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Aggregation of acetic and propionic acid in argon matrices—A matrix isolation and computational study

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Abstract

Monomeric acetic acid $\mathbf{M_A}$ and propionic acid $\mathbf{M_P}$ were isolated in argon matrices at 10 K by using a pulse deposition technique. The dimerization of the monomers was induced by warming the matrices from 10 to 40 K. Under these conditions the diffusion of small trapped molecules is rapid and the dimerization could be monitored directly by IR spectroscopy. Both carboxylic acids form the symmetrical dimers **B** with two strong C=O···HO hydrogen bridges as the thermodynamically most stable dimers. With acetic acid a less stable dimer $\mathbf{A_A}$ could be obtained if high concentrations of acetic acid in argon were used during the deposition of the matrix. On annealing this dimer rearranges to the more stable $\mathbf{B_A}$. In contrast, propionic acid does not form a corresponding less stable dimer under any experimental condition. These observations are rationalized on the basis of DFT and ab initio calculations.

Keywords: Acetic acid; Propionic acid; Matrix isolation; Dimer; DFT calculations

1. Introduction

Hydrogen bonds play a crucial role in many important chemical processes such as solvation, aggregation, and defining the shape and function of biomolecules. Carboxylic acids form stable doubly hydrogen bridged dimers which in the gas phase exist in equilibrium with the monomers [1–3]. An interesting feature of these dimers is the double proton transfer assisted by a tunneling process [4–6]. The dimers of formic acid and acetic acid have been studied in detail both experimentally and by theoretical methods. In condensed phase the situation is more complicated. In the solid state both dimeric structures and infinite chains (catamers) bridged by hydrogen bonds are observed [7–12]. Thus, acetic acid shows a chain structure [11,13] while propionic acid crystallizes as dimers (Fig. 1) [14]. Although in many cases the structure is governed by thermodynamics and the most stable polymorph is formed, there are many complicated cases, such as acetic acid, with energetically close lying structures with dimer and catamer motifs [8]. The liquid phase of formic acid consist mainly of short chains, but no significant amounts of dimers were observed by neutron diffraction [15].

Infrared spectroscopy in low temperature inert gas matrices provides an ideal means for the investigation of small hydrogen-bonded systems [16–20]. Monomeric species are trapped from the gas phase in a large excess (>1000:1) of inert gas. All experiments described here were performed using solid argon as inert gas matrix. At temperatures below 20 K the diffusion of even small molecules is inhibited and monomeric species can be characterized spectroscopically. The largest problem is the isolation of monomers with only small contamination by dimers and higher aggregates from a gas phase equilibrium mixture. This problem was solved in our laboratory by using a supersonic jet expansion followed by matrix isolation (pulse deposition technique). This allowed to matrix-isolate the almost pure monomers of formic acid and acetic acid [21,22]. The second step in our experiments is to allow the diffusion of the monomeric carboxylic acid in solid argon by warming the matrix to temperatures between 25 and 40 K. At these temperatures the trapped molecules become mobile and the formation of aggregates can be directly monitored by IR spectroscopy. At temperatures above 35 K argon starts to evaporate rapidly which

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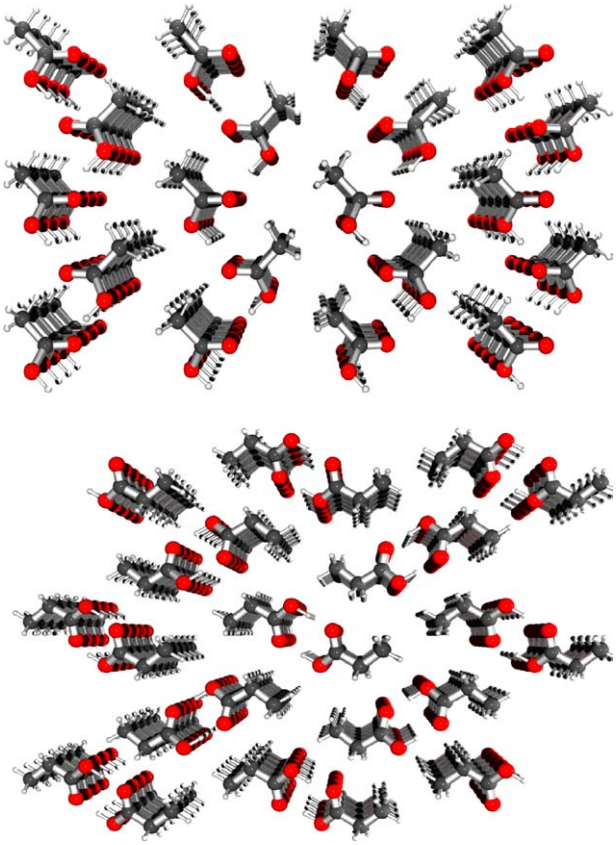
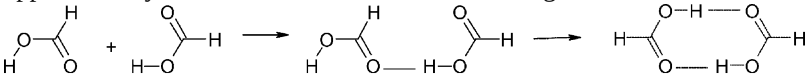


Fig. 1. Crystal structures of acetic acid (Ref. [13], top) and propionic acid (Ref. [14], bottom).

limits the available temperature range. In a typical experiment the matrix is allowed to warm from 10 to 40 K with a rate of approximately 1 K/min with monitoring changes in the matrix by IR spectroscopy.

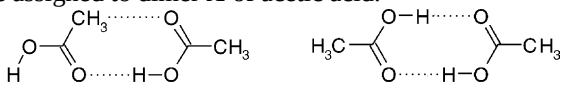
An investigation of the dimerization of formic acid monomers $\mathbf{M_F}$ using this technique revealed that the symmetrical doubly bridged dimer $\mathbf{B_F}$ is formed in a two-step process. The first, less stable intermediate is dimer $\mathbf{A_F}$ with one strong OH···O=C hydrogen bridge and a weak CH···O=C interaction. This weak interaction results in an activation barrier of approximately 2 kcal/mol for the $\mathbf{A_F} \rightarrow \mathbf{B_F}$ rearrangement.



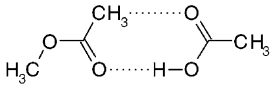
$\mathbf{M_F}$ $\mathbf{A_F}$ $\mathbf{B_F}$

The formation of dimer $\mathbf{A_F}$ as the primary dimer was later confirmed by independent studies in superfluid helium droplets at 0.38 K [23,24]. Dimer $\mathbf{A_F}$ was also predicted to be the most likely structure formed by following the minimum energy path.

The matrix IR spectra of both monomeric [25,26] and dimeric [27] acetic acid were reported in literature. The vibrational spectra were assigned by isotopic labeling. Grenie et al. provide evidence that in addition to the symmetrical doubly bridged dimer an open dimer of the type OH···OH is present in the matrix and assigned a band at 3416 cm^{-1} to this dimer [27]. Recently Emmeluth and Suhm investigated the formation of the less stable dimers of acetic acid in supersonic jet expansions [2]. By using mixtures of acetic acid and methyl acetate (where the acidic OH group is replaced by OCH_3) they were able to record IR bands of a mixed dimer of type **A** with a strong OH···O=C and a weak CH_3···O=C interaction. In addition, IR bands at 1769, 1319, and 1237 cm^{-1} were assigned to dimer **A** of acetic acid.



$\mathbf{A_A}$ acetic acid dimers $\mathbf{B_A}$



mixed dimer methyl acetate / acetic acid

Here we present a matrix isolation and computational study of the aggregation of acetic acid and propionic acid with the focus on the question whether the less stable dimers **A** are intermediates of the formation of the doubly bridged symmetrical dimers **B**. The isolation of almost pure monomers **M** in combination with controlled annealing experiments allowed to obtain clean spectra of the monomers and the dimers.

2. Experimental

A description of the matrix-isolation technique used is given elsewhere [28]. The pulse deposition unit used for acetic acid, built similar to Chen's [29] and Maier's [30] construction, was described previously [31]. To avoid uncontrolled aggregation of the sample in the matrix during deposition the spectroscopic window has to be held at the lowest temperature possible (9 K). After the deposition and recording a spectrum, the aggregation is initiated by switching off the helium compressor. This leads to a *free warm-up* of the matrix at a rate of approximately 1 K min^{-1} during which additional spectra are continuously recorded using only 50 scans per spectrum. All spectra were recorded by using a Bruker Equinox 55 or IFS 66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1}. Calculations were performed on a workstation (HP SuperDome 32000, operating system HPUX 11.i) with the Gaussian 98 program package [32] using the B3LYP [33–35] functional with the cc-pVTZ [36,37] basis set, the mPW1LYP functional with the 6-311++G^{**}, or MP2 ab initio theory with the 6-311++G^{**} basis set.