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Conformational Memory in Photodissociation of Formic Acid

Leonid Khriachtchev,* Ermelinda Maçôas,† Mika Pettersson, and Markku Räsänen

Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

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Selective laser control of chemical reactions is a practical and fundamental challenge.[1,2] As an elegant approach, one can consider potentially different photodissociation channels and chemical reactivity of various conformers (rotational isomers) of a given molecule. Experimental evidence of photodissociation channels specific to rotational isomers has very recently been reported for gas-phase cation 1-$C_3H_7I^+$ suggesting that dissociation of the gauche and anti forms produces different isomers of the $C_3H_7^+$ ion (2-$C_3H_7^+$ and cyclo-$C_3H_7^+$, respectively).[3]

Rotational isomers have extensively been studied in rare-gas solids.[4] Various forms can be efficiently interconverted by using selective excitation of their fundamental and combination modes when the energy exceeds the isomerization barrier.[5−7] Formic acid (FA) is one of the simplest species exhibiting rotational isomerism with the lowest-energy trans form and the higher-energy cis isomer.[8] By exciting the first O−H stretching overtone of *trans*-HCOOH isolated in solid Ar, we prepared the cis isomer and reported its vibrational spectrum.[9] In UV photolysis of *trans*-FA in the gas phase and in solid Ar, the $H_2O + CO$ channel dominates the $H_2 + CO_2$ channel.[10,11] It is shown in the present work that 193-nm photolysis of *cis*-FA in solid Ar represents the opposite case, that is, the photodissociation process is dominated by the $H_2 + CO_2$ channel. This demonstrates that the CO/CO_2 photodissociation products can be efficiently controlled with selective narrow-band IR radiation.

In the experiments, gaseous HCOOH/Ar mixtures (~1/1000) were prepared in a bulb and then deposited onto a CsI window. The experiments were carried out at 8 K as provided by a closed-cycle helium cryostat (DE-202A, APD). The IR absorption spectra were recorded with a Nicolet 60 SX FTIR spectrometer (resolution of 0.5 cm^{-1}). The species were photodissociated with the 193-nm radiation of an excimer laser (MPB, MSX-250) and the second-harmonic radiation of an optical parametric oscillator (OPO Sunlite, Continuum). The *trans*-FA-to-*cis*-FA conversion was achieved while pumping the first OH stretching overtone by using the narrow-band (~0.1 cm^{-1}) OPO idler radiation with a pulse energy density of ~5 mJ/cm^2 and a repetition rate of 10 Hz. This overtone band is split into two components (~6930 and ~6934 cm^{-1}) by matrix site effect, and each site group can be pumped selectively.[5,6] As reported previously, *cis*-FA relaxes back to *trans*-FA in solid Ar on a time scale of minutes, presumably via a phonon-assisted tunneling mechanism.[9] This tunneling process requires that the two main site groups of *trans*-FA should be periodically pumped to maintain considerable concentration of the cis isomer; therefore, we switched the pumping frequency between ~6930 and ~6934 cm^{-1} every 20 s. As a result of the pumping, the *trans*-FA bands decrease and the *cis*-FA bands increase, and in our experiment the steady-state proportion of the cis form was ~50%.

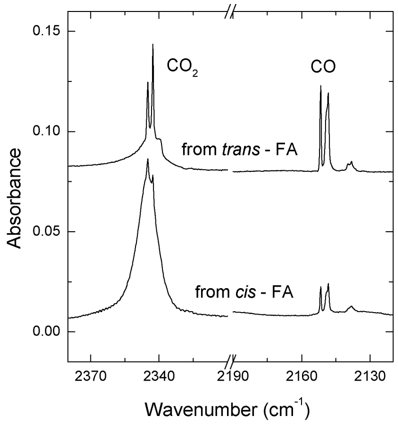

Figure 1. Photodissociation products obtained from the trans and cis isomers of FA. Note the change by a factor of 12 for the CO/CO_2 product ratio between the two conformers.

The central observation of this work concerns the clear difference in photolysis products obtained from the trans and cis isomers of FA. When the trans form was irradiated at 193 nm, the IR spectrum shows CO (mainly complexed with H_2O) and CO_2 (mainly monomeric) products in a certain proportion agreeing well with ref 11. Upon simultaneous UV and IR irradiation, the CO/CO_2 product ratio changes by a factor of ~4 in favor of CO_2 as judged by the integrated IR absorption bands. It immediately follows that the CO_2 channel is much more efficient in the *cis*-FA photodissociation than for the other isomer.

To estimate the branching ratios of the photodissociation channels numerically, we use for the matrix-isolated species the known gas-phase ratio of the CO_2 and CO absorption intensities that is about 10.[12−15] Under this assumption, the proportion of the CO product obtained from *trans*-FA is as high as 83%, and the rest is CO_2. When IR pumping enriches the cis isomer, the proportion of the CO_2 photodissociation channel increases to ~50%. It is easy to extract spectrally the pure *cis*-FA product from the sum product obtained upon IR pumping by subtracting the pure *trans*-FA product obtained without IR pumping. The result of this extraction procedure is presented in Figure 1 where the pure results of *trans*-FA and *cis*-FA photolysis are presented. It was estimated that the proportion of the CO_2 product in the *cis*-FA photodissociation is as high as 72%. Thus, in the present case of 193-nm photolysis in solid Ar, the photodissociation branching ratio between the trans and cis isomers differs by a factor of 12.

Now, we discuss possible reasons for the observed conformational selectivity of photodissociation. The computational energy barriers for the reactions of *trans*-FA to produce the alternative CO and CO_2 products are very close (~270 kJ/mol),[10] which is essentially smaller than the 193-nm photon energy (~630 kJ/mol). The energy difference between the trans and cis isomers (21.4 kJ/mol) as well as the trans-to-cis isomerization barrier (~50 kJ/mol)

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* Corresponding author. E-mail: Leonid.Khriachtchev@Helsinki.Fi.
† Permanent address: Department of Chemistry − CQC, University of Coimbra, P-3049 Coimbra, Portugal.

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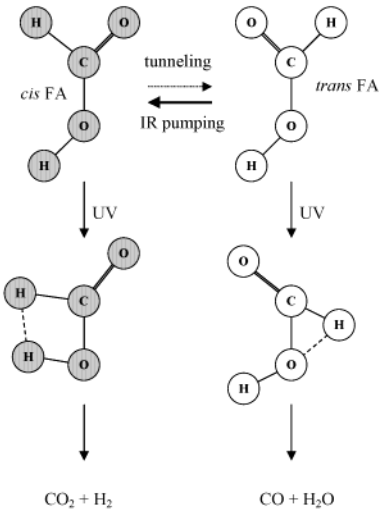

Figure 2. UV photodissociation of FA with conformational memory. Transition states are taken from ref 16. IR pumping is achieved by exciting the OH stretching first overtone at 6930 and 6934 cm^{-1}. Back-tunneling occurs in the time scale of minutes at 8 K.

is small in this scale. Energetically, the selectivity of photodissociation shows that the reaction occurs faster than the randomization of the torsion coordinate mixing the conformers. This selective photodissociation process of the trans and cis isomers of FA is illustrated in Figure 2 using the theoretical transition states connected with the initial geometry.[16] The proposed scheme applies to the vibrationally excited ground electronic state, and it emphasizes the idea of conformational (geometrical) memory of the precursor structure in formation of the transition state. The central participation of the ground state in the formation of products was shown in the 193-nm photolysis of *trans*-FA in the gas phase where vibrationally excited CO and CO_2 were detected.[10] Coupling of molecular modes with lattice phonons might be an important factor in energy relaxation,[17] and this possibly explains the smaller CO-to-CO_2 ratio for the photodissociation of *trans*-FA in solid Ar (∼5) compared with that for the gas phase (∼11).[10]

According to the gas-phase data, the 193-nm radiation can lead to the OH + HCO product.[10] In the present solid-phase study, we did not observe any isolated OH radicals after photolysis (3554 cm^{-1} in solid Ar),[18] which suggests either a small branching ratio for this reaction in solid phase or a small cage-exit probability with the available excess energy (∼2 eV). If the dissociating OH radical does not escape from the cage, the OH + HCO pair possibly recombines back to FA. We irradiated *trans*-FA with lower-energy photons (234 nm). As a result, the CO-to-CO_2 ratio increased to 6.0. It can be interpreted that the 234-nm photon energy (512 kJ/mol) is not sufficient for the OH + HCO channel with the computational transition state being 543 kJ/mol high in energy.[10] The observed increase of the CO-to-CO_2 ratio under 234-nm irradiation indicates that the OH + HCO photodissociation channel rather limits selectivity of the final photodissociation products than establishes it, which is in accord with the proposed model of photodissociation with geometrical memory in the highly vibrationally excited ground electronic state.[19] No reasons are seen to explain why the radical reactions can provide selective CO and CO_2 products, depending on the initial form of FA or why the radical pairs formed in photodissociation can be conformation-dependent. However, we cannot completely exclude a selective mechanism involving electronically excited states.

The band shapes of the CO_2 products detected in photolysis of the two conformers are different. As obtained from *trans*-FA, the CO_2 product exhibits two bands at 2342.8 and 2345.0 cm^{-1} that are assigned to CO_2 monomers in a double-substitutional site.[20,21] The CO_2 band obtained from *cis*-FA is broad, and we tentatively connect this broadening with formation of the CO_2-H_2 complex. This distinction in band shapes emphasizes the difference in photodissociation process between the two conformers. It seems that the H_2 formation for the cis form does not provide H_2 molecules with large kinetic energy. In contrast, the H_2 formation from *trans*-FA might involve repulsive configurations leading to kinetically hot H_2 and its cage exit.

In conclusion, the present data make a strong case of selective optical control of chemical reactions that are dependent on rotational isomerism. Our experiments directly show the different photodissociation channels of trans and cis forms of formic acid in solid Ar, which are essentially $H_2O + CO$ and $H_2 + CO_2$, respectively. This selective photodissociation process features the conformational memory when the transition state is reached before randomization of the torsional motion. We believe that a variety of photochemical processes can be controlled in this way.

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