induces considerable changes in the IR absorption spectrum (see Figure 2). According to our assignment (see Table 1), the bands pointing upward in the presented difference spectrum correspond to previously unreported *cis*-AA, while the bands pointing downward correspond to the known *trans* conformer. The observed blue shifts of the hydroxyl (59 cm^{–1}) and carbonyl (28 cm^{–1}) stretching modes (νOH and νC=O, respectively) in the product with respect to the *trans* conformer are very characteristic for various carboxylic acids.¹⁴ The νC=O and the COH angular deformations (δCOH) are the most intense bands of *cis*-AA. These bands are observed at 1807 cm^{–1} (νC=O) and 1272 cm^{–1} (δCOH), in good agreement with the ab initio estimations (1833 and 1310 cm^{–1}, respectively). In general, the experimental difference spectrum showing bands of both conformers of AA agrees very well with the spectrum simulated by ab initio calculations with respect to band positions and relative intensities (see Figure 2), thus giving strong support to the identification of the product of IR irradiation. The detailed discussion of the spectra of *cis*-AA exceeds the scope of this Communication.

In the equilibrium established under resonant IR irradiation, about 10% of the initial concentration of the *trans* conformer in the matrix is converted into the *cis* form. Once the IR irradiation is stopped,

[†] University of Helsinki.

[‡] University of Coimbra.

[§] Present address: Department of Chemistry, University of Jyväskylä, P. O. Box 35, FIN-40014 University of Jyväskylä, Finland.

Table 1. Observed Frequencies of *cis*-AA and *trans*-AA Isolated in an Ar Matrix at 8 K as Compared with the Predicted Values at the MP2/6-311++G(2d,2p) Level

assignment ^a	<i>trans</i> -AA		<i>cis</i> -AA	
	obs.	calc.	obs.	calc.
ν OH	3563.8	3793.6	3622.6	3859.5
ν HCH ₂ s.	3051 ^b	3236.9		3229.7
ν HCH ₂ a.	2996 ^b	3196.0		3178.0
ν CH ₃	2944 ^b	3115.3		3099.4
ν C=O	1779.0	1805.2	1807.4	1832.6
δ HCH ₂ a.	1438.8	1506.3	1448.3	1514.3
δ HCH ₂ s.	1433.6	1501.0	1444.5	1501.2
δ CH ₃	1379.4	1434.5	1368.3	1421.5
ν C–O	1259.4	1352.7	1192.9	1218.4
(?)			1285.4	
δ COH	1179.8	1210.4	1271.9	1309.5
γ CH ₃ a.	1047.2	1084.6	1042.4	1078.7
γ CH ₃ s.	985.5	1011.7	982.2	1002.9
ν C–C		871.8	848.6	864.9
τ C–O	637.8	663.4	458.0	468.2
δ OCO	580.4	586.3		600.7
γ C=O	534.2	553.1		605.2
δ CC=O	428 ^b	427.0		436.0
τ CH ₃		80.2		95.2

^a The ab initio Cartesian force constants and optimized geometries were used for the normal coordinate analysis. ^b Values taken from ref 10. Symbols: ν , stretching; δ , bending; γ , rocking; τ , torsion.

cis-AA decays back to the *trans* form in a minute time scale. As measured in the dark in solid Ar at 8 K, the *cis*-AA concentration follows a one exponential decay with a rate constant $k_t(\text{CH}_3\text{COOH}) = 2.1 \times 10^{-2} \text{ s}^{-1}$. According to the ab initio calculations, the barrier for the *cis* \rightarrow *trans* isomerization is $\sim 2550 \text{ cm}^{-1}$,⁶ which gives a negligible rate for the overbarrier reaction at 8 K ($\sim 10^{-186} \text{ s}^{-1}$, estimated using the Arrhenius formula with the torsional frequency of *cis*-AA for the preexponential factor). The overbarrier reaction may become significant only above 100 K. This shows that the *cis* \rightarrow *trans* isomerization occurs through the barrier.

The reaction coordinate for the rotational isomerization in AA is most probably described by the O=C–O–H dihedral angle, which is the internal coordinate for the O–H torsional motion. Similarly to formic acid,¹⁶ the tunneling reaction in acetic acid presumably takes place mainly from the torsional ground state of the *cis* conformer, because the population of the excited torsional levels is very low at the matrix temperature. The observed *cis* \rightarrow *trans* reaction for AA isolated in an Ar matrix at 8 K is 1 order of magnitude faster than the corresponding process for formic acid under the same experimental conditions,¹⁶ which definitely complicates its experimental observation. The relative values of the tunneling rates of formic and acetic acid can be simply explained by differences in the torsional potential of these molecules. The one-dimensional potential energy surfaces calculated for the rotational isomerization of these molecules at the same MP2/6-311++G(2d,2p) level of theory show that the *cis* to *trans* barrier height is 370 cm^{-1} lower for AA. The permeability of the reaction barrier from the torsional ground state of *cis*-AA, calculated using the ab initio potential and the WKB approximation,¹⁷ is higher by a factor of ~ 30 as compared with formic acid.¹⁶ This agrees quite well with our results on the *cis* \rightarrow *trans* tunneling rates of acetic and formic acid in solid Ar. However, it is understood that the real situation is not so simple, and many other parameters (in addition to the barrier permeability) should be considered.¹⁶

IR-induced isomerization of CH_3COOD isolated in solid Ar was also studied. The $2\nu\text{OD}$ mode at 5170 cm^{-1} was used to excite this molecule over the isomerization barrier, resulting in the *trans* \rightarrow *cis* conversion. As a result of deuteration, it was found that the *cis* \rightarrow *trans* back reaction slows down by a factor of $\sim 3 \times 10^4$ as compared with CH_3COOH [$k_t(\text{CH}_3\text{COOD}) \approx 7.3 \times 10^{-7} \text{ s}^{-1}$]. This value agrees reasonably well with the estimated 7 orders of magnitude lower barrier permeability upon deuteration. This is our final proof of the conversion of *cis*-AA to *trans*-AA via tunneling.

In conclusion, the *cis* conformer of acetic acid was produced in solid Ar by exciting the OH (OD) stretching overtone modes of two isotopic forms of the *trans* conformer (CH_3COOH , CH_3COOD). The experimental evidence for the preparation of the *cis* form is supported by the theoretical vibrational analysis. It is shown that the *cis* to *trans* tunneling reaction occurs in the solid environment even at the lowest temperatures used (8 K). For CH_3COOH , the tunneling rate is $\sim 2 \times 10^{-2} \text{ s}^{-1}$, which means that in several minutes the *cis* conformer produced by IR irradiation is fully converted back to *trans* in dark. Deuteration of the hydroxyl group increases the lifetime of the unstable conformer dramatically (by $\sim 3 \times 10^4$).

Acknowledgment. The Academy of Finland is thanked for financial support. E.M.S.M. and R.F. acknowledge the Portuguese Foundation for Science and Technology (Ph.D. grant SFRH/BD/4863/2001 and project POCTI/43366/QUI/2001).

References

- (1) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*; W. H. Freeman Co.: New York, 1980.
- (2) Huff, J. B.; Askew, B.; Duff, R. J.; Rebek, J. *J. Am. Chem. Soc.* **1988**, *110*, 5908–5909.
- (3) Tadayoni, B. M.; Parris, K.; Rebek, J. *J. Am. Chem. Soc.* **1989**, *111*, 4503–4505.
- (4) Goez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2336–2337.
- (5) Khriachtchev, L.; Maçôas, E. M. S.; Pettersson, M.; Räsänen, M. *J. Am. Chem. Soc.* **2002**, *124*, 10994–10995.
- (6) Senet, M. L. *Mol. Phys.* **2001**, *99*, 1311–1321.
- (7) Weltner, W. *J. Am. Chem. Soc.* **1955**, *77*, 3941–3950.
- (8) van Eijck, B. P.; van Opheusden, J.; van Schaik, M. M. M.; van Zoeren, E. *J. Mol. Spectrosc.* **1981**, *86*, 465–479.
- (9) Burneau, A.; Génin, F.; Quilès, F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5020–5029.
- (10) Berney, C. V.; Redington, R. L.; Lin, K. C. *J. Chem. Phys.* **1970**, *53*, 1713–1721.
- (11) Sato, H.; Hirata, F. *J. Mol. Struct. (THEOCHEM)* **1999**, *113*, 461–462.
- (12) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Räsänen, M. *J. Am. Chem. Soc.* **1997**, *119*, 11715–11716.
- (13) Khriachtchev, L.; Lundell, J.; Isoniemi, E.; Räsänen, M. *J. Chem. Phys.* **2000**, *113*, 4265–4273.
- (14) Maçôas, E. M. S.; Lundell, J.; Pettersson, M.; Khriachtchev, L.; Fausto, R.; Räsänen, M. *J. Mol. Spectrosc.* **2003**, *219*, 70–80.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (16) Pettersson, M.; Maçôas, E. M. S.; Khriachtchev, L.; Lundell, J.; Fausto, R.; Räsänen, M. *J. Chem. Phys.* **2002**, *117*, 9095–9098.
- (17) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall Ltd.: London, 1980.

JA038341A