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# Interactions of sulfuric acid with common atmospheric bases and organic acids: Thermodynamics and implications to new particle formation

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## ABSTRACT

Interactions of the three common atmospheric bases, dimethylamine ((CH<sub>3</sub>)<sub>2</sub>NH), methylamine (CH<sub>3</sub>NH<sub>2</sub>), ammonia (NH<sub>3</sub>), all considered to be efficient stabilizers of binary clusters in the Earth's atmosphere, with H<sub>2</sub>SO<sub>4</sub>, the key atmospheric precursor, and 14 common atmospheric organic acids (COAs) (formic, acetic, oxalic, malonic, succinic, glutaric acid, adipic, benzoic, phenylacetic, pyruvic, maleic acid, malic, tartaric and pinonic acids) have been studied using the density functional theory (DFT) and composite high-accuracy G3MP2 method. The thermodynamic stability of mixed (COA)(H<sub>2</sub>SO<sub>4</sub>), (COA)(B1), (COA)(B2) and (COA)(B3) dimers and (COA)(H<sub>2</sub>SO<sub>4</sub>)(B1), (COA)(H<sub>2</sub>SO<sub>4</sub>)(B2) and (COA)(H<sub>2</sub>SO<sub>4</sub>)(B3) trimers, where B1, B2 and B3 refer to (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub> and NH<sub>3</sub>, respectively, have been investigated and their impacts on the thermodynamic stability of clusters containing H<sub>2</sub>SO<sub>4</sub> have been studied. Our investigation shows that interactions of H<sub>2</sub>SO<sub>4</sub> with COA, (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub> and NH<sub>3</sub> lead to the formation of more stable mixed dimers and trimers than (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> and (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>(base), respectively, and emphasize the importance of common organic species for early stages of atmospheric nucleation. We also show that although amines are generally confirmed to be more active than NH<sub>3</sub> as stabilizers of binary clusters, in some cases mixed trimers containing NH<sub>3</sub> are more stable thermodynamically than those containing CH<sub>3</sub>NH<sub>2</sub>. This study indicates an important role of COA, which coexist and interact with that H<sub>2</sub>SO<sub>4</sub> and common atmospheric bases in the Earth atmosphere, in formation of stable pre-nucleation clusters and suggests that the impacts of COA on new particle formation (NPF) should be studied in further details.

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## Introduction

The relevance of secondary aerosols formed in the Earth's atmosphere via nucleation to cloud properties, precipitation, global climate change and adverse public health impacts, including various respiratory and cardiovascular diseases and lung cancer, is well-established (Terzano et al., 2010; Zhang et al., 2012; Almeida et al., 2013; Dunn et al., 2016). Nucleation or new particle formation (NPF) is a key process largely controlling concentrations of cloud condensation nuclei (CCN) in the Earth's atmosphere and affecting the Earth's climate via indirect radiative effects (Kazil et al., 2010; Pierce and Adams, 2007; Wang and Penner, 2009; Yu and Luo, 2009; Almeida et al., 2013; Dunn et al., 2016; Yu et al., 2018). Origin and chemical composition of newly born atmospheric nanoparticles, as well as rates, at which

they are produced in the Earth's atmosphere, are the major sources of uncertainties in the assessment of the global climate change, global climate modeling, air quality modeling and health impacts of atmospheric aerosols (Zhang et al., 2010; Yu et al., 2012). The physics and chemistry of the secondary atmospheric aerosol formation is quite complex because atmospheric nucleation is a multicomponent process, which involves (unknown) stabilizing species in addition to sulfuric acid, the key atmospheric nucleation precursor, and water, the dominant constituent of condensable vapors in the Earth's atmosphere (e.g. Zhang et al., 2012).

NPF correlate well with measured concentrations of gaseous  $\text{H}_2\text{SO}_4$ . In particular, gaseous  $\text{H}_2\text{SO}_4$  in concentrations exceeding  $10^5$  molecules/cm<sup>3</sup> is needed in order to initiate in the Earth's atmosphere NPF (Zhang et al., 2012). However, binary sulfuric acid-water nucleation (BHN) can explain NPF in the clean free troposphere only. However, nucleation in the

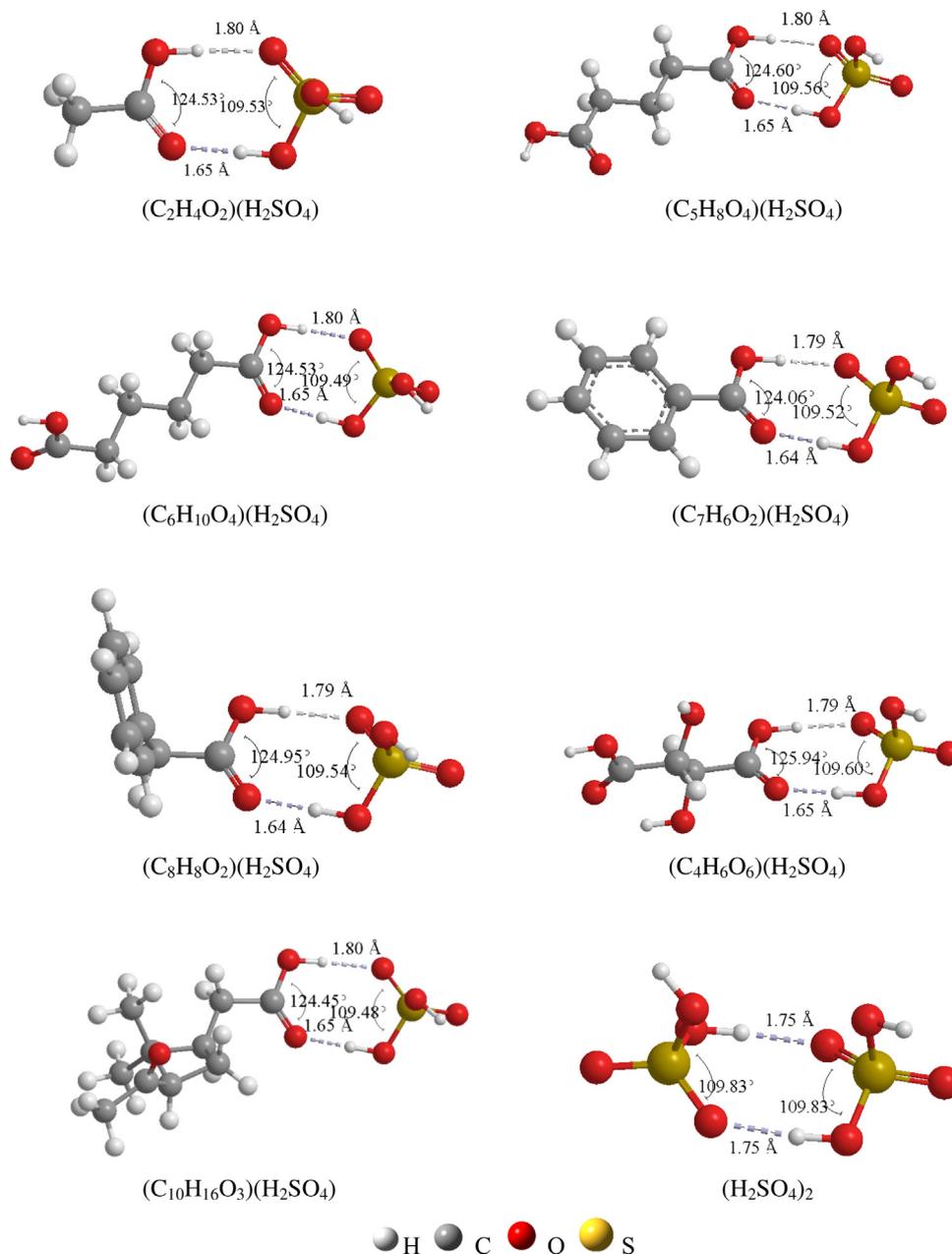
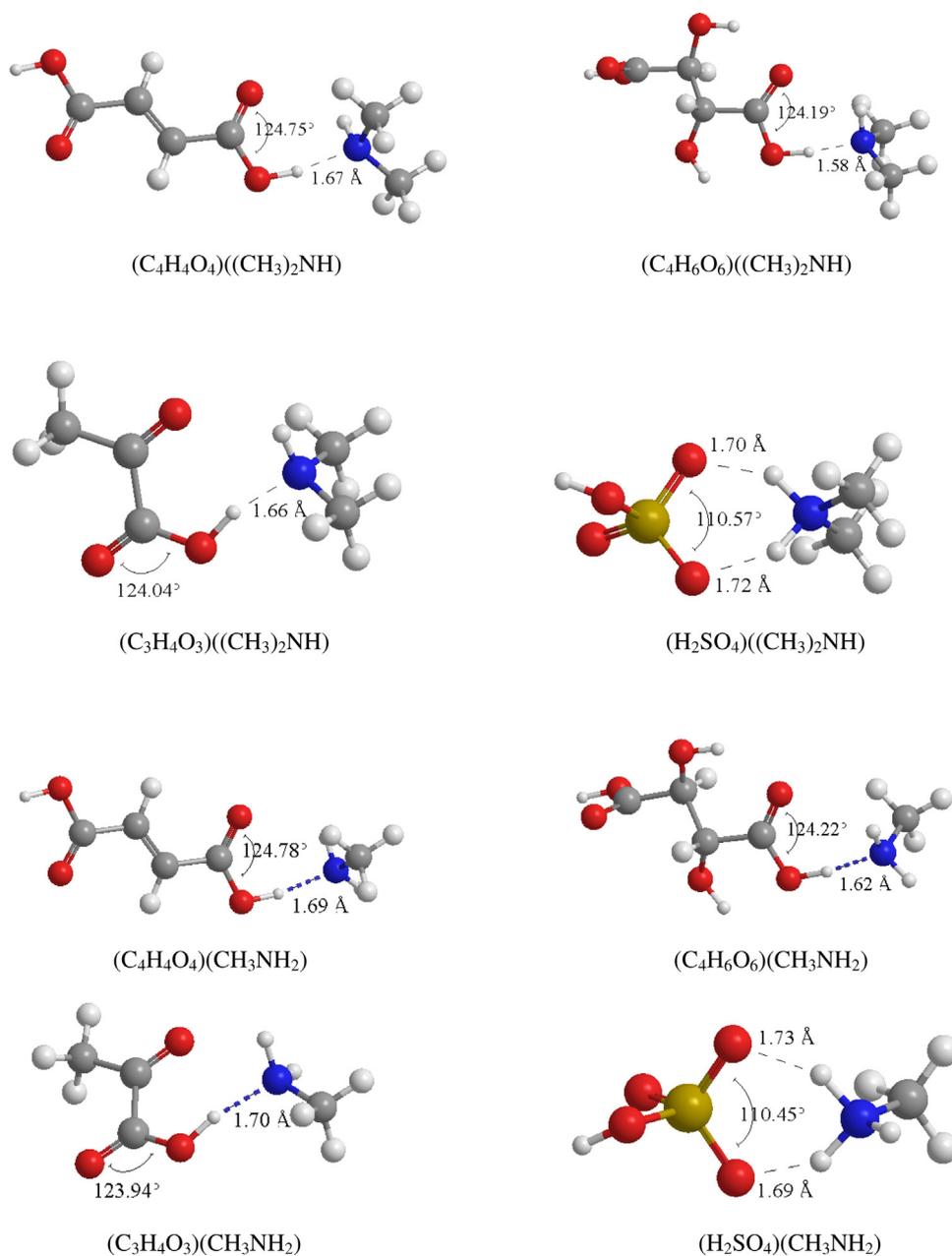


Fig. 1 – Equilibrium geometries of most stable isomers of hydrogen bonded complexes of common organic acids (COA) with  $\text{H}_2\text{SO}_4$  at G3MP2 level of theory. Bond lengths and bonding angles are given in angstrom (Å) and degree (°), respectively.

**Table 1 – Comparison of Gibbs free energy changes (kcal/mol) for the  $\text{H}_2\text{SO}_4 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)$ ,  $\text{H}_2\text{SO}_4 + \text{CH}_3\text{NH}_2 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{CH}_3\text{NH}_2)$  and  $\text{H}_2\text{SO}_4 + (\text{CH}_3)_2\text{NH} \rightleftharpoons (\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})$  reactions obtained using different high accuracy composite, ab initio and DFT methods and experimental data (Exp.).**

Reaction	G3MP2	G3	PW91PW91/6-311+G(3df,3pd)	Exp.
$\text{H}_2\text{SO}_4 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)$	-6.34	-7.14	-7.77 <sup>a</sup>	-8.5 <sup>b</sup>
$\text{H}_2\text{SO}_4 + \text{CH}_3\text{NH}_2 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{CH}_3\text{NH}_2)$	-9.95	-9.73	-11.03 <sup>a</sup>	–
$\text{H}_2\text{SO}_4 + (\text{CH}_3)_2\text{NH} \rightleftharpoons (\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})$	-13.11	-14.38	-11.38 <sup>a</sup>	–

<sup>a</sup> Nadykto et al., 2011;  
<sup>b</sup> Hanson and Eisele, 2002.



**Fig. 2 – Equilibrium geometries of most stable isomers of hydrogen bonded complexes of GOA with (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub> and NH<sub>3</sub> at G3MP2 level of theory. Bond lengths and bonding angles are given in angstrom (Å) and degree (°), respectively.**

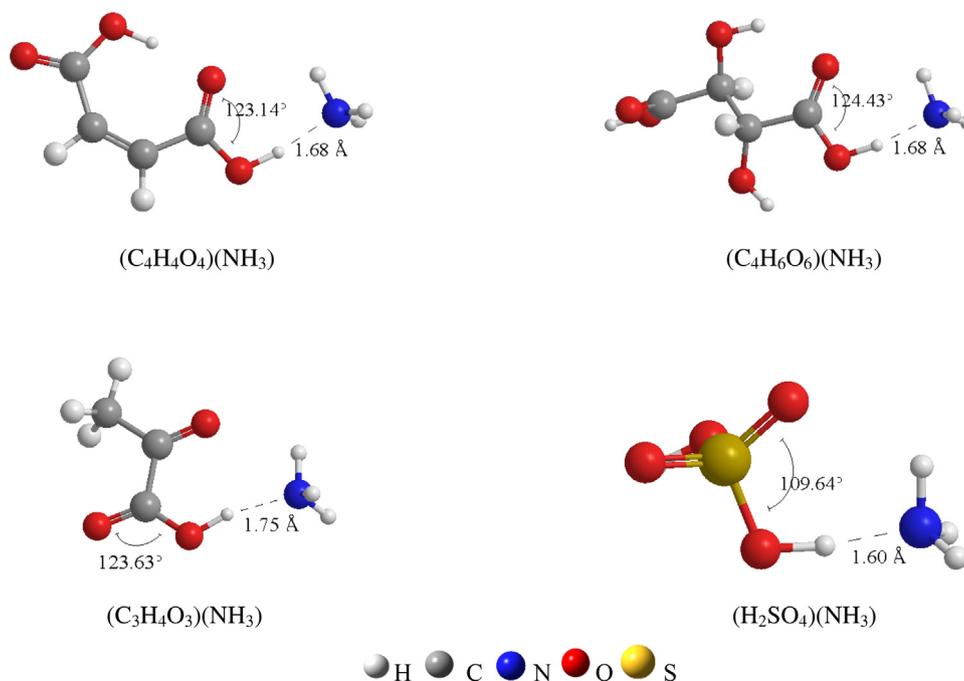


Fig. 2 – Continued

planetary boundary layer (PBL), where gaseous concentrations of pollutants such as sulfur dioxide, ammonia, various anthropogenic and biogenic volatile organic compounds are quite high may occur at much lower gaseous  $\text{H}_2\text{SO}_4$  concentration than in clean free atmosphere due to the involvement of gas-phase trace species acting as stabilizers of binary clusters enhancing concentrations of stable nucleating clusters formed via the gas-to-particle conversion.

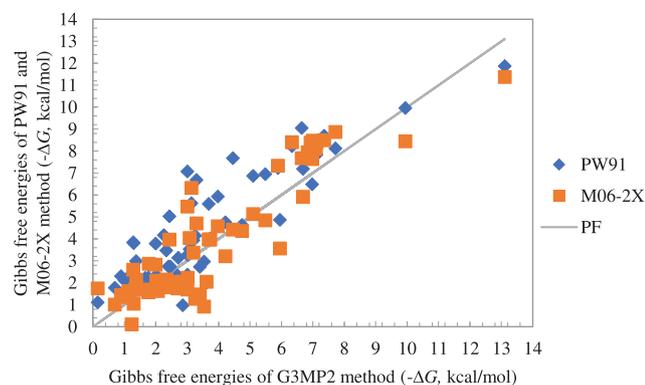
After several decades of research, a number of mechanisms of the gas-to-particle conversion in the Earth's atmosphere have been suggested and a number of species have been proposed as stabilizers/catalysts of the binary  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  nucleation. However, specific mechanisms of gas-to-particle conversion and chemical composition of nucleated particles is still remain a subject of ongoing debates (Kulmala et al., 2013; Nie et al., 2014; Zhang, 2010, 2012; Dunn et al., 2016; Yu et al., 2018). Ammonia, perhaps the most abundant base in the atmosphere, has been considered as a principle stabilizer of binary clusters since 1990s. However, it was discovered that the widely used ternary homogeneous nucleation (THN) theory (Napari et al., 2002) grossly overestimates nucleation rates and contains errors (Yu, 2006). While the original THN model has been successfully corrected, the revised THN rates appeared to be much lower than those predicted earlier. Newer models, which are based on more comprehensive THN thermodynamics derived from measurements and quantum-chemical calculations (e.g. Dunn et al., 2016; Yu et al. 2018), indicate that ammonia is likely a major contributor to NPF.

Other candidate mechanisms include ternary nucleation of amines with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  (ATHN) (Ortega et al., 2008; Loukonen et al., 2010; Nadykto et al., 2011), ion mediated nucleation (IMN) of  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$ -ion (Yu and Turco, 2000; Yu, 2006; Yu et al., 2012), nucleation of iodine-containing vapors (O'Dowd et al., 2002), and organics-enhanced nucleation (Zhang et al., 2004). Interaction of amines with sulfuric acid leads to the formation of very stable pre-nucleation clusters, and, thus, ATHN can play an important role in NPF. However, Nadykto et al. (2014, 2011) have shown that while amine- $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  clusters are obviously more stable than  $\text{NH}_3$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  competitors, the actual effect of amines on atmospheric nucleation strongly depends on ambient concen-

trations of amines. The concentrations of amines at certain sites in China and other countries with high pollution level can be as large as 7.2 pptV (Nanjing, Zheng et al., 2015) and 79.1 pptV (Shanghai, Yao et al., 2016), their values at the global scale are likely much smaller (e.g. Dunn et al., 2016; Zhang et al., 2012).

Although it is well-known that a large fraction of aerosol particles in the Earth's atmosphere contains organic species (Adachi and Buseck, 2008; Jung and Kawamura, 2011; Mäkelä et al., 2001; Nadykto and Yu, 2007; Sellegri et al., 2005; Smith et al., 2008; Sun and Ariya, 2006; Kürten et al., 2016; Schnitzhofer et al., 2014), the possible role of organic molecules in the atmospheric nucleation has long been underestimated or neglected. The importance of organic species in general and common organic acids in particular has been pointed out in the pioneering experiments of Zhang et al. (2004), where a considerable enhancement in nucleation rates due to the presence of organic acids has been observed. Nadykto and Yu (2007) and Xu et al. (2010) have shown that common atmospheric organics are capable of stabilizing small  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  clusters and thus, may promote NPF. Their conclusions have been confirmed in a number of more recent studies (e.g. Elm et al., 2017; Nadykto et al., 2018).

Benzoic, maleic, malic, pyruvic, phenylacetic, tartaric and other acids considered in this paper represent the common atmospheric organic species, which are present in the Earth's atmosphere due to the fossil fuel and biomass burning, vegetation and anthropogenic emissions from a few sources (Friedman et al., 2017; Mayol-Bracero et al., 2002; Pio et al., 2005) and are found in all the gas-phase, particulate matter and precipitation (Avery Jr. et al., 2006; Barsanti and Pankow, 2006; Hsieh et al., 2008; Huang et al., 2005). While the presence of the organic acids studied in the present paper in the atmospheric particulate matter and rainwater is well established, only a few in-situ measurements of gas-phase concentrations of these species are currently available (Friedman et al., 2017). The estimated atmospheric concentrations of these species are in the range of  $\sim 10^9$ - $10^{12}$   $\text{cm}^{-3}$  that is close to the typical range of atmospheric concentrations of  $\text{NH}_3$  and at least  $10^2$ - $10^4$  higher than typical concentrations of amines in the Earth's atmosphere.



**Fig. 3** – Comparison of calculated Gibbs free energies ( $-\Delta G$ ) given in Tables 2 and 3 predicted using G3MP2 method (baseline) and DFT PW91PW91/6-311++G(3df,3pd) (PW91) and M062X/6-311++G(3df,3pd) (M06-2X) methods. PF denotes a perfect fit.

The main problem in understanding how particles are nucleating in the Earth's atmosphere is the lack of the experimental data and methods, which are sensitive enough to follow the first steps of particle formation. Today, valuable information on the thermodynamics of first nucleation steps can be obtained using quantum-chemical methods, which in contrast to still widely used bulk liquid/capillarity approximation are capable of accounting for the actual chemical identities of nucleating species and are sensitive enough to predict first nucleation steps (Ortega, et al., 2008; Xu et al., 2010; Loukonen et al., 2010; Elm et al., 2017; Almeida et al., 2013; Nadykto et al., 2004, 2014, 2018; Nadykto and Yu, 2007)

In the present paper, interactions of 14 common atmospheric organic acids (formic ( $\text{CH}_2\text{O}_2$ ), acetic ( $\text{C}_2\text{H}_4\text{O}_2$ ), oxalic ( $\text{C}_2\text{H}_2\text{O}_4$ ), malonic ( $\text{C}_3\text{H}_4\text{O}_4$ ), succinic ( $\text{C}_4\text{H}_6\text{O}_4$ ), glutaric acid ( $\text{C}_5\text{H}_8\text{O}_4$ ), adipic ( $\text{C}_6\text{H}_{10}\text{O}_4$ ), benzoic ( $\text{C}_6\text{H}_5\text{COOH}$ ), phenylacetic ( $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ), pyruvic ( $\text{C}_3\text{H}_4\text{O}_3$ ), maleic acid ( $\text{C}_4\text{H}_4\text{O}_4$ ), malic ( $\text{C}_4\text{H}_6\text{O}_5$ ), tartaric ( $\text{C}_4\text{H}_6\text{O}_6$ ) and pinonic acid ( $\text{C}_{10}\text{H}_{16}\text{O}_3$ )) with methylamine  $\text{CH}_3\text{NH}_2$ , dimethylamine ( $(\text{CH}_3)_2\text{NH}_2$ ) and ammonia, important catalysts of BHN in the Earth's atmosphere, and  $\text{H}_2\text{SO}_4$ , the key atmospheric precursor, have been studied using DFT and high-accuracy G3MP2 composite method. The formation of mixed dimers and trimers containing  $\text{H}_2\text{SO}_4$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$  and 14 common atmospheric organic acids has been investigated and enthalpy, entropy and stepwise Gibbs free energy changes, key properties controlling NPF thermochemistry, have been calculated. The thermochemical analysis of cluster formation, which was focused on impacts of organic acids on cluster stability, has been carried out and atmospheric implications of the obtained results have been discussed.

## 1. Methods

In order to ensure the quality of the conformational sampling, a comprehensive conformational search has been carried out using the basin hopping algorithm, as implemented in Biovia Materials Studio 8.0 (Dassault Systèmes BIOVIA, 2013) and our own conformational search machine, which is based on the mesh created around clusters, with molecules to be attached to the cluster being placed in the mesh nodes, and blind search algorithm. The number of initial/guess geome-

**Table 2** – Enthalpy ( $\Delta H$ ) and Gibbs free energy changes ( $\Delta G$ ) of the formation of mixed dimers consisting of  $\text{H}_2\text{SO}_4$  and COA at temperature of 298.15 K and pressure of 101.3 KPa.

Reaction	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{H}_2\text{SO}_4)_2$	-17.11 <sup>a</sup> -16.30 <sup>b</sup> -18.02 <sup>c</sup>	<b>-6.98<sup>a</sup></b> -6.48 <sup>b</sup> -7.77 <sup>c</sup>
$\text{CH}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{CH}_2\text{O}_2)(\text{H}_2\text{SO}_4)$	-16.19 <sup>a</sup> -18.02 <sup>b</sup> -17.76 <sup>c</sup>	<b>-5.89<sup>a</sup></b> -7.23 <sup>b</sup> -7.33 <sup>c</sup>
$\text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_2\text{H}_4\text{O}_2)(\text{H}_2\text{SO}_4)$	-17.14 <sup>a</sup> -19.05 <sup>b</sup> -18.79 <sup>c</sup>	<b>-6.95<sup>a</sup></b> -8.18 <sup>b</sup> -8.29 <sup>c</sup>
$\text{C}_2\text{H}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_2\text{H}_2\text{O}_4)(\text{H}_2\text{SO}_4)$	-12.71 <sup>a</sup> -12.95 <sup>b</sup> -13.30 <sup>c</sup>	-3.08 <sup>a</sup> -3.53 <sup>b</sup> -4.04 <sup>c</sup>
$\text{C}_3\text{H}_4\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_3\text{H}_4\text{O}_4)(\text{H}_2\text{SO}_4)$	-18.82 <sup>a</sup> -18.39 <sup>b</sup> -20.26 <sup>c</sup>	<b>-6.74<sup>a</sup></b> -7.66 <sup>b</sup> -8.14 <sup>c</sup>
$\text{C}_4\text{H}_6\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_4\text{H}_6\text{O}_4)(\text{H}_2\text{SO}_4)$	-16.89 <sup>a</sup> -17.97 <sup>b</sup> -18.13 <sup>c</sup>	<b>-6.65<sup>a</sup></b> -9.05 <sup>b</sup> -7.67 <sup>c</sup>
$\text{C}_5\text{H}_8\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_5\text{H}_8\text{O}_4)(\text{H}_2\text{SO}_4)$	-17.24 <sup>a</sup> -18.96 <sup>b</sup> -18.73 <sup>c</sup>	<b>-6.93<sup>a</sup></b> -7.73 <sup>b</sup> -8.38 <sup>c</sup>
$\text{C}_6\text{H}_{10}\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_6\text{H}_{10}\text{O}_4)(\text{H}_2\text{SO}_4)$	-18.14 <sup>a</sup> -18.94 <sup>b</sup> -19.74 <sup>c</sup>	<b>-7.72<sup>a</sup></b> -8.12 <sup>b</sup> -8.87 <sup>c</sup>
$\text{C}_7\text{H}_6\text{O}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_7\text{H}_6\text{O}_2)(\text{H}_2\text{SO}_4)$	-17.70 <sup>a</sup> -19.58 <sup>b</sup> -19.19 <sup>c</sup>	<b>-7.36<sup>a</sup></b> -8.69 <sup>b</sup> -8.49 <sup>c</sup>
$\text{C}_8\text{H}_8\text{O}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_8\text{H}_8\text{O}_2)(\text{H}_2\text{SO}_4)$	-17.39 <sup>a</sup> -19.22 <sup>b</sup> -18.78 <sup>c</sup>	<b>-7.10<sup>a</sup></b> -8.44 <sup>b</sup> -8.11 <sup>c</sup>
$\text{C}_3\text{H}_4\text{O}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_3\text{H}_4\text{O}_3)(\text{H}_2\text{SO}_4)$	-11.92 <sup>a</sup> -10.29 <sup>b</sup> -11.86 <sup>c</sup>	-2.86 <sup>a</sup> -0.97 <sup>b</sup> -2.04 <sup>c</sup>
$\text{C}_4\text{H}_4\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{SO}_4)$	-14.12 <sup>a</sup> -14.43 <sup>b</sup> -14.22 <sup>c</sup>	-4.75 <sup>a</sup> -4.63 <sup>b</sup> -4.36 <sup>c</sup>
$\text{C}_4\text{H}_6\text{O}_5 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_4\text{H}_6\text{O}_5)(\text{H}_2\text{SO}_4)$	-16.81 <sup>a</sup> -18.56 <sup>b</sup> -19.02 <sup>c</sup>	<b>-7.00<sup>a</sup></b> -7.86 <sup>b</sup> -8.47 <sup>c</sup>
$\text{C}_4\text{H}_6\text{O}_6 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_4\text{H}_6\text{O}_6)(\text{H}_2\text{SO}_4)$	-17.20 <sup>a</sup> -18.81 <sup>b</sup> -18.49 <sup>c</sup>	<b>-6.84<sup>a</sup></b> -7.81 <sup>b</sup> -7.95 <sup>c</sup>
$\text{C}_{10}\text{H}_{16}\text{O}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{C}_{10}\text{H}_{16}\text{O}_3)(\text{H}_2\text{SO}_4)$	-17.38 <sup>a</sup> -18.71 <sup>b</sup> -18.08 <sup>c</sup>	<b>-7.12<sup>a</sup></b> -7.84 <sup>b</sup> -8.39 <sup>c</sup>

Reactions shown in bold leading to the formation of mixed dimers are more stable thermodynamically than  $(\text{H}_2\text{SO}_4)_2$ .

$\text{CH}_2\text{O}_2$ : formic acid;  $\text{C}_2\text{H}_4\text{O}_2$ : acetic acid;  $\text{C}_2\text{H}_2\text{O}_4$ : oxalic acid;  $\text{C}_3\text{H}_4\text{O}_4$ : malonic acid;  $\text{C}_4\text{H}_6\text{O}_4$ : succinic acid;  $\text{C}_5\text{H}_8\text{O}_4$ : glutaric acid;  $\text{C}_6\text{H}_{10}\text{O}_4$ : adipic acid;  $\text{C}_6\text{H}_5\text{COOH}$ : benzoic acid;  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ : phenylacetic acid;  $\text{C}_3\text{H}_4\text{O}_3$ : pyruvic acid;  $\text{C}_4\text{H}_4\text{O}_4$ : maleic acid;  $\text{C}_4\text{H}_6\text{O}_5$ : malic acid;  $\text{C}_4\text{H}_6\text{O}_6$ : tartaric acid;  $\text{C}_{10}\text{H}_{16}\text{O}_3$ : pinonic acid.

<sup>a</sup> G3MP2 method;

<sup>b</sup> PW91PW91/6-311++G(3df,3pd) method;

<sup>c</sup> M06-2X/6-311++G(3df,3pd) method.

**Table 3 – Enthalpy and Gibbs free energy changes of the formation of mixed dimers consisting of (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>3</sub> and COA at temperature of 298.15 K and pressure of 101.3 KPa.**

Reaction	$\Delta H$ (kcal/mol) (X=(CH <sub>3</sub> ) <sub>2</sub> NH)	$\Delta G$ (kcal/mol) (X=(CH <sub>3</sub> ) <sub>2</sub> NH)	$\Delta H$ (kcal/mol) (X=CH <sub>3</sub> NH <sub>2</sub> )	$\Delta G$ (kcal/mol) (X=CH <sub>3</sub> NH <sub>2</sub> )	$\Delta H$ (kcal/mol) (X=NH <sub>3</sub> )	$\Delta G$ (kcal/mol) (X=NH <sub>3</sub> )
CH <sub>2</sub> O <sub>2</sub> + X ⇌ (CH <sub>2</sub> O <sub>2</sub> )(X)	-11.55 <sup>a</sup> -13.45 <sup>b</sup> -13.56 <sup>c</sup>	-3.20 <sup>a</sup> -3.93 <sup>b</sup> -3.37 <sup>c</sup>	-10.90 <sup>a</sup> -13.01 <sup>b</sup> -12.35 <sup>c</sup>	-2.34 <sup>a</sup> -3.47 <sup>b</sup> -2.15 <sup>c</sup>	-9.41 <sup>a</sup> -11.79 <sup>b</sup> -10.81 <sup>c</sup>	-1.38 <sup>a</sup> -2.98 <sup>b</sup> -2.14 <sup>c</sup>
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + X ⇌ (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )(X)	-11.04 <sup>a</sup> -12.42 <sup>b</sup> -12.69 <sup>c</sup>	-2.72 <sup>a</sup> -3.14 <sup>b</sup> -2.04 <sup>c</sup>	-10.34 <sup>a</sup> -12.03 <sup>b</sup> -11.63 <sup>c</sup>	-1.77 <sup>a</sup> -2.24 <sup>b</sup> -1.57 <sup>c</sup>	-8.95 <sup>a</sup> -10.95 <sup>b</sup> -10.20 <sup>c</sup>	-0.90 <sup>a</sup> -2.30 <sup>b</sup> -1.44 <sup>c</sup>
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> + X ⇌ (C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> )(X)	-12.91 <sup>a</sup> -17.27 <sup>b</sup> -15.73 <sup>c</sup>	-3.01 <sup>a</sup> -7.07 <sup>b</sup> -5.47 <sup>c</sup>	-12.39 <sup>a</sup> -16.19 <sup>b</sup> -14.64 <sup>c</sup>	-3.30 <sup>a</sup> -6.68 <sup>b</sup> -4.70 <sup>c</sup>	-10.31 <sup>a</sup> -13.86 <sup>b</sup> -12.21 <sup>c</sup>	-2.44 <sup>a</sup> -5.03 <sup>b</sup> -3.96 <sup>c</sup>
C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> + X ⇌ (C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> )(X)	-12.1 <sup>a</sup> -14.15 <sup>b</sup> -15.59 <sup>c</sup>	-4.22 <sup>a</sup> -4.75 <sup>b</sup> -3.21 <sup>c</sup>	-13.06 <sup>a</sup> -17.69 <sup>b</sup> -15.08 <sup>c</sup>	-4.46 <sup>a</sup> -7.67 <sup>b</sup> -4.42 <sup>c</sup>	-10.07 <sup>a</sup> -12.22 <sup>b</sup> -11.39 <sup>c</sup>	-2.00 <sup>a</sup> -3.78 <sup>b</sup> -2.82 <sup>c</sup>
C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> + X ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> )(X)	-11.52 <sup>a</sup> -12.40 <sup>b</sup> -12.24 <sup>c</sup>	-3.26 <sup>a</sup> -4.15 <sup>b</sup> -1.27 <sup>c</sup>	-10.76 <sup>a</sup> -11.99 <sup>b</sup> -11.90 <sup>c</sup>	-2.26 <sup>a</sup> -4.17 <sup>b</sup> -1.88 <sup>c</sup>	-9.27 <sup>a</sup> -10.84 <sup>b</sup> -11.16 <sup>c</sup>	-1.30 <sup>a</sup> -3.80 <sup>b</sup> -1.04 <sup>c</sup>
C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> + X ⇌ (C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> )(X)	-11.34 <sup>a</sup> -12.75 <sup>b</sup> -12.24 <sup>c</sup>	-3.02 <sup>a</sup> -3.27 <sup>b</sup> -2.23 <sup>c</sup>	-10.64 <sup>a</sup> -12.36 <sup>b</sup> -11.92 <sup>c</sup>	-2.07 <sup>a</sup> -2.10 <sup>b</sup> -1.62 <sup>c</sup>	-9.18 <sup>a</sup> -11.24 <sup>b</sup> -10.42 <sup>c</sup>	-1.13 <sup>a</sup> -2.26 <sup>b</sup> -1.62 <sup>c</sup>
C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> + X ⇌ (C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> )(X)	-12.12 <sup>a</sup> -13.12 <sup>b</sup> -14.36 <sup>c</sup>	-3.62 <sup>a</sup> -2.00 <sup>b</sup> -2.04 <sup>c</sup>	-11.41 <sup>a</sup> -12.12 <sup>b</sup> -11.71 <sup>c</sup>	-2.69 <sup>a</sup> -2.34 <sup>b</sup> -1.74 <sup>c</sup>	-9.97 <sup>a</sup> -11.04 <sup>b</sup> -11.43 <sup>c</sup>	-1.78 <sup>a</sup> -2.80 <sup>b</sup> -2.86 <sup>c</sup>
C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> + X ⇌ (C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> )(X)	-11.77 <sup>a</sup> -12.81 <sup>b</sup> -12.59 <sup>c</sup>	-3.54 <sup>a</sup> -2.96 <sup>b</sup> -0.91 <sup>c</sup>	-10.98 <sup>a</sup> -12.40 <sup>b</sup> -12.05 <sup>c</sup>	-2.47 <sup>a</sup> -2.73 <sup>b</sup> -1.98 <sup>c</sup>	-9.42 <sup>a</sup> -11.25 <sup>b</sup> -10.54 <sup>c</sup>	-1.36 <sup>a</sup> -2.25 <sup>b</sup> -1.69 <sup>c</sup>
C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> + X ⇌ (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )(X)	-11.58 <sup>a</sup> -12.90 <sup>b</sup> -12.17 <sup>c</sup>	-3.41 <sup>a</sup> -2.72 <sup>b</sup> -1.47 <sup>c</sup>	-10.79 <sup>a</sup> -12.45 <sup>b</sup> -11.87 <sup>c</sup>	-2.41 <sup>a</sup> -2.74 <sup>b</sup> -1.79 <sup>c</sup>	-9.10 <sup>a</sup> -11.30 <sup>b</sup> -10.83 <sup>c</sup>	-1.24 <sup>a</sup> -2.22 <sup>b</sup> -0.10 <sup>c</sup>
C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> + X ⇌ (C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> )(X)	-10.27 <sup>a</sup> -11.26 <sup>b</sup> -10.88 <sup>c</sup>	-1.67 <sup>a</sup> -2.22 <sup>b</sup> -1.69 <sup>c</sup>	-9.22 <sup>a</sup> -10.66 <sup>b</sup> -10.15 <sup>c</sup>	-0.70 <sup>a</sup> -1.77 <sup>b</sup> -1.00 <sup>c</sup>	-7.46 <sup>a</sup> -9.23 <sup>b</sup> -8.39 <sup>c</sup>	-0.16 <sup>a</sup> -1.10 <sup>b</sup> -1.74 <sup>c</sup>
C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> + X ⇌ (C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> )(X)	-14.54 <sup>a</sup> -16.80 <sup>b</sup> -16.43 <sup>c</sup>	-6.69 <sup>a</sup> -7.19 <sup>b</sup> -5.91 <sup>c</sup>	-11.59 <sup>a</sup> -14.51 <sup>b</sup> -15.75 <sup>c</sup>	-3.14 <sup>a</sup> -5.62 <sup>b</sup> -6.32 <sup>c</sup>	-11.65 <sup>a</sup> -14.32 <sup>b</sup> -13.01 <sup>c</sup>	-3.69 <sup>a</sup> -5.59 <sup>b</sup> -3.97 <sup>c</sup>
C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> + X ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> )(X)	-14.71 <sup>a</sup> -14.30 <sup>b</sup> -13.87 <sup>c</sup>	-5.96 <sup>a</sup> -4.86 <sup>b</sup> -3.56 <sup>c</sup>	-8.86 <sup>a</sup> -13.49 <sup>b</sup> -12.68 <sup>c</sup>	-1.29 <sup>a</sup> -3.84 <sup>b</sup> -2.59 <sup>c</sup>	-12.23 <sup>a</sup> -12.58 <sup>b</sup> -13.18 <sup>c</sup>	-3.74 <sup>a</sup> -4.01 <sup>b</sup> -3.96 <sup>c</sup>
C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> + X ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> )(X)	-14.71 <sup>a</sup> -17.93 <sup>b</sup> -15.88 <sup>c</sup>	-5.10 <sup>a</sup> -6.86 <sup>b</sup> -5.13 <sup>c</sup>	-14.03 <sup>a</sup> -17.30 <sup>b</sup> -15.35 <sup>c</sup>	-5.49 <sup>a</sup> -6.95 <sup>b</sup> -4.84 <sup>c</sup>	-12.00 <sup>a</sup> -15.48 <sup>b</sup> -13.42 <sup>c</sup>	-3.98 <sup>a</sup> -5.93 <sup>b</sup> -4.57 <sup>c</sup>
C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> + X ⇌ (C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> )(X)	-11.31 <sup>a</sup> -12.45 <sup>b</sup> -11.95 <sup>c</sup>	-3.01 <sup>a</sup> -2.37 <sup>b</sup> -1.69 <sup>c</sup>	-10.56 <sup>a</sup> -12.05 <sup>b</sup> -11.68 <sup>c</sup>	-2.02 <sup>a</sup> -2.39 <sup>b</sup> -2.09 <sup>c</sup>	-9.04 <sup>a</sup> -10.94 <sup>b</sup> -10.11 <sup>c</sup>	-1.01 <sup>a</sup> -2.10 <sup>b</sup> -1.35 <sup>c</sup>
H <sub>2</sub> SO <sub>4</sub> + X ⇌ (H <sub>2</sub> SO <sub>4</sub> )(X)	-21.93 <sup>a</sup> -21.43 <sup>b</sup> -21.32 <sup>c</sup>	-13.11 <sup>a</sup> -11.87 <sup>b</sup> -11.37 <sup>c</sup>	-19.04 <sup>a</sup> -19.20 <sup>b</sup> -18.85 <sup>c</sup>	-9.95 <sup>a</sup> -9.96 <sup>b</sup> -8.44 <sup>c</sup>	-14.45 <sup>a</sup> -16.73 <sup>b</sup> -16.28 <sup>c</sup>	-6.34 <sup>a</sup> -8.22 <sup>b</sup> -8.40 <sup>c</sup>

<sup>a</sup> G3MP2 method;<sup>b</sup> PW91PW91/6-311++G(3df,3pd) method;<sup>c</sup> M06-2X/6-311++G(3df,3pd) method.

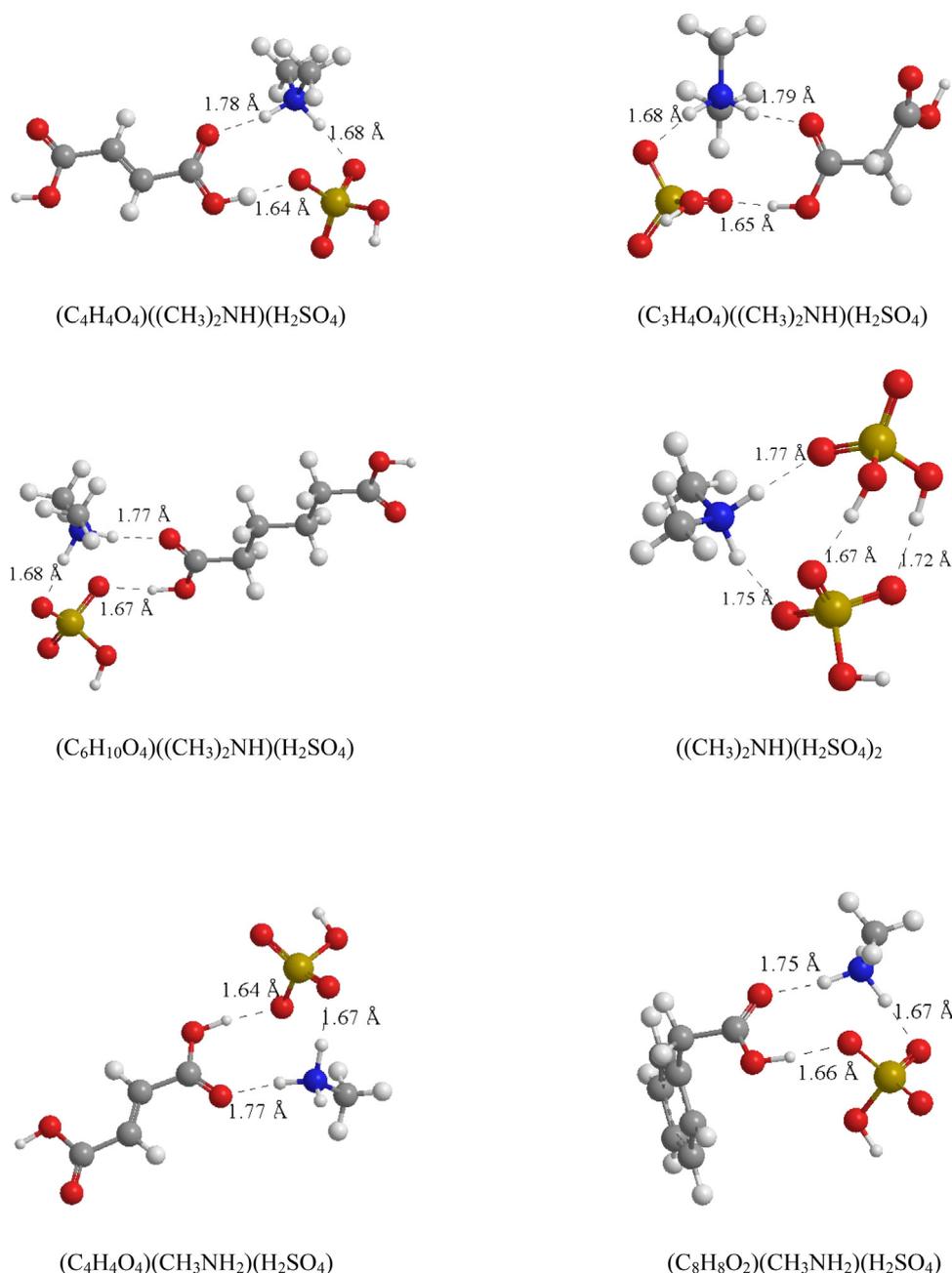
tries for each cluster class varied depending on the cluster size from 150 to 200 to ~1000. The initial geometries were treated using the semi-empirical PM6 method first. The most stable isomers located within 15 kcal/mol of the intermediate global minimum of the Gibbs free energy were re-optimized with PW91PW91/CBSB7 method. Most stable isomers located within 5 kcal/mol of the intermediate global minimum at the PW91PW91/CBSB7 level of theory were optimized using G3MP2 and DFT PW91PW91/6-311 + G(3df,3pd) and M06-2X/6-

311 + G(3df,3pd) methods to obtain the final results. Cartesian geometries of most stable isomers of clusters being studied here are included in Appendix A. Supplementary data. The computations have been carried out using Gaussian 09 suite of programs (Frisch et al., 2009).

Table 1 shows that G3MP2 data for the H<sub>2</sub>SO<sub>4</sub> + NH<sub>3</sub> ⇌ (H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>), H<sub>2</sub>SO<sub>4</sub> + CH<sub>3</sub>NH<sub>2</sub> ⇌ (H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) and H<sub>2</sub>SO<sub>4</sub> + (CH<sub>3</sub>)<sub>2</sub>NH ⇌ (H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH) reactions are in a reasonable agreement with experimental data and DFT

**Table 4 – Enthalpy and Gibbs free energy changes of the formation of mixed trimers consisting of H<sub>2</sub>SO<sub>4</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>3</sub> and COA at temperature of 298.15 K and pressure of 101.3 KPa at G3MP2 level of theory.**

Reaction	$\Delta H$ (kcal/mol) (X=(CH <sub>3</sub> ) <sub>2</sub> NH)	$\Delta G$ (kcal/mol) (X=(CH <sub>3</sub> ) <sub>2</sub> NH)	$\Delta H$ (kcal/mol) (X=CH <sub>3</sub> NH <sub>2</sub> )	$\Delta G$ (kcal/mol) (X=CH <sub>3</sub> NH <sub>2</sub> )	$\Delta H$ (kcal/mol) (X=NH <sub>3</sub> )	$\Delta G$ (kcal/mol) (X=NH <sub>3</sub> )
CH <sub>2</sub> O <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (CH <sub>2</sub> O <sub>2</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.14	-8.91	-20.95	-11.05	-17.95	-8.06
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.31	-9.18	-19.30	-8.26	-18.24	-8.45
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-18.17	-8.14	-17.57	-8.96	-12.96	-3.30
C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-21.29	-10.11	-20.90	-11.50	-18.34	-8.67
C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.36	-9.22	-18.98	-8.05	-17.98	-8.13
C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.94	-9.64	-21.76	-11.86	-18.70	-8.74
C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-21.22	-9.91	-21.13	-11.22	-19.07	-9.05
C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-17.88	-7.54	-19.93	-8.79	-17.37	-7.04
C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.84	-9.64	-21.72	-11.96	-17.06	-6.85
C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-18.25	-7.83	-16.76	-6.24	-14.22	-3.48
C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-24.11	-13.39	-22.83	-12.16	-21.57	-12.13
C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.18	-9.01	-18.83	-7.68	-16.35	-6.32
C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-21.08	-9.75	-19.69	-8.67	-17.42	-5.92
C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> )(H <sub>2</sub> SO <sub>4</sub> )(X)	-20.49	-9.33	-19.21	-8.20	-17.12	-6.87
H <sub>2</sub> SO <sub>4</sub> + (H <sub>2</sub> SO <sub>4</sub> )(X) ⇌ (H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> (X)	-27.99	-14.76	-30.91	-17.82	-28.27	-14.94



**Fig. 4 – Equilibrium geometries of most stable isomers of mixed (COA)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH), (COA)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) and (COA)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) trimers at G3MP2 level of theory. Bond lengths and bonding angles are given in angstrom (Å) and degree (°), respectively.**

PW91PW91/6-311+G(3df,3pd) method widely used in the atmospheric nucleation studies

## 2. Results and discussion

Fig. 1 and Table 2 present the equilibrium geometries of the most stable isomers of mixed sulfuric acid-COA dimers and enthalpies and Gibbs free energy changes of COA + H<sub>2</sub>SO<sub>4</sub> ⇌ (COA)(H<sub>2</sub>SO<sub>4</sub>) reactions, respectively.

As it may be seen from Fig. 1, in most cases the intermolecular OH-bonds in (H<sub>2</sub>SO<sub>4</sub>)-COA complexes are very close

to those in the (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>. In most cases bonds in (H<sub>2</sub>SO<sub>4</sub>)-COA are ~4%-6% shorter than those in (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>, indicating that (H<sub>2</sub>SO<sub>4</sub>)-COA complexes are as stable as or more stable than the sulfuric acid dimer. The comparison of the thermochemical data in Table 2 fully confirms the above-mentioned conclusion. In particular, the dimerization free energies of (COA)(H<sub>2</sub>SO<sub>4</sub>) are within ~1 kcal/mol of that of the (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> formation, with the exceptions for the oxalic (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>), maleic (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) and pyruvic acid (C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>). Although a difference in the thermodynamic stability in the favor of (H<sub>2</sub>SO<sub>4</sub>)-COA clusters compared to (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> is relatively small and does not exceed 1 kcal/mol in all the cases studied here, (COA)(H<sub>2</sub>SO<sub>4</sub>)

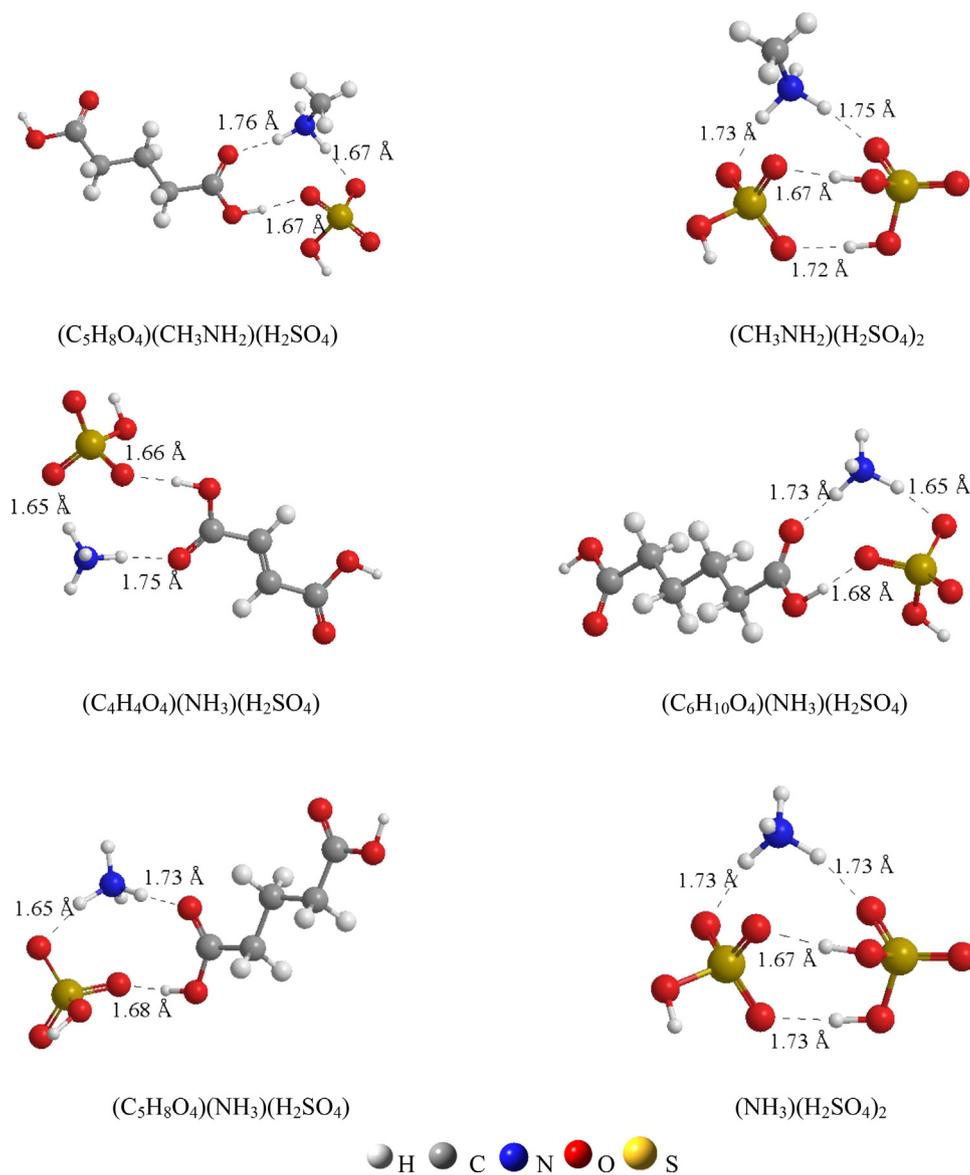


Fig. 4 – Continued

are much more abundant than (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> under typical atmospheric conditions due much larger atmospheric concentrations of COA compared to H<sub>2</sub>SO<sub>4</sub>.

As seen from Table 2, DFT PW91PW91 and M06-2X calculations and composite high accuracy G3MP2 data lead to identical conclusions about the enhanced stability of dimers containing sulfuric acid due to the presence of organic acids and the abundance of mixed dimers in the Earth's atmosphere.

Fig. 2 and Table 3 show the equilibrium geometries of the most stable isomers of mixed (CH<sub>3</sub>)<sub>2</sub>NH-COA, CH<sub>3</sub>NH<sub>2</sub>-COA and NH<sub>3</sub>-COA dimers and enthalpies and Gibbs free energy changes of COA + (CH<sub>3</sub>)<sub>2</sub>NH ⇌ (COA)((CH<sub>3</sub>)<sub>2</sub>NH), COA + CH<sub>3</sub>NH<sub>2</sub> ⇌ (COA)(CH<sub>3</sub>NH<sub>2</sub>) and COA + NH<sub>3</sub> ⇌ (COA)(NH<sub>3</sub>) reactions, respectively.

As it may be seen from Fig. 2, the intermolecular OH-bonds in (CH<sub>3</sub>)<sub>2</sub>NH-COA and CH<sub>3</sub>NH<sub>2</sub>-COA complexes are considerably shorter than those in the (CH<sub>3</sub>)<sub>2</sub>NH-H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>NH<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> dimers, while the OH-bonds in NH<sub>3</sub>-COA complexes are longer than those in the NH<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>. However, it is worth not-

ing that two OH-bonds are formed both in (CH<sub>3</sub>)<sub>2</sub>NH-H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>NH<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> dimers. This is a clear indication that the stability of (CH<sub>3</sub>)<sub>2</sub>NH-COA, CH<sub>3</sub>NH<sub>2</sub>-COA and NH<sub>3</sub>-COA complexes is not as high as that of the H<sub>2</sub>SO<sub>4</sub>-base dimers. The comparison of the thermochemical data presented in Table 3 shows clearly that none of the (CH<sub>3</sub>)<sub>2</sub>NH-COA, CH<sub>3</sub>NH<sub>2</sub>-COA and NH<sub>3</sub>-COA complexes are nearly as stable as H<sub>2</sub>SO<sub>4</sub>-base dimers. This indicates that in most cases organic acids considered in the present study are likely incapable of “self-nucleation” even if such efficient stabilizers as (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub> and NH<sub>3</sub> are present in the nucleating vapor mixture and that the possible role of these COA is likely limited to stabilization of binary and, possibly, ternary clusters because a very large difference in the thermochemical stability between (COA)(X) and (H<sub>2</sub>SO<sub>4</sub>)(X), where X = (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>3</sub>, cannot be offset by the  $\frac{[\text{COA}]}{[\text{H}_2\text{SO}_4]}$  concentration ratios < 10<sup>6</sup> translated into ~6.82 kcal/mol difference in the Gibbs free energy at T = 298.15 K.

As seen from Fig. 3, DFT PW91PW91/6-311++G(3df,3pd) and M06-2X/6-311++G(3df,3pd) methods agree with G3MP2 within  $\sim 1.5$  kcal/mol on average. Although the deviation of M06-2X from G3MP2 is a little bit smaller than that of PW91PW91, both DFT methods are in agreement with G3MP2.

Fig. 4 and Table 4 present equilibrium geometries of most stable isomers of mixed (COA)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH), (COA)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) and (COA)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) trimers, and enthalpy and Gibbs free energy changes associated with their formation.

As it may be seen from Table 4, a few organic acids studied here could possibly serve as a replacement of H<sub>2</sub>SO<sub>4</sub> in the formation of mixed (COA)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH), (COA)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) and (COA)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) trimers. While the Gibbs free energies of CH<sub>2</sub>O<sub>2</sub> + (H<sub>2</sub>SO<sub>4</sub>)(X)  $\rightleftharpoons$  (CH<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(X) reactions, where X = (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>3</sub>, are not as high as those of H<sub>2</sub>SO<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub>)(X)  $\rightleftharpoons$  (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>(X), the difference in atmospheric concentrations of COA and H<sub>2</sub>SO<sub>4</sub> could probably make [(C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH)], [(CH<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)], [(C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)], [(C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)], [(C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)], [(C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)], [(CH<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)], [(C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)], [(C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)], [(C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)], [(C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)], [(C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)] comparable to [(H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>((CH<sub>3</sub>)<sub>2</sub>NH)], [(H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>(CH<sub>3</sub>NH<sub>2</sub>)] and [(H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>(NH<sub>3</sub>)]. Another interesting observation is that the replacement of NH<sub>3</sub> with CH<sub>3</sub>NH<sub>2</sub>, a more efficient BHN stabilizer, does not necessarily lead to a great enhancement in the cluster stability. For example, the Gibbs free energy changes of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> + (H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)  $\rightleftharpoons$  (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>), C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)  $\rightleftharpoons$  (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) and C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>)  $\rightleftharpoons$  (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) reactions are larger than those for C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> + (H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)  $\rightleftharpoons$  (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>), C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)  $\rightleftharpoons$  (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) and C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>)  $\rightleftharpoons$  (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>SO<sub>4</sub>)(CH<sub>3</sub>NH<sub>2</sub>) reactions. All Gibbs free energy changes for (COA)(H<sub>2</sub>SO<sub>4</sub>)((CH<sub>3</sub>)<sub>2</sub>NH) are higher than those for (COA)(H<sub>2</sub>SO<sub>4</sub>)(NH<sub>3</sub>) that indicates that (CH<sub>3</sub>)<sub>2</sub>NH can enhance the stability of these ternary clusters better than NH<sub>3</sub>. As it may be seen from the comparison of data in Tables 2–4, no systematic dependency of the stabilizing effect of COA on its molecular weight or size has been found in the present study.

### 3. Conclusions

In this paper, the impact of 14 common atmospheric organic acids (COA) (formic (CH<sub>2</sub>O<sub>2</sub>), acetic (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), oxalic (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>), malonic (C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>), succinic (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>), glutaric acid (C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>), adipic (C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>), benzoic (C<sub>6</sub>H<sub>5</sub>COOH), phenylacetic (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH), pyruvic (C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>), maleic acid (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>), malic (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>), tartaric (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>) and pinonic acid (C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>)) on NPF involving H<sub>2</sub>SO<sub>4</sub>, the key atmospheric precursor, and three common atmospheric bases, dimethylamine ((CH<sub>3</sub>)<sub>2</sub>NH), methylamine (CH<sub>3</sub>NH<sub>2</sub>) and ammonia (NH<sub>3</sub>), have been investigated using DFT PW91PW91 and M06-2X and composite high-accuracy G3MP2 methods.

The present study leads us to the following conclusions regarding COA-containing clusters and their role in NPF follows:

(1) Mixed dimers (COA)(H<sub>2</sub>SO<sub>4</sub>) are typically as stable as or more stable than pure (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> dimers. This conclusion is

supported by both DFT and G3MP2 calculations. While the stability of (COA)(H<sub>2</sub>SO<sub>4</sub>) and (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> is quite close, the (COA)(H<sub>2</sub>SO<sub>4</sub>) are much more abundant than (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub> under typical atmospheric conditions due much larger concentrations of COA.

- (2) In most cases, interaction of COA with H<sub>2</sub>SO<sub>4</sub> and common atmospheric bases such as methylamine, dimethylamine and ammonia leads to the formation of mixed trimers that more stable thermodynamically than (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>(base) clusters.
- (3) The net effect of a COA on NPF and the importance of a specific COA for atmospheric nucleation strongly depend on the [COA]/[H<sub>2</sub>SO<sub>4</sub>] and [COA]/[base] concentration ratios, and seem to be not dependent of the molecular weight or size of the COA.
- (4) Although amines are generally confirmed as more active stabilizers of binary clusters than NH<sub>3</sub>, in some cases mixed trimers containing NH<sub>3</sub> are more stable than those containing methylamine CH<sub>3</sub>NH<sub>2</sub>. In contrast, dimethylamine (CH<sub>3</sub>)<sub>2</sub>NH enhance production of stable pre-nucleation clusters of sulfuric acid with COA better than ammonia in all the cases studied here.
- (5) Model predictions of G3MP2 and DFT PW91PW91 and M06-2X methods are in an agreement within  $\sim 1.5$  kcal/mol, and the key conclusions made based on G3MP2 results and DFT data are identical.

The present study leads us to conclude that interaction of common organic acids with the key atmospheric nucleation precursor H<sub>2</sub>SO<sub>4</sub> and common atmospheric bases (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, and NH<sub>3</sub> is important and, thus, should be studied further. Accurate measurements of atmospheric concentrations of the COA are also needed in order to gain a deep and insightful understanding the role of these common organic species in NPF.

Further research is needed to extend the present study to larger pre-nucleation clusters containing more organic acid, sulfuric acid, and possibly, water molecules so that the derived thermodynamic data can be incorporated in the framework of kinetic nucleation models providing explicit simulations of cluster formation and evolution (e.g. Dunn et al., 2016; Yu et al., 2018). Such nucleation models constrained by quantum-derived thermochemical data for pre-nucleation clusters can be then implemented, after the proper validation, in global models to study the new particle formation in the planetary atmosphere (Yu and Luo, 2009; Dunne et al., 2016; Yu et al., 2018).

### Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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## Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.03.033.

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