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UV-light induced conformational changes of 2-pyridinecarboxylic acid in low-temperature argon matrices

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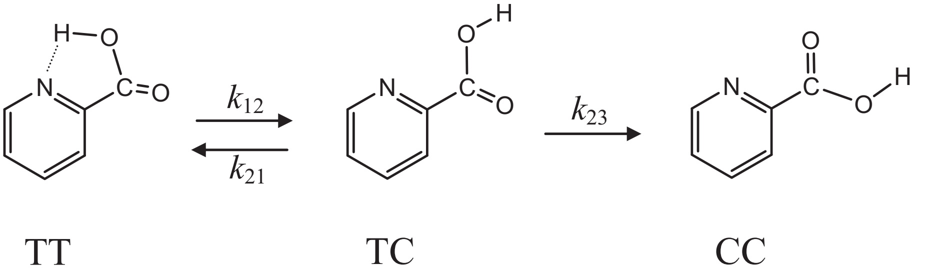
HIGHLIGHTS

- Conformations of 2-pyridinecarboxylic acid are investigated by IR spectroscopy.
- Stabilization due to intramolecular hydrogen bonding is examined by DFT method.
- Conformational changes in argon matrices occur upon UV irradiation.
- Photoreaction pathways are derived from kinetic analysis of IR absorbance changes.

GRAPHICAL ABSTRACT



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ABSTRACT

Conformational changes of 2-pyridinecarboxylic acid (2-picolinic acid) upon UV irradiation have been investigated by low-temperature matrix-isolation infrared spectroscopy. Only one conformer having an intramolecular hydrogen bond of COOH···N in the pyridine ring is found to exist in argon matrices after deposition before UV irradiation, in contrast to a reported feature in the CCl_4 solution. The hydrogen bond is broken by UV irradiation, resulting in two less stable conformers; one increases immediately at the early irradiation stage while the other increases slowly during the prolonged irradiation time. The conformations around the OC—OH and C—COOH bonds of the photoproducts are identified by assignments of the IR bands measured in an argon matrix with an aid of the density-functional-theory calculation. The proposed photoreaction pathways of the conformational changes based on this observation are supported by a kinetic analysis of the IR absorbance changes with the reactants and the photoproducts against the irradiation time.

Introduction

Pyridinecarboxylic acids (2-picolinic acids; see Fig. 1) are used for food supplements and active agents in drugs as metal complexes and heterodimers with other carboxylic acids [1–4]. Since pyridinecarboxylic acid, abbreviated as PA, has a hydrogen donor in the carboxy group and a hydrogen acceptor of the lone pair at the N atom in the pyridine ring, it remains controversial whether they exist predominantly as a neutral form or a zwitterionic form in an isoelectric aqueous solution. As for 3-PA, where a COOH group is bonded at the third position of the pyridine ring, it was once considered to be present predominantly as a neutral form [5,6], but it has later been concluded that PAs are predominantly present as a zwitterionic form [7–10].

In contrast to the results in aqueous solutions, PAs are expected to be present as a neutral form in non-polar solutions. If this is true, only 2-PA among the three neutral forms of PAs has a conformer named TT in Fig. 2, being stabilized by an intramolecular hydrogen bond (IMHB, hereafter) of COOH···N in the pyridine ring. The former letter T denotes *trans* conformation of the O atom in the C═O group against the N atom in the pyridine ring, while the latter

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T denotes *trans* conformation of the O—H group against the C═O group. Ōki et al. reported the infrared (IR) absorption bands of 2-PA in CCl_4 solution and identified a non-hydrogen-bonded conformer, named TC in Fig. 2, besides the hydrogen-bonded conformer TT [11]. However, the resolution of their observed assignments of the two C═O stretching bands to TT and TC in the CCl_4 solution did not seem to provide correct identification of the slight difference in the position of the hydrogen atom in the COOH group in view of the wide widths of the IR bands in the solution. In addition, the relative energy of the less stable conformer is estimated to be 15.3 kJ mol^{-1} higher than that of TT [12] by a quantum chemical calculation at the DFT/B3PW91/6-311++G** level, implying that the population of TC is so small that its identification is hard at room temperature judging from the Boltzmann distribution law.

The finding for 2-PA that the *trans* conformation around the OC—OH bond (TT) is more stable than the *cis* conformation (TC) totally contrasts with general carboxylic acids, because the *trans* conformation is destabilized by the repulsion of lone pairs in the two O atoms in the COOH group. For example, the less stable conformers, *trans*, in formic acid [13–15], acetic acid [13,16,17], propionic acid [13,18], and benzoic acid [19] are produced from the more stable conformers, *cis*, by IR radiation and return to *cis* in darkness through hydrogen-atom tunneling. Another example is reported that the *trans* conformer of 2-chlorobenzoic acid produced from the *cis* conformer by UV irradiation is unable to exist stably even in a low-temperature argon matrix in spite of the stabilization due to the IMHB of COOH···Cl [20]. It is assumed that the *trans* conformer immediately returns to the *cis* conformer through hydrogen-atom tunneling. Thus, it is required to confirm that the most stable conformer of 2-PA, where the C—Cl part of 2-chlorobenzoic acid is replaced by the N atom in the pyridine ring, is *trans* around the OC—OH bond in the COOH group and that the *cis* conformer of 2-PA is negligible at room temperature.

In the present study, we have investigated the conformation of 2-PA monomer using the low-temperature matrix-isolation IR spectroscopy. 2-PA has two possible conformations, *trans* and *cis*, around the C—COOH and OC—OH bonds, resulting in the four conformers shown in Fig. 2. To confirm that only TT exists stably at room temperature, we have measured IR spectra of a low-temperature argon-matrix sample and performed vibrational assignments with an aid of the density-functional-theory (DFT) calculation. In addition, we have measured the IR spectra of less stable conformers produced from the most stable conformer by UV irradiation and determined their conformations around the C—COOH and OC—OH bonds by comparison of the observed spectra with the spectral patterns obtained by the DFT calculation. This combined technique is one of the most effective methods to stabilize less stable conformers with a small amount of population and distinguish slight differences due to conformational changes, as shown in our recent papers and the references therein [21–26].

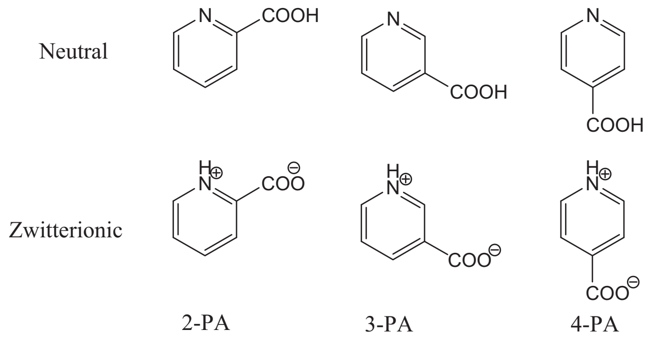

Fig. 1. Three structural isomers and their zwitterionic forms of PA.

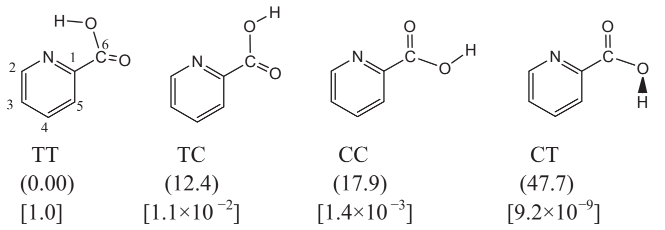

Fig. 2. Four possible conformers of 2-PA and numbering of carbon atoms. The numbers in parentheses represent calculated relative energies in kJ mol^{-1}. The numbers in square brackets represent population ratios according to the Boltzmann distribution law at the deposition temperature of 298 K using the calculated relative Gibbs energies.

Experimental and computational methods

A solid sample of 2-PA (purity > 98%) was purchased from Wako Pure Chemical Industries and used after vacuum distillation to remove impurities. Since the vapor pressure of 2-PA is insufficient to premix with pure argon gas (Taiyo Toyo Sanso, 99.9999% purity), a small amount of the solid sample was placed on the way to a deposition nozzle, and argon was flowed over the sample at room temperature. The mixed gas was deposited through a stainless steel pipe on a CsI plate cooled by a closed-cycle helium-refrigeration unit of IWATANI (Model CW303). The temperature for deposition was controlled to be 20 K, whereas every spectrum was measured at 10 K.

IR spectra were measured with an FTIR spectrometer (JEOL, JIR-WINSPEC50). The IR beam of the spectrometer was introduced into the matrix sample through a KBr window and detected with a liquid-nitrogen cooled MCT placed on the opposite side of the vacuum chamber. The spectral resolution was 0.5 cm^{-1}, and the number of accumulations was 64. A super high-pressure mercury lamp (Ushio, BA-H500) was used to induce conformational changes through a water filter to remove IR radiation. The radiation wavelength was adjusted using a shorter-wavelength cut-off optical filter (HOYA) of UV28 ($\lambda > 270$ nm). See Ref. [26] for other experimental detail.

The DFT calculations were carried out using the Gaussian 09 W program [27] with the 6-31++G** basis set, where Becke's three-parameter hybrid density functional [28] was used in combination with the Lee–Yang–Parr correlation functional (B3LYP) [29] to optimize the geometrical structures and to calculate relative energies and IR spectral patterns. Scaling factors of 0.98 and 0.95 were used in the regions lower and higher than 2000 cm^{-1}, respectively.

Results and discussion

Optimized geometrical structures of 2-PA by DFT calculations

The four conformers of 2-PA shown in Fig. 2 were optimized by the DFT calculations. Among the four conformers, only CT is non-planar so as to avoid the steric hindrance between two H atoms; one is in the O—H group and the other is bonded to the pyridine ring. Optimized geometrical parameters of the four conformers are listed in Table 1, where the numbering of carbon atoms is denoted in Fig. 2.

Calculated relative energies of the four conformers are listed in Fig. 2 after correction of zero-point vibrational energy, showing that TT is the most stable conformer. This result is in contrast to the fact that general carboxylic acids prefer *cis* to *trans* conformation about the OC—OH bond in the COOH group [13–19], as described in Introduction, implying that TT of 2-PA is strongly stabilized by the IMHB of COOH···N in spite of the repulsion between