Contribution of methane sulfonic acid to new particle formation in the atmosphere

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HIGHLIGHTS

- Interactions between MSA and atmospheric nucleation precursors were studied.
- The complexes have large binding energies and are thermodynamically favorable.
- The effect of atmospheric heights on stability was investigated.
- MSA shows almost the same capability in nucleation as H_2SO_4.

ARTICLE INFO

ABSTRACT

Methane sulfonic acid (MSA) is present in substantial concentrations in the gas phase over oceans and coastal regions. We present an investigation into the contribution of MSA to new particle formation with the common atmospheric aerosol nucleation precursors including MSA, methanol, formic acid, acetone, dimethylether, formaldehyde, methyl formate, by making use a quantum chemical approach. Density functional theory calculations indicate that these bimolecular complexes are characterized by the presence of strong inter-molecular hydrogen bonds (SO−H···O) with large binding energies and thermodynamic equilibrium constants. Topological analysis employing quantum theory of atoms in molecules shows that the charge density of the SO−H···O hydrogen bonds of the MSA complexes falls in the range of hydrogen bonding criteria, but the Laplacian at bond critical points exceeds the range, which is due to the strong hydrogen bonding interactions. In all the studied complexes, the electrostatic interactions are found to be the main attractive force by localized molecular orbital energy decomposition analysis. All these indicate the environmental fate of MSA could play the role of nucleation centers in new particle formation. The effect of the atmospheric heights (0−12 km) was also considered. The Gibbs free energy of formation decreases with the increase of the atmospheric height owing to the decrease of the atmospheric temperature and pressure. The calculated Gibbs free energies of formation within the atmospheric temperature and pressure range could help to understand the atmospheric pollution.

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1. Introduction

New particle formation (NPF) is an important source of atmospheric aerosols, and it can affect human health and impact climate change (Kulmala, 2003; Saxon and Diaz-Sanchez, 2005). NPF contributes over half of the atmosphere's cloud condensation nuclei (CCN), which influences cloud properties and Earth's energy balance (Bianchi et al., 2016). Furthermore, NPF is known as a two-step process: an initial nucleation step to form a critical nucleus and

then a growth step where the size of the critical clusters increases rapidly (Wang et al., 2010; Zhang, 2010; Temelso et al., 2012; Zhang et al., 2012). The composition and population in the initial nucleation is critical and it would affect the NPF events and the nucleation rate.

Many studies have been carried out to investigate the initial nucleation mechanisms, but the species involved in the atmospheric nucleation are still highly unknown (Kulmala et al., 2012, 2013). Inter-molecular interactions, namely, hydrogen bonding, have been found to be responsible for the aerosol particle formation (Kjaergaard et al., 2003; Kirkby et al., 2011; Vaida, 2011; Kulmala et al., 2013). Homogeneous nucleation, ion-induced nucleation and ion-mediated nucleation have been proposed as

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potential candidates for atmospheric nucleation. A latest study shows that neutral nucleation is more than 10 times faster than ion-induced nucleation (Bianchi et al., 2016). Because of the important role of neutral nucleation in both the tropospheric and the stratospheric budgets of atmospheric gases, the investigation of sulfur has been a subject of intense scientific interest for many years (Langner and Rodhe, 1991). Atmospheric gas phase sulfuric acid (H_2SO_4) is an important component of atmospheric aerosols, which has been known as a primary driver of NPF (Klemperer and Vaida, 2006; Van Loon et al., 2008; Schobesberger et al., 2013). Its gaseous concentrations in the atmosphere are 10^6–10^7 molecules cm^{-3}, which is a necessary condition for NPF (Sipilä et al., 2010; Zhang et al., 2012). This means that the critical cluster should contain one or two H_2SO_4 or H_2SO_4–containing molecules. In recent studies, the nucleation between organic matters with H_2SO_4, water (H_2O), or ammonia (NH_3) has been received great attention. Zhang et al. have found that NPF of H_2SO_4 would be enhanced in the present of organic acids (Zhang et al., 2004). Later on, they demonstrated that there were one cis-pinonic acid and three to five H_2SO_4 molecules in the critical nucleus (Zhang et al., 2009). In the study of Schobesberger et al., the stable clusters contained one to four oxidized organics and one to three H_2SO_4 molecules (Schobesberger et al., 2013). Moreover, Kulmala et al. affirmed that H_2SO_4 should be coupled with a stabilizing component such as ammonia, amines, or organic compounds (Kulmala et al., 2013).

Dimethyl sulfide (($CH_3)_2S$, noted as DMS) is the most abundant biogenic sulfur compound emitted over the oceans into the atmosphere by phytoplankton (Simpson et al., 1999; Kappler and Schäfer, 2014). It can also be naturally produced via bacterial transformation of dimethyl sulfoxide (($CH_3)_2SO$, noted as DMSO) waste disposing into sewers (Glindemann et al., 2006). DMS can be oxidized in the marine atmosphere to various compounds, such as sulfur dioxide (SO_2), DMSO, dimethyl sulfone (($CH_3)_2SO_2$, noted as $DMSO_2$), methane sulfonic acid (CH_3SO_3H, noted as MSA) and H_2SO_4 (Lucas and Prinn, 2005). The gas phase MSA in the atmosphere is one of the main oxidation products of ocean released DMS and it is predominantly formed heterogeneously through the oxidation of DMSO (von Glasow and Crutzen, 2004; Barnes et al., 2006). The concentrations of MSA in the atmosphere are about 10^5–10^7 molecules cm^{-3}, which is about 10–100% of those of H_2SO_4 (Eisele and Tanner, 1993; Berresheim et al., 2002). Atmospheric MSA is expected to become relatively more important for the initial stages of NPF (Wang, 2007; Perraud et al., 2015).

The lifetime of MSA in the atmosphere is very long, and it cannot be photochemically decomposed. Therefore, it is expected to be removed from the atmosphere via either wet or dry deposition (Andreae, 1986; Baker et al., 1991). It is interesting to investigate the environmental fate of MSA by interacting with the atmospheric relevant compounds. The interactions between MSA and amines/ammonia have been found as a source of NPF in the atmosphere (Chen et al., 2016). In the present study, the interaction of the common atmospheric aerosol nucleation precursors including methanol (CH_3OH), formic acid (HCOOH), acetone (CH_3COCH_3), dimethylether (CH_3OCH_3), formaldehyde (HCHO), and methyl formate ($HCOOCH_3$) with MSA have been studied using the density functional theory (DFT), quantum theory of atoms in molecules (QTAIM), and localized molecular orbital energy decomposition analysis (LMO-EDA). These common atmospheric aerosol nucleation precursors are chosen because they are the most abundant organic compounds in the atmosphere (Yu, 2000; Legreid et al., 2007; Zhang et al., 2012; Jardine et al., 2014; Mellouki et al., 2015). Among them, 11.9% of the top 20 oxygenated volatile organic chemicals (OVOCs) emissions (by mass) from anthropogenic sources (in the U.K.) in 2010 is methanol, while 7.5% is acetone, 4.5% is formaldehyde, 0.7% is dimethylether (Mellouki

et al., 2015). 1–9% of the total gaseous and aerosol organic acid concentrations are atmospheric formic acid (Yu, 2000). Moreover, volatile ester is one of the important OVOCs (Legreid et al., 2007; Jardine et al., 2014). In the atmosphere, 2% of the measured OVOCs concentrations is esters (Legreid et al., 2007). Methyl formate represents the simplest ester and as such its study allows for the investigation of the role of the ester functionality on NPF. The implications of the present results are discussed for the initial stages of the atmospheric aerosol nucleation.

2. Computational methods

DFT calculations employing the B3LYP-D3 functional were carried out with the Gaussian 09 (Revision E.01) program (Frisch et al., 2013). Dunning's augmented-correlation consistent polarized valence-only triple-zeta (aug-cc-pVTZ) basis set was employed in all calculations except for the sulfur atoms (Dunning, 1989). The recommended tight d function was included for the sulfur atoms to improve the energy convergence (Wilson and Dunning, 2003, 2004). For each stable structure, harmonic frequencies were calculated to confirm that the structures are indeed minima and to estimate the zero-point vibrational energy (ZPVE) contribution to the binding energies (BEs). BEs of different bimolecular complexes have been estimated using a super-molecular approach, namely, the energy of the complex minus the two monomer energies, $BE = E(A \cdots B) - E(A) - E(B)$. However, the results are not corrected for the basis set superposition errors (BSSEs) by the counterpoise (CP) correction (Boys and Bernardi, 1970). The commonly used CP correction has been found to be important for small basis sets, but not for larger basis sets, such as aug-cc-pVTZ (Feller, 1992; Dunn et al., 2004). For example, the BSSEs calculated with aug-cc-pVTZ basis set in the carboxylic acid–aldehyde complexes were smaller than 1.3 kJ mol^{-1}, which was about 1.8–3.2% to the total binding energies (Zhang and Du, 2016). In addition, geometry optimization calculations with B3LYP, M06-2X, ωB97X-D were also performed for comparison. In order to obtain explicit estimates of thermodynamic constants, two additional options: an extremely tight optimization convergence criteria (opt = verytight) and a very high accuracy grid integration (integral = ultrafine) were used in all optimization calculations. The calculations with these two options have been shown to give good frequencies and thermochemical corrections to the electronic energies for the hydrogen bonded complexes (Hansen et al., 2014a, b).

The topological analysis of the electron density, $\rho(r)$, and its Laplacian function, $\nabla^2\rho(r)$ constitute a powerful tool to investigate the nature of the chemical bonds (Parthasarathi et al., 2006; Lane et al., 2013). According to Bader theory, the presence of a bond critical point (BCP) is an indicator of the existence of a bonding interaction (Bader, 1991). Topological analysis of the charge density was carried out by utilizing the AIM2000 program package. The hydrogen bonding interactions were investigated using the localized molecular orbital energy decomposition analysis (LMO-EDA), which is implemented in the GAMESS (US) program (Schmidt et al., 1993). The total interaction energy (E^{INT}) is divided into electrostatic energy (E^{ES}), exchange energy (E^{EX}), repulsion energy (E^{REP}), polarization energy (E^{POL}) and dispersion energy (E^{DISP}) (Su and Li, 2009). However, the LMO-EDA analysis does not give the dispersion contribution to the net binding energy. The dispersion term in the LMO-EDA analysis is defined using the change in the correlation functionals on going from monomers to complexes (Su and Li, 2009). In fact, the dispersion term in LMO-EDA is "correlation energy". In order to be in line with LMO-EDA (Su and Li, 2009; Su et al., 2014), the term is still called as dispersion energy.