



Hydrogen bonding in the carboxylic acid–aldehyde complexes



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ABSTRACT

Carboxylic acids have been recognized as important precursor species in atmospheric new particle formation. To clearly understand how aerosols form at the molecular level we investigated the hydrogen bonding interactions in the complexes between carboxylic acids and aldehydes using density functional theory methods. The geometric optimization shows that the Z-type carboxylic acid and aldehyde subunits are linked together through a classical O–H···O and a weak C–H···O hydrogen bond, which forms ring structures, and the E-type carboxylic acid and aldehyde subunits are linked through an O–H···O hydrogen bond with no ring structure. The binding energies and OH-stretching frequency calculations show that the carboxylic acid (Z)–aldehyde complexes are bonding stronger than the carboxylic acid (E)–aldehyde complexes. In addition, atoms in molecules (AIM) theory and natural bond orbital (NBO) analyses were performed to further interpret the intermolecular properties of the carboxylic acid–aldehyde complexes. This study helps to elucidate the nature of the hydrogen bond in these complexes and reveal their roles in atmospheric new particle formation.

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1. Introduction

Atmospheric aerosols, which is defined as microscopic particles suspended in Earth's atmosphere, have become a major environmental problem and have received enhanced attention in the recent years, mainly on account that they degrade visibility, negatively affect human health, and directly and indirectly influence climate by absorbing and reflecting solar radiation and modifying cloud formation. However, how aerosols form at the molecular level is still far from well understood [1–3]. It is generally accepted that new particle formation consists of two distinct stages: first molecular complexes and pre-nucleation clusters form to reach the point of “critical nucleus” and second the critical nucleus grows to a detectable nanometer sized aerosol particle [4]. This process in the atmosphere through nucleation of gas phase species and continuous condensational growth is a crucial process. It has been discovered that intermolecular hydrogen bonding is partly responsible for the formation of atmospherically relevant clusters. The study of the thermodynamic stability of the clusters could provide useful information about the initial steps of particle formation.

In a recent study of atmospheric new particle formation and growth at an urban site of Beijing, it is found that the particle growth was limited by the concentrations of the oxidized organic

vapors [5]. The first indication of the participation of organic gases in the nucleation process was reported by Zhang et al., which showed an enhanced nucleation of sulfuric acid in the presence of organic acids [1]. Carboxylic acids have been recognized as important precursor species in atmospheric new particle formation [6]. It has been reported that carboxylic acids form stable hydrogen bonded dimers that exist in the vapor phase in equilibrium with monomers [7]. Elm et al. studied the molecular interaction of pinic acid with sulfuric acid and found that pinic acid cannot be a key species in the first steps in nucleation, but the favorable interactions between sulfuric acid and pinic acid imply that pinic acid can contribute to the subsequent growth of an existing nucleus by condensation [8]. Since oxygenated organic compounds could contribute to the nucleation and growth of atmospheric particles, it is helpful to study the interaction between the oxygenated organic compounds. Gou et al. have investigated the complex between formic acid (HCOOH) and formaldehyde (HCHO) using the Fourier transform microwave (FTMW) spectra [9]. The hydrogen bonding in the complex could be responsible for the interaction between them in the atmosphere.

In the present study, we choose formic acid (HCOOH), acetic acid (CH₃COOH) and trifluoroacetic acid (CF₃COOH) as the hydrogen bond donors, formaldehyde (HCHO) and acetaldehyde (CH₃CHO) as the acceptors to study the hydrogen bond interactions between the carboxylic acids and aldehydes. The geometry and interaction energies were obtained using computational methods. We calculated the OH-stretching frequency of the donor monomer

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and its redshift upon formation of the complex. The red shift is a typical feature of hydrogen bond formation. In addition, atoms in molecules (AIM) analysis were carried out to investigate the electronic densities and the hydrogen bond interactions in the complexes. Natural bond orbital (NBO) analysis was performed to explain the donor–acceptor charge delocalization that takes place between the lone pair of the acceptor and proximal antibonding orbital of the donor and to evaluate the direction and magnitude of the hydrogen bond interactions in the complexes.

2. Computational methods

All the calculations were carried out using Gaussian 09 software. Optimized geometries and energies for the three carboxylic acids, formic acid (HCOOH), acetic acid (CH₃COOH) and trifluoroacetic acid (CF₃COOH), and the two aldehydes, formaldehyde (HCHO) and acetaldehyde (CH₃CHO), and their complexes were calculated employing the B3LYP, B3LYP-D3 and M06-2X methods combined with the aug-cc-pVTZ basis set [10], using the options “opt = verytight” and “integral = ultrafine”. Harmonic vibrational frequency calculations were made by using the three methods with aug-cc-pVTZ basis set to confirm the energy minima for all the structures of the complexes and monomers studied here and to obtain the zero-point vibrational energies (ZPVE). The counterpoise (CP) correction scheme proposed by Boys and Bernardi was employed in consideration of effects of the Basis Set Superposition Error (BSSE) [11]. Binding energies (BE) of the complexes were obtained through subtracting the energies of the two isolated monomers from the energy of the dimer. The BE of the complexes were corrected for the BSSE and ZPVE correction. Enthalpies and Gibbs free energies of formation for all the complexes at 298 K and 1 atm were obtained employing standard statistical mechanics.

The quantum theory of atoms in molecules (AIM) theory, which was performed based on topological analysis of the electron charge density, has been employed in clarifying the characterization of the intermolecular hydrogen bonding interactions in a variety of molecular complexes [12]. The topological parameters and the molecular graphs were obtained by implementing in the AIM 2000 software with the structure at the B3LYP-D3/aug-cc-pVTZ level. The wave functions computed at the B3LYP-D3/aug-cc-pVTZ level of theory were used to calculate the electron density $\rho(r)$ and Laplacian $\nabla^2\rho(r)$ at the bond critical points (BCPs) [13,14]. Natural bond orbital (NBO) analysis provides a deep insight into the property of electronic structure and bonding of molecules. The NBO calculations were performed using the NBO program, as implemented in Gaussian 09, at the B3LYP-D3/aug-cc-pVTZ level.

3. Results and discussion

3.1. Geometric parameters and energies

Optimized geometries of the carboxylic acids, aldehydes and their O—H···O bonded complexes at the B3LYP-D3/aug-cc-pVTZ level of theory are depicted in Fig. 1. We also optimized the geometries of the acid–aldehyde complexes with no O—H···O hydrogen bond. These structures obtained at the B3LYP-D3/aug-cc-pVTZ level of theory are shown in supplementary material. The discussion in this paper is mainly focused on the complexes with O—H···O hydrogen bonds, because they have lower energy and are more stable. There are two types of conformer of the COOH group in the acids, the O atom and H atom on the different sides of C—O bond (Z-type) or on the same side of C—O bond (E-type). The acid (Z)-aldehyde complexes possess a hydrogen bond pair, O—H···O hydrogen bond and C—H···O hydrogen bond, which forms a

seven- or an eight-membered cyclic ring. While the acid (E)-aldehyde complexes only possess O—H···O hydrogen bond, which do not form any cyclic ring, except that the CF₃COOH (E)-aldehyde complexes form an eight-membered cyclic ring due to the O—H···O hydrogen bond and the interaction between F atom and CH.

Selected geometric parameters, including the OH bond length in complexes R(OH), the change in the OH bond length upon complexation $\Delta r(\text{OH})$, the intermolecular hydrogen bond distance R(HB) and the hydrogen bond angle $\theta(\text{HB})$, obtained at the B3LYP-D3/aug-cc-pVTZ level of theory are listed in Table 1. The parameters at the B3LYP/aug-cc-pVTZ and M06-2X/aug-cc-pVTZ level of theory are listed in Table S1 in supplementary material. In the ideal hydrogen bonded complex, the hydrogen bond angle is supposed to be 180°. The carboxylic acid–aldehyde complexes with cyclic rings possess a hydrogen bond angle closer to 180° than those with no cyclic ring. The hydrogen bond angle in the HCOOH (Z)-HCHO (A) complex is only tilt 3.3°, while the hydrogen bond angle in the HCOOH (E)-HCHO (A) complex is tilt 11.0°. For the HCOOH (Z)-CH₃CHO (A) complex, the hydrogen bond angle is only tilt 1.8°, while the hydrogen bond angle is tilt 9.6° for the HCOOH (Z)-CH₃CHO (B) complex. Furthermore, the carboxylic acid–acetaldehyde complexes with a seven-membered cyclic ring possess a hydrogen bond angle closer to 180° than those with an eight-membered cyclic ring. However, in the complexes having a seven-membered cyclic ring with the same carboxylic acid subunit but different aldehyde subunits, such as the HCOOH (Z)-HCHO (A) and HCOOH (Z)-CH₃CHO (A) complexes, the hydrogen bond angles are quite close to each other, with the difference of only about 1.5–1.6°.

The intermolecular hydrogen bond distance of the O—H···O bonded carboxylic acid–aldehyde complexes are in the range of 1.6586–1.8424 Å. The intermolecular hydrogen bond distance in the HCOOH (Z)-CH₃CHO (A) complex (1.7247 Å) is shorter than that in the HCOOH (Z)-CH₃CHO (B) complex (1.7652 Å), which indicates that the bonding upon formation of the seven-membered ring structure is stronger than that of the eight-membered ring structure. Gou et al. investigated five isotopologues of the 1:1 complex between HCOOH and HCHO using the Fourier transform microwave spectroscopy [9]. The HCOOH–HCHO complex was determined to be planar, with its two subunits held together through an O—H···O hydrogen bond and a C—H···O weak hydrogen bond, and this complex is quite rigid. The intermolecular hydrogen bond distance in the HCOOH (Z)-CH₃CHO (A) complex is larger than HCOOH (Z)-HCHO (A), suggesting that the CH₃CHO subunit is a stronger hydrogen acceptor than HCHO. Among the HCOOH (Z)-HCHO (A), CH₃COOH (Z)-HCHO (A) and CF₃COOH (Z)-HCHO (A) complexes, the intermolecular hydrogen bond distance of CF₃COOH (Z)-HCHO (A) is the shortest, indicating that CF₃COOH is the strongest hydrogen bond donor of the three acids.

Besides, the change in the OH bond length upon complexation is larger in the stronger complexes hydrogen bonded. For example, the O—H bond length in the CF₃COOH (Z)-HCHO (A) and CF₃COOH (E)-HCHO (A) complexes increase by 0.0261 and 0.0185 Å for the stronger and the weaker bonding, respectively. In the case of the CF₃COOH (Z)-CH₃CHO (A) and CF₃COOH (Z)-CH₃CHO (B) complexes, the O—H bonds are elongated by 0.0323 and 0.0257 Å, respectively. For the HCOOH (E)-HCHO (A) and HCOOH (E)-CH₃CHO (A) complexes, the O—H bonds are lengthened by 0.0132 and 0.0166 Å, respectively. The relative strength of the hydrogen bonds indicated by the different geometric parameters is consistent with each other.

The B3LYP-D3/aug-cc-pVTZ calculated binding energies (BE), zero point vibrational energy (ZPVE), basis set superposition error (BSSE), enthalpies of formation ($\Delta H_{298\text{K}}^0$), Gibbs free energies of formation ($\Delta G_{298\text{K}}^0$) and equilibrium constants (K_{eq}) at 298 K for the lowest energy conformers of the carboxylic acid–aldehyde

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