

Stabilization of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ Clusters by Organic Acids

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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 study, bonding among formic, acetic and benzoic acids, sulfuric acid, ammonia and water is studied using Density Functional Theory (DFT) at PW91PW91/6-311++G(3df,3pd) level. The stabilizing effect of formic, acetic, and benzoic 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

Keywords Organics enhanced nucleation, binary clusters, ternary clusters, nucleation precursors

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 and human health impacts. 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 of H_2SO_4 and H_2O cannot 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

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alternative nucleation mechanism in the lower atmosphere since 1990s. While the original THN [1] 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 [2–4] 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 [5]. Other species that may be involved in atmospheric nucleation are ions, iodine-containing vapors, and organics.

In this paper, the thermodynamic stability of hydrogen-bonded complexes of formic, acetic, and benzoic acids with free and hydrated sulfuric acid has been studied. This study has been carried out using the quantum theory at DFT PW91PW91/6-311 ++ G(3df,3pd) level.

Results and Discussion

Tables 1 and 2 present changes in the Gibbs free energy associated with the cluster formation. Calculations have been performed at temperature of 298.15K and pressure of 101.3 kPa.

As seen from Table 1, hydrates of the sulfuric acid are stable thermodynamically and hydration free energies obtained in the present study are consistent with the experiments [6]. 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 ($-7.77 \text{ kcal mole}^{-1}$) is in agreement with experimental data [7] ($\sim -8.5 \text{ kcal mole}^{-1}$) and its value is $\sim 3.2 \text{ kcal mole}^{-1}$ more negative than that given in the B3LYP study [8]. The affinity of ammonia to binary sulfuric acid–water clusters gradually decreases as the water content grows. 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 [5]. 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 ($-11.5\text{--}13.8 \text{ kcal mole}^{-1}$) is much larger than sulfuric acid dimerization ($-5.58 \text{ kcal mole}^{-1}$) and $(\text{H}_2\text{SO}_4) + \text{NH}_3 = (\text{H}_2\text{SO}_4)(\text{NH}_3)$ ($-7.77 \text{ kcal mole}^{-1}$). The stabilizing effect of ammonia on the formation of small $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters is likely to increase with the number of sulfuric acid molecules in the cluster. Thermochemistry of H_2SO_4 and NH_3 in small $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ 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.

As seen from Table 2, the interaction of formic acid, acetic and benzoic 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, acetic, and benzoic acids form thermodynamically stable complexes with ammonia.

Table 1 Enthalpies, entropies, and Gibbs free energy changes associated with reactions among clusters composed of atmospheric precursors (sulfuric acid, water, and ammonia) calculated at $T = 298.15\text{K}$ and $P = 101.3\text{kPa}$. Superscripts (a), (b), (c), (d), (e), and (f) refer to studies [9], [10], [6], [8], [7], and [11], respectively. Superscript* refers to experimental data

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	-32.08	-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) ^{e*}
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + \text{NH}_3 \rightleftharpoons (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})(\text{NH}_3)$	-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

This indicates that formic, acetic, and benzoic acids may efficiently stabilize small sulfuric acid–water complexes and they can interact actively with ammonia. This suggests that the involvement of these acids, with or without ammonia, in

Table 2 Enthalpy, entropy, and Gibbs free energy changes associated with reactions among clusters composed of atmospheric precursors (sulfuric acid, water, and ammonia) and formic, acetic, and benzoic acids calculated at temperature of 298.15K and pressure of 101.3 kPa

Reaction	ΔH (kcal mole ⁻¹)	ΔS (cal mole ⁻¹ K ⁻¹)	ΔG (kcal mole ⁻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

clustering and subsequent nucleation of sulfuric acid and water should be studied in further detail.

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