

## COMMUNICATIONS

***Cis*→*trans* conversion of formic acid by dissipative tunneling in solid rare gases: Influence of environment on the tunneling rate**M. Pettersson<sup>a)</sup>*Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014, University of Helsinki, Finland*

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The relaxation of the higher-energy *cis* conformer of formic acid to the lower-energy *trans* form by a tunneling mechanism has been investigated in low-temperature rare gas matrices. In the temperature range 8–60 K, the tunneling takes place dominantly from the vibrational ground state of the *cis* form and the temperature dependence of the tunneling rate constant is influenced by the interactions with the environment. The temperature-dependent tunneling rates for HCOOH and DCOOH in solid Ar, Kr, and Xe are measured including data for molecules in different local environments within each host. It was found that the medium and the local environment has a significant influence on the tunneling rate. © 2002 American Institute of Physics.

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In reaction kinetics, tunneling of atoms is often negligible compared with over-barrier transitions. At very low temperatures, however, the population of energy states above the barrier becomes exceedingly small and tunneling becomes comparatively more important.<sup>1</sup> In a condensed environment, phonons participate in a tunneling reaction and the environment should have some effect on tunneling reactions.<sup>2,3</sup> However, in several previous experiments it was found that the tunneling rate constant was unaffected by the change of solvent.<sup>1,4–6</sup> In this work, we have studied the conversion of *cis* formic acid (HCOOH) to *trans* formic acid in solid rare gases (Ar, Kr, Xe). This reaction is dominated by tunneling from the vibrational ground state at temperatures below 60 K. The results show that the tunneling rate depends strongly on the environment.

The samples were made by mixing vapors of formic acid (FA) (KEBO lab, >99%) or its isotopomers (IT Isotope 95%–98% deuteration) with rare gases (Rg) Ar (AGA, 99.9999%), Kr (Air Liquid, 99.95%), Xe (AGA, 99.997%) in the gas phase in a proportion FA/Rg≈1/1000. The gas mixture was deposited on a CsI substrate at 15 K (Ar), 25 K (Kr) or 35 K (Xe) yielding highly monomeric matrices with respect to FA. Thickness of the sample was typically about 100 μm. After deposition, the samples were cooled to ~8 K

which was the lower limit for the cryostat (APD DE 202 A). The spectra were measured with a FTIR spectrometer (Nicolet 60 SX) with a resolution of 1 or 0.25 cm<sup>-1</sup>.

FA has energy minima in two planar forms differing by orientation of the hydroxyl group as shown in Fig. 1. The interconversion of the conformers involves mainly the torsional motion of the hydroxyl group. In the gas phase, *cis*-FA is 1365±30 cm<sup>-1</sup> higher in energy than *trans*-FA.<sup>7</sup> The barrier from *trans* to *cis* has been calculated to be ~4200 cm<sup>-1</sup>.<sup>8</sup> In this work, *cis*-FA was prepared by exciting the vibrational transitions of *trans*-FA in rare-gas matrices with narrowband infrared radiation of an optical parametric oscillator (Sunlite, Continuum, FWHM ~0.1 cm<sup>-1</sup>). The excitation energy flows into the torsional coordinate inducing the conformer conversion.<sup>9</sup> The IR spectra of *cis* and *trans* FA differ significantly from each other making it possible to distinguish them easily in rare-gas matrices.<sup>9</sup> FA is trapped in several sites corresponding to different local environments and the corresponding IR absorption frequencies differ typically a few cm<sup>-1</sup> as illustrated in Fig. 2 for *cis*-FA in solid Xe. *Cis*-FA was generated site-selectively by irradiating molecules in a separate site at a time similarly to our matrix-isolation studies on HONO.<sup>10</sup> In this way, the tunneling kinetics of FA in different sites could be investigated. There was no interconversion between different site groups either in IR pumping or in relaxation by tunneling.

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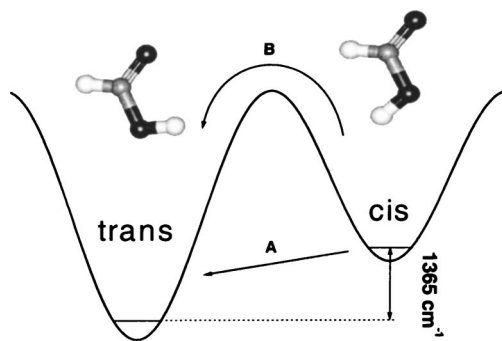


FIG. 1. *Cis* and *trans* formic acid and the torsional potential which connects the two conformers. The energy difference between the conformers is the experimental gas phase result from the Ref. 7. The arrows represent the conformer conversion processes by (A) tunneling and (B) over-barrier reactions.

Once formed, *cis*-FA converts back to *trans*-FA in a timescale of minutes even below 20 K.<sup>9</sup> At these temperatures, this reaction occurs purely via tunneling. Indeed, according to the *ab initio* calculations, the barrier ( $E_a$ ) for the *cis*→*trans* isomerization is  $\sim 2800\text{ cm}^{-1}$ ,<sup>8</sup> which gives, according to the Arrhenius formula  $k=A*\exp(-E_a/kT)$  and using the torsional frequency for the pre-exponential factor  $A$ , a rate constant of  $\sim 10^{-16}\text{ s}^{-1}$  even at 60 K. This rate is more than 13 orders of magnitude smaller than what is observed in our experiments. The over-barrier reaction should become significant at temperatures only above  $\sim 110\text{ K}$ . The torsional mode, which mainly corresponds to the tunneling coordinate, is the lowest frequency vibration in *cis*-FA at  $\sim 500\text{ cm}^{-1}$ .<sup>9</sup> It follows that, at the highest temperatures of our experiments (60 K) the population of the first excited torsional level is  $< 10^{-5}$ . We have estimated by using the WKB approximation<sup>1</sup> for the penetration probability and *ab initio* calculated (MP2/6-311++G(2d,2p), GAUSSIAN 98)<sup>11</sup> torsional potential that the permeability of the barrier from the first excited torsional level is  $\sim 4$  orders of magnitude higher than from the ground state. Therefore, at low temperatures the tunneling reaction takes place essentially from the ground vibrational state of *cis*-FA and the tunneling from the thermally excited vibrational states may become important only at temperatures above 60 K. In this respect, FA is an

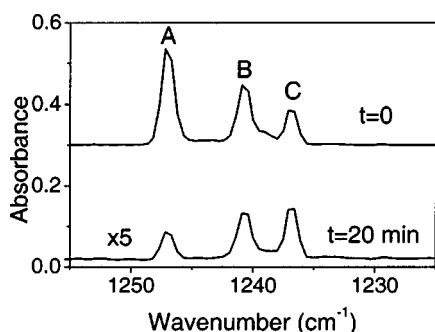


FIG. 2. IR absorption of *cis*-HCOOH in the CO-COH deformation fundamental region in solid Xe at 8 K. A, B, and C denote the absorptions corresponding to various sites (local environment). The lower trace was measured 20 min after the upper trace showing the different tunneling rates for the three sites.

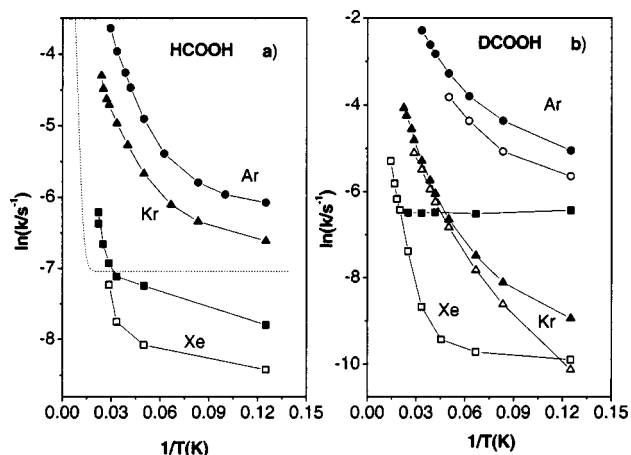


FIG. 3. Arrhenius plots for tunneling of (a) HCOOH and (b) DCOOH in various matrices. Data for two representative sites for each host are shown as solid and open symbols. The data for two sites shown in plot (a) for Xe as solid and open squares correspond to labels A and B in Fig. 2, respectively. For comparison, a simulated temperature dependence for tunneling from two lowest intramolecular vibrational states is shown as a dotted line.

ideal system to study the effect of the environment on tunneling.

The kinetics of the tunneling reaction was measured by FTIR spectroscopy after the *trans*→*cis* IR pumping was stopped by following the decrease in intensity of the CO-COH deformation absorption band of *cis* FA at  $\sim 1250\text{ cm}^{-1}$  (see Fig. 2). As an additional complication, it was found that the spectrometer glowbar radiation increases the rate of the *cis*→*trans* conversion significantly. By using an interference filter that blocks the radiation above  $\sim 1500\text{ cm}^{-1}$ , the effect of glowbar was suppressed and tunneling rates could be reliably measured. It was also estimated that the room temperature blackbody radiation from the cryostat windows did not affect the results. The Arrhenius plots for HCOOH and DCOOH in various rare-gas solids including representative examples of different sites (indicated by solid and open symbols) are presented in Fig. 3. The isomerization rate for HCOOH was also measured in Ar and it was at least three orders of magnitude smaller at 8 K than for HCOOH.

The major conclusion drawn from Fig. 3 is that the tunneling rate depends crucially on the solid host and in most cases also on the local matrix morphology (matrix-site effect). The temperature dependencies are also in definite contrast with the behavior that tunneling from the thermally excited intramolecular vibrational levels would show. To make this clear we show in Fig. 3(a) by a dotted line the simulated temperature dependence assuming tunneling from the two lowest torsional levels and four orders of magnitude higher tunneling probability from the first excited level than from the ground state. Clearly, comparing this result with the experiments suggests that the experimental temperature dependencies originate from the interaction of FA with the environment. For HCOOH, the tunneling rate decreases from Ar to Xe by one order of magnitude at 8 K. The rates for the two representative sites in solid Xe differ by a factor of  $\sim 2$  at 8 K (see also Fig. 2). In Ar and Kr matrices the molecules in various sites have the same rates within the experimental error. For DCOOH, the different sites show different tunnel-

ing rates in all the hosts. The tunneling rate for DCOOH in Ar is more than two orders of magnitude higher than in Kr at 8 K. The rates for molecules in different sites in Xe differ by a factor of  $\sim 30$  at 8 K. It is also interesting to compare the tunneling rates of HCOOH and DCOOH in the same host. It is seen that the tunneling rates change considerably despite the deuteration of the carbon bound hydrogen shifts down the torsional frequency less than 2%. In solid Ar at 8 K, DCOOH tunnels three times faster than HCOOH. In Kr matrices, the trend is opposite: HCOOH tunnels  $\sim 30$  times faster than DCOOH. In Xe host, the difference in rate constants depends strongly on which sites are compared.

These observations demonstrate that both changing the solid host, and changing the local environment within the same host can influence strongly the tunneling rates, the differences in the rate constants exceeding two orders of magnitude at 8 K. Related phenomena have been reported for reorientation of  $\text{NH}_3\text{D}^+$  ions in Tutton salts.<sup>12</sup> In those experiments, however, the tunneling system was defined by the environment (rotation of  $\text{NH}_3\text{D}^+$  between the inequivalent sites). In the present case, the tunneling system (internal rotation of formic acid) is well defined without the environment and therefore the effect of environment on the tunneling reaction is probed.

Next, we try to qualitatively understand different factors influencing the tunneling rate. Due to the large asymmetry of the torsion potential (see Fig. 1) the tunneling process involves excited vibrational states of *trans*-FA. In this respect, the energy difference between the *cis* and *trans* isomers and the vibrational level structure of *trans* are important to consider. It should be noticed that the two isomers have markedly different dipole moments (3.79 D for *cis*; 1.42 D for *trans*)<sup>7</sup> and hence their solvation energies are different. We estimated the solvation energies of *trans* and *cis*-FA in various hosts within the frame of the polarized continuum (PCM) model in GAUSSIAN 98 (Ref. 11) at the MP2/aug-cc-pvTZ level using the calculated gas phase structures and the dielectric constants of the rare gases [1.63 (Ar); 1.88 (Kr); 2.19 (Xe)].<sup>13</sup> The differences for solvation energies of the *cis* and *trans* forms are  $319\text{ cm}^{-1}$  (Ar),  $412\text{ cm}^{-1}$  (Kr), and  $508\text{ cm}^{-1}$  (Xe) indicating that solvation in a dielectric medium has a significant effect on the energetics. According to similar calculations performed on the transition state, the *cis*→*trans* barrier increases from Ar to Kr by  $43\text{ cm}^{-1}$  and from Kr to Xe by  $44\text{ cm}^{-1}$ . The vibrational energy level structure of *trans* FA relative to the ground state of *cis*-FA is shown in Fig. 4 for HCOOH/Ar, DCOOH/Ar and HCOOH/Xe. The position of the ground state of *cis*-FA estimated by the solvation calculations is shown with a dashed line in Fig. 4. Due to the limited accuracy of the solvation model the position of the ground state of *cis*-FA should be considered qualitative. Therefore, the discussion below is mostly hypothetical with respect to the exact energetics. In solid Ar, the smallest energy gap for the relaxation from the ground state of *cis*-HCOOH is connected with the first excited state of the  $\nu_8$  mode (C–H out of plane wag) of the *trans* form. In contrast, in solid Xe, solvation lowers the energy of *cis*-FA and the most energetically favorable relaxation channel occurs to the first excited states of  $\nu_7$  (OCO scissors) and  $\nu_9$  (torsion)

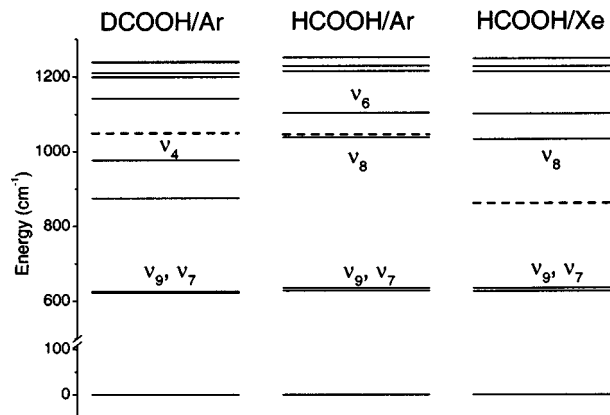


FIG. 4. Vibrational level structure of *trans* HCOOH and *trans* DCOOH as determined from their infrared spectra. The energy of the ground state of *cis* FA estimated by using the gas-phase energetics (Ref. 7) and *ab initio* calculated solvation energies for the two conformers is shown with a dashed line. The labels for selected vibrational states correspond to torsion ( $\nu_9$ ), OCO scissor ( $\nu_7$ ), C–H out-of-plane wag ( $\nu_8$ ), C–D rocking ( $\nu_4$ ), and COH–CO deformation ( $\nu_6$ ) modes (Ref. 9).

modes. In solid Ar, one-phonon emission is sufficient to dissipate the excess energy (Debye frequency of Ar= $93\text{ cm}^{-1}$ ) while in Xe, a higher-order multiphonon process is required (Debye frequency of Xe= $64\text{ cm}^{-1}$ ).<sup>14</sup> We can conclude from these examples that at least three factors contribute to the observed differences in the tunneling rates: (1) Change in the barrier height due to solvation which, according to the calculations, is relatively small in this case. (2) Due to differences in solvation energies, in different environments phonon-assisted tunneling may occur between different levels. The coupling between vibrational levels can vary strongly and therefore the effect on the tunneling rate can be large. (3) Change of the magnitude of the energy gap between the tunneling levels changes the order of the phonon process providing the energy dissipation. The differences of the rates between HCOOH and DCOOH should mainly originate from the change of the intrinsic level structure upon deuteration (see Fig. 4). The site effect can be explained on the same basis: It is plausible to assume that molecules in various sites have different solvation energies because the cavity size and geometry are key factors in the solvation. Additionally, coupling with phonons can be different for various sites.

The temperature dependencies of the rate constants are roughly described as  $k(T) \propto T^3$  or  $T^4$ . Previously, roughly  $T^4$  dependence was observed for translational tunneling of the acidic protons in benzoic acid dimers.<sup>15</sup> Theoretically, it was shown that  $T^2$  or  $T^3$  dependencies may arise from two-phonon emission/absorption and Raman processes.<sup>16,17</sup> Recently, a much stronger temperature dependence was reported for the  $\text{D} + \text{HD} \rightarrow \text{D}_2 + \text{H}$  reaction in solid HD (Ref. 18) and the origin of the effect was considered theoretically.<sup>3,19</sup> The present observations should be valuable in testing theories for the temperature dependence of dissipative tunneling. In addition to the fundamental value the observed phenomenon can be used for solid-phase stabilization of desired species affected by tunneling decay by choosing a suitable environment.<sup>20</sup> It is interesting to note that

indirect evidence of the influence of environment on a *cis*–*trans* isomerization tunneling reaction of hydroquinone in Ar and Xe matrices has been recently reported.<sup>21</sup>

In summary, it has been shown here that despite the relatively high energy barrier ( $\sim 2800\text{ cm}^{-1}$ ) *cis*-FA converts to *trans*-FA in timescale of minutes even at 8 K via pure tunneling mechanism. The tunneling rate depends strongly on the solid host and even on the local environment within a particular host, the differences in the tunneling rate constants exceeding two orders of magnitude at 8 K.

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