

Strong hydrogen bonding between atmospheric nucleation precursors and common organics

Alexey B. Nadykto ^{*}, Fangqun Yu

Atmospheric Sciences Research Center, State University of New York at Albany, 251 Fuller Road, Albany 12203, NY, USA

Received 5 May 2006; in final form 8 December 2006

Available online 20 December 2006

Abstract

While atmospheric aerosols are known to contain a significant fraction of organic substances, the influence of organics on the formation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters and subsequent nucleation in the atmosphere is poorly understood. In the present Letter, bonding among formic and acetic acids, sulfuric acid, ammonia and water is studied using density functional theory at PW91PW91/6-311++G(3df,3pd) level. The stabilizing effect of formic and acetic acids is found to be close that of ammonia that indicates that the common organic substances may efficiently stabilize small $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters and their involvement, alongside with or without ammonia, in the atmospheric nucleation should be studied further.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

New particle formation frequently observed in various locations in the atmosphere is an important source of atmospheric aerosols that are responsible for climate change [1,2] and human health impacts [3,4]. Although nucleation phenomena have been intensively studied in the past, there are still major uncertainties concerning nucleation mechanisms and species involved in the atmospheric nucleation. Nucleation in the Earth's atmosphere is essentially multicomponent. Nucleation rates are very sensitive to the concentration of H_2SO_4 vapor, which is likely a principal nucleation agent. However, binary homogeneous nucleation [5] of H_2SO_4 and H_2O can not explain some of the nucleation events observed in the lower atmosphere. Ternary homogeneous nucleation (THN) involving H_2SO_4 and H_2O as the key nucleation agents and NH_3 as a principal stabilizer of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters has been considered as an alternative nucleation mechanism in the lower atmosphere since 1990s. While the original THN [6] predicts that NH_3 at ppt level can increase the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$

nucleation rate by up to ~ 30 orders of magnitude, the laboratory experiments [7–9] indicate that the presence of NH_3 at ppb–ppm levels enhances the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation by up to ~ 2 orders of magnitude only [10]. Other species that may be involved in atmospheric nucleation are ions [11], iodine-containing vapors [12], and organics [13].

It is well known that nucleation rates are very sensitive to the thermodynamics of initial steps of the cluster formation, where reliable thermodynamic data are often lacking. It is clear that a theoretical tool that could predict, with sufficient degree of confidence, the thermodynamic properties of nucleating particles/clusters is urgently needed. Theoretical foundation of the commonly used bulk liquid model did not experience significant changes since being developed back in 19th century by Lord Kelvin (W. Thomson). The applicability of such an approach for the description of initial steps of the cluster formation is generally limited. Therefore, an accurate theoretical treatment of molecular clusters requires a more rigorous method, such as quantum mechanics.

Recent experiments [13] show that the presence of organic benzoic ($\text{C}_7\text{H}_6\text{O}_2$), *p*-toluic ($\text{C}_8\text{H}_8\text{O}_2$), and *m*-toluic ($\text{C}_8\text{H}_8\text{O}_2$) acids, which likely work as a catalyst, can enhance the nucleation of H_2SO_4 and H_2O . Having a large

^{*} Corresponding author. Fax: +1 518 437 8758.

E-mail address: alexn@asrc.cestm.albany.edu (A.B. Nadykto).

number of organics species in the atmosphere, one faces a complicate choice problem. We have selected formic and acetic acids, which are among the most abundant organic acids in the atmosphere. For example, in Denmark they account for $18\% \pm 8\%$ of the total acidity in rain [14]. In this Letter, thermodynamic stability of hydrogen bonded complexes of formic and acetic acids with free and hydrated sulfuric acid is studied and compared to that of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{CH}_2\text{O}_2\text{-H}_2\text{O}$, $\text{C}_2\text{H}_4\text{O}_2\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ complexes, unary H_2SO_4 , CH_2O_2 , $\text{C}_2\text{H}_4\text{O}_2$ and mixed $\text{CH}_2\text{O}_2\text{-C}_2\text{H}_4\text{O}_2$ dimers. This study has been carried out using the Density Functional Theory (DFT) at PW91PW91/6-311++G(3df,3pd) level.

2. Methods

In order to select a reasonable computational method, several DFT and ab initio tests have been performed. Comparison of computed structural data for reactants with experiments demonstrates a very good predictivity of PW91PW91(PW91), B3LYP and MP2 methods. A considerable disagreement of theoretical results with recent experimental data has been observed in the case of $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$ only. B3LYP and MP2 over-estimate the length of longest O–H bond controlling the cluster stability by ~ 0.1 and 0.13 angstroms, respectively, while PW91 results are in excellent, within ~ 0.01 angstroms, agreement with experimental data [15]. Since vibrational frequencies are input parameters in the calculations of enthalpies and entropies controlling the cluster stability, accurate determination of vibrational frequencies is critically important. Comparison of theoretical results with the experimental data shows a very good agreement of PW91/6-311++G(3df,3pd), which over-performs B3LYP/6-311++G(3df,3pd), with experiments in all the cases studied. Dipole moment relates directly to the distribution of atomic charges. While direct measuring atomic charges is problematic, dipole moments can be measured with high accuracy. Comparison of theoretical results with experimental data shows that PW91/6-311++G(3df,3pd) with 4.2% average deviation, over-performs both B3LYP/6-311++G(3df,3pd) (7.2%) and MP2/6-311++G(3df,3pd) ($\sim 20\%$).

Comparison of the hydration energies computed using different density functionals with experimental data summarized in Table 1 shows that PW91 predictions agree best with experiments. PW91 over-performs B3LYP, which considerably deviates from experiments even if large 6-311++G(3df,3pd) basis set is used. This implies that uncer-

tainties in hydration energies [16–20] relates, in agreement with [21], to insufficient accuracy of B3LYP method used to predict intermolecular interaction energies in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ complexes in the past. The test results lead us to conclude that PW91 with large 6-311++G(3df,3pd) basis set, which gives quite low basis set superposition error (BSSE) [22], is a better choice.

3. Results and discussion

Fig. 1 presents equilibrium geometries of most stable isomers of hydrogen bonded complexes studied here and Tables 2 and 3 present changes in the Gibbs free energy associated with their formation. Calculations have been performed at temperature of 298.15 K and pressure of 101.3 KPa. Equilibrium geometries of sulfuric [23,24], formic [25] and acetic [26] acid dimers, mono- and di-hydrates of formic [27] and sulfuric [16,17,23,28] acids, $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ [19], and $(\text{H}_2\text{O})(\text{NH}_3)$ [29] complexes were used as initial (guess) geometries in the present study.

As seen from Table 2, hydrates of the sulfuric acid are stable thermodynamically and hydration free energies obtained in the present study are consistent with the experiments [18]. Another important detail is that the presence of ammonia is unlikely to enhance the affinity of water to $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters. As seen from Table 2, this quantity depends on the ammonia content only weakly. The affinity of ammonia to the monomer of the sulfuric acid obtained in the present study ($-7.77 \text{ kcal mol}^{-1}$) is in agreement with experimental data [20] ($\sim -8.5 \text{ kcal mol}^{-1}$) and its value is $\sim 3.2 \text{ kcal mol}^{-1}$ more negative than that given in the B3LYP study [19]. The affinity of ammonia to binary sulfuric acid–water clusters gradually decreases as the water content grow. This finding is consistent with observation showing that the effect of ammonia decreases as the saturation ratio for water and, consequently, water content in the cluster, increases [10]. Gibbs free energy associated with addition of sulfuric acid to $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_n\text{NH}_3$ clusters ($-11.5\text{--}13.8 \text{ kcal mol}^{-1}$) is much larger than sulfuric acid dimerization ($-5.58 \text{ kcal mol}^{-1}$) and $(\text{H}_2\text{SO}_4) + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)$ ($-7.77 \text{ kcal mol}^{-1}$). This may be an indication that the effect of ammonia is associated with the sulfuric acid content and increases with the number of sulfuric acid molecules in the cluster.

As seen from Table 3, the formation of mixed $\text{H}_2\text{SO}_4\text{-CH}_2\text{O}_2$ and $\text{H}_2\text{SO}_4\text{-C}_2\text{H}_4\text{O}_2$ dimers is favorable thermodynamically. ΔG associated with the formation of both $\text{H}_2\text{SO}_4\text{-CH}_2\text{O}_2$ and $\text{H}_2\text{SO}_4\text{-C}_2\text{H}_4\text{O}_2$ is negative and, thus,

Table 1

Comparison of changes in the Gibbs free energy (kcal/mol) associated with hydration of the sulfuric acid calculated using B3LYP, BLYP, MPWPW91, PBEPBE and PW91PW91 at 6-311++G(3df,3pd) level with experimental data [18]

	B3LYP	BLYP	MPWPW91	PBEPBE	PW91	Exp.
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$	-0.76	0.33	-0.77	-1.72	-2.28	-3.6 ± 1.0
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2$	-0.92	-0.49	-1.28	-2.29	-3.00	-2.3 ± 0.3

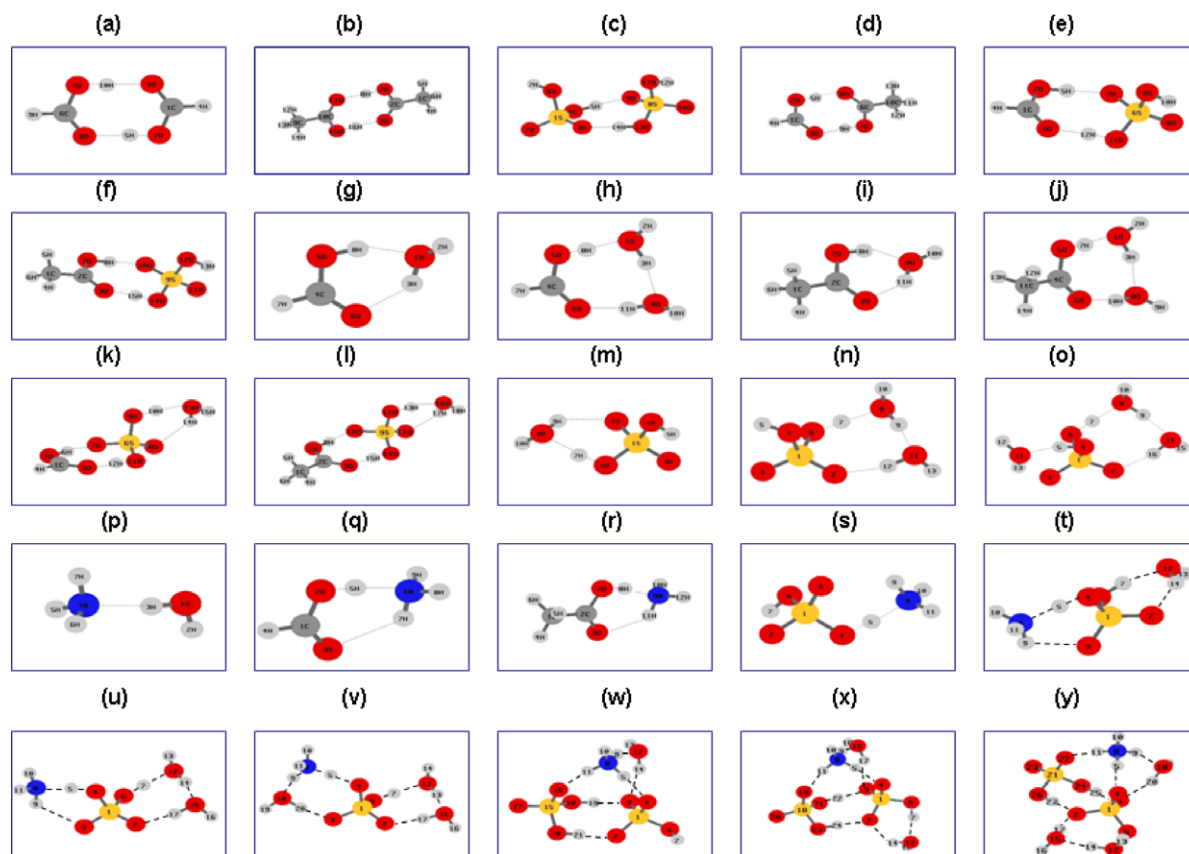


Fig. 1. Equilibrium geometries of most stable isomers calculated using DFT at PW91PW91/6-311++G(3df,3pd) level: (a) $(\text{CH}_2\text{O}_2)_2$; (b) $(\text{C}_2\text{H}_4\text{O}_2)_2$; (c) $(\text{H}_2\text{SO}_4)_2$; (d) $(\text{CH}_2\text{O}_2)(\text{C}_2\text{H}_4\text{O}_2)$; (e) $(\text{CH}_2\text{O}_2)(\text{H}_2\text{SO}_4)$; (f) $(\text{C}_2\text{H}_4\text{O}_2)(\text{H}_2\text{SO}_4)$; (g) $(\text{CH}_2\text{O}_2)(\text{H}_2\text{O})$; (h) $(\text{CH}_2\text{O}_2)(\text{H}_2\text{O})_2$; (i) $(\text{C}_2\text{H}_4\text{O}_2)(\text{H}_2\text{O})$; (j) $(\text{CH}_2\text{O}_2)(\text{H}_2\text{O})_2$; (k) $(\text{CH}_2\text{O}_2)(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$; (l) $(\text{C}_2\text{H}_4\text{O}_2)(\text{H}_2\text{O})$; (m) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$; (n) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2$; (o) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_3$; (p) $(\text{H}_2\text{O})(\text{NH}_3)$; (q) $(\text{CH}_2\text{O}_2)(\text{NH}_3)$; (r) $(\text{C}_2\text{H}_4\text{O}_2)(\text{NH}_3)$; (s) $(\text{H}_2\text{SO}_4)(\text{NH}_3)$; (t) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2(\text{NH}_3)$; (u) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2(\text{NH}_3)$; (v) $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_3(\text{NH}_3)$; (w) $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_2(\text{NH}_3)$; (x) $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_3(\text{NH}_3)$; (y) $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_3(\text{NH}_3)$.

Table 2

Enthalpies, entropies, and Gibbs free energy changes associated with reactions among clusters composed of atmospheric precursors (sulfuric acid, water and ammonia) calculated at $T = 298.15$ K and $P = 101.3$ kPa

Reaction	ΔH	ΔS	ΔG
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$	-11.76	-31.80	-2.28 (-2.5) ^a (-0.6) ^b (-3.6 ± 1.0) ^{c,*}
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2$	-12.57 ^c	-32.08 ^c	-3.00 (-1.8) ^a (-0.1) ^b (-2.3 ± 0.3) ^{c,*}
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2 + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_3$	-11.34	-31.71	-1.89 (-0.5) ^b
$(\text{H}_2\text{SO}_4)(\text{NH}_3) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})$	-10.96 (-8.87) ^d	-32.03 (-30.70) ^d	-1.41 (0.62) ^d
$(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_2$	-11.92 (-9.0) ^d	-32.34 (-30.12) ^d	-2.28 (-0.02) ^d
$(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_2 + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_3$	-11.51 (-9.45) ^d	-33.51 (-32.47) ^d	-1.52 (0.23) ^d
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})$	-11.68	-31.32	-2.31
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})_2$	-11.17	-33.40	-1.21
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})_2 + \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})_3$	-12.18	-34.00	-2.04
$\text{H}_2\text{SO}_4 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{NH}_3)$	-16.72 (-13.76) ^d	-30.01 (-30.91) ^d	-7.77 (-4.54) ^d (-8.5) ^{c,*}
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})(\text{NH}_3)$	-15.91 (-12.91) ^d	-30.23 (-31.09) ^d	-6.90 (-3.64) ^d
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2(\text{NH}_3)$	-15.27	-30.49	-6.18
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_3 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_3(\text{NH}_3)$	-15.44	-32.30	-5.81
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{H}_2\text{SO}_4)_2$	-16.16 (-13.2) ^f	-35.46 (-35.6) ^f	-5.59 (-3.1) ^a (-2.5) ^f
$(\text{H}_2\text{SO}_4)(\text{NH}_3) + (\text{H}_2\text{SO}_4) \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)$	-25.11	-45.14	-11.65
$(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O}) + (\text{H}_2\text{SO}_4) \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})$	-25.83	-44.42	-12.59
$(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4) \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})_2$	-25.08	-45.49	-11.52
$(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_3 + (\text{H}_2\text{SO}_4) \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)(\text{H}_2\text{O})_3$	-25.75	-45.98	-12.04
$(\text{H}_2\text{SO}_4)_2 + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)$	-25.67	-39.68	-13.83
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_3)(\text{H}_2\text{O})$	-5.81	-19.87	0.11

Superscripts (a), (b), (c), (d), (e) and (f) refer to studies [23], [16], [18], [19], [20], and [24], respectively. * Refers to experimental data.

Table 3

Enthalpy, entropy, and Gibbs free energy changes associated with reactions among clusters composed of atmospheric precursors (sulfuric acid, water and ammonia) and formic and acetic acids calculated at temperature of 298.15 K and pressure of 101.3 kPa

Reaction	ΔH (kcal mol ⁻¹)	ΔS (kcal mol ⁻¹ K ⁻¹)	ΔG (kcal mol ⁻¹)
CH ₂ O ₂ + CH ₂ O ₂ ⇌ (CH ₂ O ₂) ₂	-17.02	-37.99	-5.69
C ₂ H ₄ O ₂ + C ₂ H ₄ O ₂ ⇌ (C ₂ H ₄ O ₂) ₂	-17.15	-36.54	-6.26
C ₂ H ₄ O ₂ + CH ₂ O ₂ ⇌ (C ₂ H ₄ O ₂)(CH ₂ O ₂)	-17.33	-37.10	-6.27
H ₂ SO ₄ + CH ₂ O ₂ ⇌ (H ₂ SO ₄)(CH ₂ O ₂)	-17.67	-37.67	-6.44
H ₂ SO ₄ + C ₂ H ₄ O ₂ ⇌ (H ₂ SO ₄)(C ₂ H ₄ O ₂)	-18.71	-37.71	-7.46
CH ₂ O ₂ + H ₂ O ⇌ (CH ₂ O ₂)(H ₂ O)	-10.03	-32.12	-0.45
C ₂ H ₄ O ₂ + H ₂ O ⇌ (C ₂ H ₄ O ₂)(H ₂ O)	-10.08	-32.06	-0.52
(CH ₂ O ₂)(H ₂ O) + H ₂ O ⇌ (CH ₂ O ₂)(H ₂ O) ₂	-11.32	-31.96	-1.79
(C ₂ H ₄ O ₂)(H ₂ O) + H ₂ O ⇌ (C ₂ H ₄ O ₂)(H ₂ O) ₂	-10.74	-31.65	-1.31
(H ₂ SO ₄)(C ₂ H ₄ O ₂) + H ₂ O ⇌ (H ₂ SO ₄)(C ₂ H ₄ O ₂)(H ₂ O)	-11.43	-30.10	-2.45
(H ₂ SO ₄)(CH ₂ O ₂) + H ₂ O ⇌ (H ₂ SO ₄)(CH ₂ O ₂)(H ₂ O)	-11.68	-31.21	-2.37
(H ₂ SO ₄)(H ₂ O) + CH ₂ O ₂ ⇌ (H ₂ SO ₄)(H ₂ O)(CH ₂ O ₂)	-17.58	-11.06	-6.53
(H ₂ SO ₄)(H ₂ O) + C ₂ H ₄ O ₂ ⇌ (H ₂ SO ₄)(H ₂ O)(C ₂ H ₄ O ₂)	-18.37	-36.01	-7.64
H ₂ SO ₄ + (CH ₂ O ₂)(H ₂ O) ⇌ (CH ₂ O ₂)(H ₂ O)(H ₂ SO ₄)	-19.32	-36.76	-8.36
H ₂ SO ₄ + (C ₂ H ₄ O ₂)(H ₂ O) ⇌ (C ₂ H ₄ O ₂)(H ₂ O)(H ₂ SO ₄)	-20.06	-35.75	-9.40
NH ₃ + CH ₂ O ₂ ⇌ (NH ₃)(CH ₂ O ₂)	-11.63	-29.53	-2.82
NH ₃ + C ₂ H ₄ O ₂ ⇌ (NH ₃)(C ₂ H ₄ O ₂)	-10.78	-28.29	-2.35

these complexes are thermodynamically stable. Another important detail is that (H₂SO₄)(CH₂O₂), (H₂SO₄)-(C₂H₄O₂) and (H₂SO₄)(NH₃) complexes are more stable than other single-component and mixed dimers. It is important to note that ΔG associated with the formation of (H₂SO₄)(CH₂O₂) and (H₂SO₄)(C₂H₄O₂) are close to the Gibbs free energy of (H₂SO₄)(NH₃) formation. Another important detail is that in addition to the strong bonding with H₂SO₄, both CH₂O₂ and C₂H₄O₂ are able to form thermodynamically stable complexes with NH₃ and H₂O. Hydration of the sulfuric acid is ~ 0.9 – 1.8 kcal mol⁻¹ stronger than that of acetic and formic acids and it depends on the presence of ammonia only weakly.

Structure of mono- and di-hydrates of formic acid obtained in the present study agrees with that of the most stable FAZ1 and FAZ11 isomers, respectively that have been obtained in the recent B3LYP/6-311++G(d,p) study [30]. Interatomic distances in both CH₂O₂ and H₂O molecules obtained in [30] and the present study are very close; however, length of intermolecular bonds R(3–6) and R(8–10) in the monohydrate of formic acid and R(8–10), R(3–9) and R(6–11) in the di-hydrate of the formic acid obtained in the present study are 0.05–0.14 Å shorter than those given in [30]. As seen from Table 3, the Gibbs free energy associated with the formation of (H₂SO₄)(CH₂O₂)(H₂O) and (H₂SO₄)(C₂H₄O₂)(H₂O) from hydrated formic and acetic acids (-8.36 and -9.40 kcal mol⁻¹, respectively) is more negative than that the Gibbs free energy of (NH₃)(H₂SO₄) formation from (NH₃) and (H₂SO₄) (-7.77 kcal mol⁻¹). Another important detail is that the difference in the affinity of (H₂SO₄)(CH₂O₂), (H₂SO₄)(C₂H₄O₂) and (H₂SO₄)(H₂O) to H₂O does not exceed ~ 0.2 kcal mol⁻¹.

Comparison of our results with other theoretical studies shows that the B3LYP method overestimates changes in the Gibbs free energies by 1.5–3.5 kcal mol⁻¹ compared to both our results and experimental data. As seen from Table 2, problems of the B3LYP functional are caused

by the insufficiently accurate prediction of reaction enthalpies ΔH . PW91PW91 with the small DNP basis set [23] gives reasonable predictions of small mono- and di-hydration of free energies; however, the Gibbs free energy associated with the formation of the larger (H₂SO₄)₂ cluster is overestimated by ~ 2.5 kcal mol⁻¹. This suggests that the application of a more appropriate, presumably larger, basis set is necessary.

4. Conclusion

In this Letter, the formation of hydrogen bonded complexes composed of atmospheric precursors and common organics has been studied and new thermochemical data to be used in the atmospheric nucleation studies have been reported. The present study leads us to conclude that

- Interaction of formic acid and acetic acids with sulfuric acid and water leads to the formation of stable hydrogen-bonded complexes. The stability of such complexes is close to the stability of complexes of sulfuric acid with ammonia. In addition to the formation of strong hydrogen-bonded complexes with sulfuric acid and water, formic and acetic acids form thermodynamically stable complexes with ammonia. This indicates that formic and acetic acids may efficiently stabilize small sulfuric acid–water complexes and they can interact actively with ammonia. This suggests that the involvement of formic and acetic acids, alongside with or without ammonia, in clustering and subsequent nucleation of sulfuric acid and water should be studied in details further.
- The stabilizing effect of ammonia on the formation of small H₂SO₄–H₂O clusters is likely to increase with the number of sulfuric acid molecules in the cluster. Thermochemistry of H₂SO₄ and NH₃ in small H₂SO₄–H₂O–NH₃ clusters is either virtually

independent of or depends weakly on the water content. This suggests that the stabilizing effect of ammonia at initial steps of the cluster growth is associated mainly with the sulfuric acid.

Acknowledgements

NSF funded this work under Grant ATM0618124 and NOAA under Grant NA05OAR4310103.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2006.12.050](https://doi.org/10.1016/j.cplett.2006.12.050).

References

- [1] R.J. Charlson, S.E. Schwartz, J.M. Hales, et al., *Science* 255 (1992) 423.
- [2] M. Kulmala, *Science* 302 (2003) 1000.
- [3] D.B. Kittelson, W.F. Watts, J.P. Johnson, *Atmos. Environ.* 38 (2004) 9.
- [4] D. Saxon, D. Diaz-Sanchez, *Nature Immunol.* 6 (3) (2005) 223.
- [5] F. Yu, *J. Geophys. Res.* 111 (2006) D04201, doi:10.1029/2005JD006358.
- [6] I. Napari, M. Noppel, H. Vehkamäki, M. Kulmala, *J. Geophys. Res.* 107 (D19) (2002) 4381, doi:10.1029/2002JD002132.
- [7] S.M. Ball, D.R. Hanson, F.L. Eisele, P.H. McMurry, *J. Geophys. Res.* 104 (D19) (1999) 23709, doi:10.1029/1999JD900411.
- [8] T.O. Kim, T. Ishida, M. Adachi, K. Okuyama, J.H. Seinfeld, *Aerosol Sci. Technol.* 29 (1998) 112.
- [9] P.S. Christensen, S. Wedel, H. Livbjerg, *Chem. Eng. Sci.* 49 (1999) 4605.
- [10] F. Yu, *J. Geophys. Res.* 111 (2006) D01204, doi:10.1029/2005JD005968.
- [11] F. Yu, R.P. Turco, *Geophys. Res. Lett.* 27 (2000) 883.
- [12] C.D. O'Dowd et al., *Nature* 417 (2002) 632.
- [13] R. Zhang et al., *Science* 304 (2004) 1487.
- [14] K. Granby, C.S. Christensen, C. Lohse, *Atmos. Environ.* 31 (1997) 1403.
- [15] D.L. Fiacco, S.W. Hunt, K.R. Leopold, *J. Am. Chem. Soc.* 124 (16) (2002) 4504.
- [16] A.R. Bandy, J.C. Ianni, *J. Phys. Chem. A* 102 (32) (1998) 6533.
- [17] S. Re, Y. Osamura, M. Morokuma, *J. Phys. Chem. A* 103 (1999) 3535.
- [18] D.R. Hanson, F.L. Eisele, *J. Phys. Chem. A* 104 (2000) 1715.
- [19] J.C. Ianni, A.R. Bandy, *J. Phys. Chem. A* 103 (1999) 2801.
- [20] D.R. Hanson, F.L. Eisele, *J. Geophys. Res.* 107 (12) (2002) 4158, doi:10.1029/2001JD001100.
- [21] S. Tsuzuki, H.P. Lüthi, *J. Chem. Phys.* 114 (2001) 3949.
- [22] A. Müller, M. Losada, S. Leutwyler, *J. Phys. Chem. A* 108 (1) (2004) 157.
- [23] C.-G. Ding, K. Laasonen, A. Laaksonen, *J. Phys. Chem. A* 107 (41) (2003) 8648.
- [24] J.C. Ianni, A.R. Bandy, *J. Mol. Struct. (Theochem.)* 497 (2000) 19.
- [25] W. Qian, S.J. Krimm, *J. Phys. Chem. A* 105 (2001) 20.
- [26] J. Chocholousova, J. Vacek, P. Hobza, *J. Phys. Chem. A* 107 (2003) 3086.
- [27] Z. Zhou, Y. Shi, X. Zhou, *J. Phys. Chem. A* 108 (2004) 813.
- [28] A. Al Natsheh, A.B. Nadykto, K.V. Mikkelsen, F. Yu, J. Ruuskanen, *J. Phys. Chem. A* 108 (41) (2004) 8914.
- [29] J. Sadlej, R. Moszynski, J.Cz. Dobrowolski, A.P. Mazurek, *J. Phys. Chem. A* 103 (42) (1999) 8528.
- [30] S. Aloisio, P.E. Hintze, V. Vaida, *J. Phys. Chem. A* 106 (2002) 363.