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A theoretical study of temperature dependence of cluster formation from sulfuric acid and ammonia

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ABSTRACT

We have performed density functional theory (BL3YP) and *ab initio* (MP2) calculations to investigate the energetics of the cluster formation for $(NH_3)_m(H_2SO_4)$ and $(NH_3)(H_2SO_4)_n$ ($m, n = 1–6$) in the atmospherically-relevant temperature range between 200 and 300 K. For $(NH_3)_m(H_2SO_4)$ clusters, the binding increases from $m = 1$ to 6 at 200 K, while the most stable complex at 300 K is the cluster with $m = 2$. For $(NH_3)(H_2SO_4)_n$ clusters, the binding is more stable for those with larger n. There is a strong temperature dependence for the $(NH_3)_m(H_2SO_4)$ cluster formation; the lowest free energy shifts from $m = 6$ at $T = 200$ K to $m = 5$ around $T = 240$ K and further to $m = 2$ at $T \geqslant 280$ K. The temperature effects on $(NH_3)(H_2SO_4)_n$ clusters are much less stronger, while there is still a similar trend which favors larger n in the entire temperature range from 200 to 300 K.

1. Introduction

Atmospheric nucleation (formation of solid or liquid aerosols directly from gas phase species) is an important source of secondary aerosols [1]. Nucleation contributes significantly to the global production of cloud condensation nuclei (CCN) [2]. Although a large of number of observational studies have been made in the nucleation field [3], aerosol nucleation mechanisms are not well understood, especially at the molecular cluster level. Direct measurements of chemical composition of newly nucleated clusters are very limited [4] and the thermodynamics properties of formation of molecular clusters have rarely been measured [5]. From this perspective, theoretical computational studies of nucleation clusters can provide indirect yet valuable information on molecular structures and energetics of clusters formed at the very early stage of aerosol nucleation.

Atmospheric observations and laboratory studies have consistently pointed out that sulfuric acid (H_2SO_4) is the key aerosol nucleation precursor [3]. But in the boundary layer conditions, H_2SO_4 concentrations ($10^5 - 10^7$ cm^{-3}) are not sufficient to explain the measured nucleation rates, indicating that other ternary species are also involved in nucleation [6]. Ammonia (NH_3) is one of key ternary species. NH_3 is abundant in the atmosphere and is the main base compound in the atmosphere and thus has a unique capability to stabilize H_2SO_4 clusters via acid–base reactions [7]. However there are still controversies on the role of NH_3 on H_2SO_4 nucleation. Global modeling studies have shown that ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O is the dominant nucleation mechanism in the entire troposphere and lower stratosphere [8], and this nucleation mechanism has been also used to explain atmospheric observations of new particle formation in the Eastern United States [9]. However, laboratory studies also showed that the enhancement of nucleation rates by NH_3 is moderate (only at the 10–1000 range), although tens of pptv to tens ppbv level of NH_3 was used in these studies [7a–e]. Another important role of NH_3 in nucleation is that it can form H_2SO_4–NH_3 clusters initially under higher concentrations of NH_3 in the atmosphere and then ammonium components are replaced by lower concentrations of amines in the aerosol phases [10].

Molecular modeling studies with density functional theories (DFT) and *ab initio* calculations have been performed for formation of H_2SO_4 and NH_3 clusters [11], but conclusions of these studies are contradictory. Using DFT (B3LYP) calculations, Ianni and Bandy [11h] studied structures, energetics, dipoles and rotational constants of $NH_3{\cdot}H_2SO_4{\cdot}(H_2O)_n$ ($n = 0–5$) and $NH_3{\cdot}(H_2SO_4)_2{\cdot}H_2O$ clusters, and concluded that the $NH_3{\cdot}(H_2SO_4)_2{\cdot}H_2O$ cluster does not have enough free energy to initialize the atmospheric nucleation and hence NH_3 does not play roles in atmospheric aerosol nucleation. On the other hand, Kurten et al. [11d,11e] conducted *ab initio* RI-CC2 calculations to derive total energies, free energies, binding energies, and atmospheric cluster size distributions of $NH_3{\cdot}(H_2SO_4)_m{\cdot}(H_2O)_n$ ($m = 1, 2;\ n = 0–7$) clusters, and showed that NH_3 can

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strengthen the formation of clusters containing 2 H_2SO_4 and 0–2 H_2O molecules and so that NH_3 favors thermodynamics of H_2SO_4 and NH_3 binding via formation of ammonium bisulfate. Previous studies also showed that the enhancing effect of NH_3 is more pronounced for the formation of neutral clusters containing 2 H_2SO_4 molecules than larger clusters [11a,11d,11e,11i].

Recent RI-CC2 calculations by Kurten et al. [11c,12] further showed that organic amine compounds can reduce Gibbs free energy for the formation of H_2SO_4 clusters even more effectively than NH_3, so that the trace level of amines may play key roles in aerosol nucleation [11c,12]. Another DFT (PW91PW91) study by Nadykto et al. [11b] indicated that the thermochemical stability of the H_2SO_4–amines–H_2O complexes is indeed higher than that of the H_2SO_4–NH_3–H_2O complexes, in a qualitative agreement with Kurten et al. [11f]; but the enhancement in the stability due to amines is not large enough (2–3.5 kcal/mol) to overcome the difference in typical atmospheric concentrations of NH_3 and amines (two to three orders of magnitude lower than NH_3 [13]). It is possible that the uncertainties associated with calculations at different levels of the theory have caused different energetics in these studies [11b,11c,12]. Calculations also showed that organic acids may be important for the H_2SO_4 cluster formation, with or without NH_3, via hydrogen bonding between H_2SO_4 and carboxylic acids [11a,14].

For the case of the attachment of NH_3 molecules to H_2SO_4 clusters, the presence of H_2O may have small effects on the Gibbs free energy of the H_2SO_4 and NH_3 cluster formation [11a], although an addition of H_2O tends to slightly decrease the binding of NH_3 to H_2SO_4 clusters [11d,11e]. For example, the Gibbs formation free energy of an unhydrated cluster containing one H_2SO_4 and one NH_3 derived from previous DFT calculations ranged from -4.5 to -8.7 kcal/mol, whereas the formation free energy of the hydrated cluster ranged -3.6 to -7.6 kcal/mol [11a–h]. In contrast to these cited studies, recent studies indicated that hydration can increase the stability of H_2SO_4–amine clusters [3b,15].

Temperature dependence of thermodynamical properties is an important parameter needed for understanding how a specific nucleation mechanism plays roles at different altitudes (and hence different temperatures) in the atmosphere. Quantum calculations can provide such data, especially when experiments at lower temperature ranges are even more difficult to perform, because of the increased wall losses of aerosol precursors (H_2SO_4 and NH_3) at low temperatures. But computational studies are still very limited on the temperature dependence of Gibbs free energies for the cluster formation involving H_2SO_4 and NH_3 [11h,11i].

In the present study, we show MP2 and B3LYP calculations of unhydrated $(NH_3)_m(H_2SO_4)$ and $(NH_3)(H_2SO_4)_n$ $(m, n = 1–6)$ complexes at temperatures of 200, 220, 240, 260, 280, and 300 K, thus within the entire temperature range from the ground level to the lower stratosphere. We have optimized geometries of clusters and computed binding energies, enthalpies, entropies, and Gibbs free energies of the formation of these model clusters.

2. Computational methods

Geometries for $(NH_3)_m(H_2SO_4)$ and $(NH_3)(H_2SO_4)_n$ model complexes with $m, n = 1–6$ were optimized at the B3LYP [16] level with the 6-31+G(d,p) [17] basis set using ORCA [18]. A larger number of different initial geometries have been systematically constructed in a stepwise manner, exploring the configurational space in an efficient way. For the $(NH_3)_m(H_2SO_4)$ complex, a NH_3 molecule was manually added to the optimized $(NH_3)_{m-1}(H_2SO_4)$ complex of the lowest energy at different positions with various orientations. The same strategy was applied to the construction of $(NH_3)(H_2SO_4)_n$, where H_2SO_4 was added one by one. While we have tried our best to use the aufbau principle to grow clusters, one should be aware of the limits of this method in exploring the configuration space. In this perspective, a sampling scheme used by Xu and Zhang [15] can be an alternative choice. Tight SCF convergence and a large grid for integral evaluation were utilized for DFT calculations (see the detailed computational setup in Supporting Information). To refine the interaction energies, single-point calculations were carried out at the optimized geometries employing the RI-MP2 [19] (resolution of the identity MP2) method with Dunning's augmented correlation-consistent basis sets (aug-cc-pVXZ, X = D, T, Q) [20] implemented ORCA. The MP2 single-point energies were then extrapolated to the complete basis set (CBS) limit using the following equation [21]:

$$E_X^{\mathrm{MP2}} = E_{\mathrm{CBS}}^{\mathrm{MP2}} + \frac{b}{X^3} \tag{1}$$

where E_X^{MP2} is the MP2/aug-cc-pVXZ (X = D, T, Q) energy, $E_{\mathrm{CBS}}^{\mathrm{MP2}}$ is the extrapolated MP2/CBS energy, and b is a fitting parameter. Due to the technical constraint, we were unable to converge MP2/aug-cc-pVQZ calculations for $(NH_3)(H_2SO_4)_6$ clusters. Therefore, MP2/CBS energies were not available for $(NH_3)(H_2SO_4)_6$. We note that, while B3LYP- and MP2-geometry optimizations may lead to different minima for hydrogen-bonded complexes, the optimized geometries usually agree with each other [11g]. Moreover, variations in the interaction energies due to small differences in the geometry are likely marginal (1–2 kcal/mol) [22]. Therefore, we consider the above MP2/CBS//B3LYP/6-31+G(d,p) strategy as a reasonable compromise between the accuracy and efficiency.

The binding energy (ΔU) associated with the complex formation, compared to free molecules, was computed by:

$$\Delta U[(\mathrm{NH_3})_m(\mathrm{H_2SO_4})] = E[(\mathrm{NH_3})_m(\mathrm{H_2SO_4}))] - [m \times E(\mathrm{NH_3}) + E(\mathrm{H_2SO_4})] \tag{2}$$

$$\Delta U[(\mathrm{NH_3})(\mathrm{H_2SO_4})_n] = E[(\mathrm{NH_3})(\mathrm{H_2SO_4})_n)] - [E(\mathrm{NH_3}) + n \times E(\mathrm{H_2SO_4})] \tag{3}$$

where E is the electronic energy. Normal-mode analysis was performed at the optimized geometries at the B3LYP/6-31+G(d,p) level. Enthalpy changes ΔH and entropy changes ΔS were estimated in the similar way. All thermodynamics quantities were estimated assuming harmonic vibrations for temperatures T at 200, 220, 240, 260, 280, and 300 K. For example, the entropic contribution S_v by a normal mode v was calculated based on [23]:

$$S_v = Nk\left[\frac{\beta hc\tilde{v}}{e^{\beta hc\tilde{v}} - 1} - \ln(1 - e^{-\beta hc\tilde{v}})\right] \tag{4}$$

where $\beta = \frac{1}{kT}$, N is the Avogadro constant, k is the Boltzmann constant, T is temperature, h is the Planck constant, c is the speed of light, and $\tilde{v}$ is the vibrational wavenumber.

The harmonic approximation likely overestimathe partition functions for normal modes of very low frequencies, which are very anharmonic. To reduce errors in the computation of entropic contributions for those normal modes, we have adopted an ansatz, where we replaced the actual vibrational wavenumber by a cut-off value ($\tilde{v}_{\mathrm{cutoff}} = 35\ \mathrm{cm}^{-1}$) when computing entropic contributions for a normal mode, if the actual wavenumber was lower than the cut-off value. Such a treatment has been successfully employed in our previous study of kinetic isotope effects for methane reacting with hydroxyl radical in the atmosphere [24]. Estimations of the entropy of free energy without this treatment are denoted as Est1 in the present study, and those with this treatment as Est2. Both Est1 and Est2 free energies can be further refined by replacing B3LYP electronic energies by more accurate MP2/CBS counterparts, and the corresponding results are indicated as Est1(MP2) and Est2(MP2), respectively.