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Growth of Ammonium Bisulfate Clusters by Adsorption of Oxygenated Organic Molecules

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Ⓢ *Supporting Information*

ABSTRACT: Quantum chemical calculations were employed to model the interactions of the $[(NH_4^+)_4(HSO_4^-)_4]$ ammonium bisulfate cluster with one or more molecular products of monoterpene oxidation. A strong interaction was found between the bisulfate ion of this cluster and a carboxylic acid, aldehyde, or ketone functionality of the organic molecule. Free energies of adsorption for carboxylic acids were in the −70 to −73 kJ/mol range, while those for aldehydes and ketones were in the −46 to −50 kJ/mol range. These values suggest that a small ambient $[(NH_4^+)_4(SO_4^-)_4]$ cluster is able to adsorb an oxygenated organic molecule. While adsorption of the first molecule is highly favorable, adsorption of subsequent molecules is less so, suggesting that sustained uptake of organic molecules does not occur, and thus is not a pathway for continuing growth of the cluster. This result is consistent with ambient measurements showing that particles below ~1 nm grow slowly, while those above 1 nm grow at an increasing rate presumably due to a lower surface energy barrier enabling the uptake of organic molecules. This work provides insight into the molecular level interactions which affect sustained cluster growth by uptake of organic molecules.
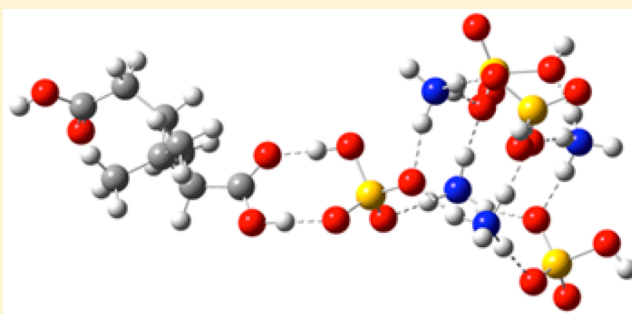
■ INTRODUCTION

Atmospheric new particle formation is a gas-to-particle conversion process that contributes substantially to the number concentration of ambient particles.[1,2] The overall process involves the formation of a small molecular cluster that may subsequently grow to a large enough size where it can serve as a cloud condensation nucleus.[3−5] Sulfuric acid and water are believed to be the primary vapors involved in particle formation,[6−11] but binary nucleation of these species alone does not account for all observed nucleation events.[7] Tertiary species such as ammonia[7,12−14] and amines[8,15−17] have been shown to assist particle formation.[18−21] Recent ambient measurements have shown that the growth rate of particles with a diameter smaller than ~1 nm is slow and appears to be determined by the collision rate of sulfuric acid molecules with the particle surface. The growth rate increases with increasing particle diameter in the 1−5 nm range,[22,23] presumably due to the uptake of condensable organic molecules, which often have much higher ambient concentrations than sulfuric acid. Since these small nuclei coagulate rapidly with larger pre-existing aerosol particles in the atmosphere, their rate of growth relative to coagulation determines whether they survive to form cloud condensation nuclei or not.

In previous work, we have explored the formation and growth of molecular clusters containing sulfuric acid, ammonia (or an amine), and water.[24−26] These studies have focused primarily on clusters that contain equal numbers of sulfuric acid and ammonia molecules, since these partially neutralized species are the main ones detected in nucleation experiments.[7−10] In these clusters, proton transfer yields ammonium and bisulfate ions, and the calculated free energies of cluster formation are very negative owing to strong electrostatic forces between the ions.[25−27] Similarly, cluster growth by stepwise addition of sulfuric acid and ammonia is driven by proton transfer.[24] Water exists as neutral molecules in these clusters. For clusters containing six or fewer bisulfate ions, the most probable number of water molecules per cluster under typical ambient conditions is significantly less than the number of bisulfate ions per cluster.[24] Nonetheless, water does provide a slight enhancement of cluster stability, and its presence in these types of clusters, albeit in small amounts, has been inferred experimentally.[28]

Globally, a substantial portion of the mass of atmospheric particles is carbonaceous, and much of it is derived from the oxidation of biogenic precursors.[9,29−31] Particularly important for new particle formation are the oxidation products of monoterpenes such as α-pinene, which are emitted from coniferous vegetation.[32−34] The chemistry of monoterpene oxidation is complex, typically encompassing more than 1000 unique molecular formulas among the products.[35−38] These products contain functional groups such as carboxylic acids, aldehydes, ketones, peroxides, and alcohols.[39] Oxidation products with very low vapor pressures may assist formation and early growth of new particles in the atmosphere,[30,40] while products with somewhat higher vapor pressures can partition from the gas phase onto pre-existing aerosol.[41] It has been suggested that low volatility organics cannot nucleate and grow new particles on their own but require sulfuric acid as a stabilizing molecule to further decrease the volatility[42] since organic molecules are often too hydrophobic to interact strongly with each other. Indeed, sulfuric acid−organic mixtures exhibit enhanced nucleation and growth rates relative to the individual components.[3,43,44]

Computational studies of the interactions of sulfuric acid, ammonia, amines, and water across all manner of compositions and charges have given significant insight into the nature of atmospheric nucleation and the chemistry which drives it.[45−52] The interaction of sulfuric acid with small organic acids has also been the focus of computational[52−59] and experimental studies.[42,60−62] Owing to the difficulties of calculating the potential energy surfaces for large molecules using quantum chemical methods, computational studies have been limited to small clusters composed of fewer than about 8 total molecules. For example, Xu and Zhang investigated the clustering reactions of succinic acid and oxalic acid (and other small carboxylic acids) with sulfuric acid, water, and ammonia and found that organic acids bind very strongly to both sulfuric acid and ammonia.[56] Additional work by these authors has indicated ammonia and amines bind strongly to small carboxylic acids and water.[57] Recently, Wang and Wexler suggested particle growth can be enhanced by surface adsorption of organic molecules to small molecular salt clusters.[63] They suggest the strong intermolecular interactions between salts and organics are sufficient to overcome the surface free energy barrier and enable the growth of new particles.

In the work described here, the structures and free energies of interaction between several first-generation monoterpene oxidation products and an atmospherically relevant salt cluster are explored. We use the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster discussed in our previous work,[25] since it represents a balance between a large enough cluster to study adsorption and the significant computational resources needed to perform these calculations. Water is not included in these calculations. We note that very few molecules (less than the number of bisulfate ions) are expected to be present in clusters of this size and composition under ambient conditions.[25,64,65] Recent experimental measurements of cluster hydration using ion mobility mass spectrometry,[28] vibrational spectroscopy,[61] and electrical mobility[64] also suggest that only a few water molecules will be present in clusters in the size range of the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster used as our surrogate in the present study.

■ COMPUTATIONAL METHODS

Molecular clusters derived from an initial "salt" cluster containing 4 ammonia molecules and 4 sulfuric acid molecules plus 1−8 organic molecules were constructed using optimized geometries taken from our previous work.[25,39] The $[(NH_4^+)_4(HSO_4^-)_4]$ cluster is characterized by transfer of a proton from each sulfuric acid molecule to an ammonia molecule to give a product with the formula $[(NH_4^+)_4(HSO_4^-)_4]$. The structure of this cluster was obtained from individual optimized monomers of ammonia and sulfuric acid using our previously described multistep configuration searching method. The salt cluster structure was generated using Austin Model 1 (AM1) semiempirical theory[66] by configuration sampling with a 10 000 point extended distance Metropolis Monte Carlo based search as implemented in the HyperChem 8.0.8 GUI-based modeling package,[67] followed by optimization using the density functional theory (DFT) method PW91[68,69] in Gaussian09 (rev. C.03)[70] and the 6-31++G(d,p) basis set. Structures for the organic molecules were taken from our previous work on oligomer formation from the oxidation products of α-pinene.[39] For the present study, these molecules include cis-pinic acid, cis-pinonic acid, terpenylic acid, norpinic acid, pinalic-4 acid, pinonaldehyde and 2,2-dimethyl-3-formylcyclobutylmethanoic acid. We note that the structure for the cluster containing 8 cis-pinic acid molecules was only optimized with AM1 due to computational limitations. All calculations and Monte Carlo simulations were performed in the NVT ensemble at standard state conditions (298 K and 1 atm pressure).

To confirm the validity of our choice of DFT method and modest basis set, a comparison of the experimental binding energies (taken as Gibbs free energies) of positively charged ammonium bisulfate clusters from Froyd and Lovejoy[71] are compared to our previously calculated geometries. Additionally, we have chosen not to correct our PW91 energetics for BSSE using the counterpoise (CP) correction of Boys and Bernardi.[72] While PW91/6-31++G(d,p) overestimates the binding energies by ∼3−9 kJ/mol relative to the experimental data from Froyd and Lovejoy,[71] it captures the trends in the reactivity properly (see Table S1 in Supporting Information). We have previously benchmarked this method/basis set combination against other DFT methods and MP2 with and without the CP correction method[72] and found that while the absolute values of thermodynamic potentials changes from method to method and with the CP correction, the overall trends in the data did not. Furthermore, the computational approach used here was shown to provide quantitative agreement with experimental measurements of ammonium bisulfate cluster reactivity.[24,26] It was recently shown that significant uncertainty in atmospheric cluster thermochemistry can arise with different DFT method/basis set combinations.[73−75] In these studies, PW91 with a larger basis set was shown to perform admirably against higher level data and the limited experimental data sets available relative to other DFT methods and further reinforces the use of PW91 for the present work. While some reduction in accuracy can be expected with the smaller basis set used here, an ∼10 kJ/mol computational error will not affect the global conclusions of this work.

The choice of initial "salt" cluster represented a balance between size of the cluster and number of adsorbed organic molecules that could be studied within the framework of DFT. If a larger salt cluster had been used, then the maximum number of adsorbed organic molecules able to be studied would have likely been smaller to keep the task computationally feasible. We point out that none of the initial salt clusters

studied will have a high atmospheric concentration at equilibrium, as cluster growth is not an equilibrium process.

The starting conditions for organic molecular adsorption were chosen to promote interaction of the organic molecule with a bisulfate ion in the cluster. This interaction is consistent with previous modeling studies[56,57] and our own test calculations for producing minimum-energy structures. For the organic molecules having two terminal groups (*cis*-pinic acid, *cis*-pinonic acid, pinonaldehyde, and pinalic-4 acid), interactions of the cluster with both end groups were studied.

To explore the effect of adding multiple organic molecules to the salt cluster, *cis*-pinic acid was selected for study. *cis*-Pinic acid is one of the more abundant products of monoterpene oxidation and has both α- and β-carboxylic acid termini. Starting from the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster with a single adsorbed *cis*-pinic acid molecule, sequential *cis*-pinic acid molecules were added to the remaining bisulfate ions (three total); each new structure optimized before adding the next *cis*-pinic acid molecule. This was done using both acid end groups of the molecule, creating two different cluster systems. As a test of each position on the cluster, the bisulfate ions were numbered and the *cis*-pinic acid molecules were placed on different combinations of bisulfate ions. For example, the first *cis*-pinic acid was placed on bisulfate ion 1 and then the second was placed on bisulfate ions 2, 3, and 4, with each system being individually optimized. This resulted in a total of 8 different geometries. The results of this indicate that for a given number of *cis*-pinic acid molecules the bisulfate ion they were interacting with did not matter; i.e., the difference in electronic energy between the six possible 2 *cis*-pinic acid cluster systems is less than ∼4 kJ/mol. This was only done for the α-terminus of cis-pinic acid because it is the more energetically favorable end of the molecule, although we would expect similar results for the β-terminus. From the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster with 4 *cis*-pinic acid molecules, a second layer of *cis*-pinic acid molecules was added one at a time to the free carboxylic acid end of the adsorbed *cis*-pinic acid molecules; this was done until there were a total of 7 *cis*-pinic acid molecules with each cluster being optimized individually. In order to keep the task of covering such a large potential energy surface computationally reasonable, we only optimized at the DFT level the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster with up to 7 organic molecules attached. Adding the eighth molecule proved too computationally intensive at the DFT level. For this reason, we computed only a cursory structure for this cluster using the AM1 level of theory for visualization. The Cartesian coordinates for all molecules and clusters studied in this work are available in the Supporting Information.

■ RESULTS AND DISCUSSION

Adsorption of a Single Organic Molecule. Figure 1a shows the structure of the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster interacting with the α-carboxylic acid group on the end of a *cis*-pinic acid molecule. Protons from the bisulfate ion and carboxylic acid group form a hydrogen-bonded ring which links the two functionalities together. This interaction is similar to that observed in dimers of small carboxylic acids such as acetic acid and formic acid.[76,77] The structure in Figure 1a is characteristic of all clusters studied in this work that involve the interaction of a bisulfate ion with a carboxylic acid. Figure 1b shows the structure of the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster interacting with the alkyl carboxy group on a pinonaldehyde molecule. Here, a single hydrogen bond links the bisulfate
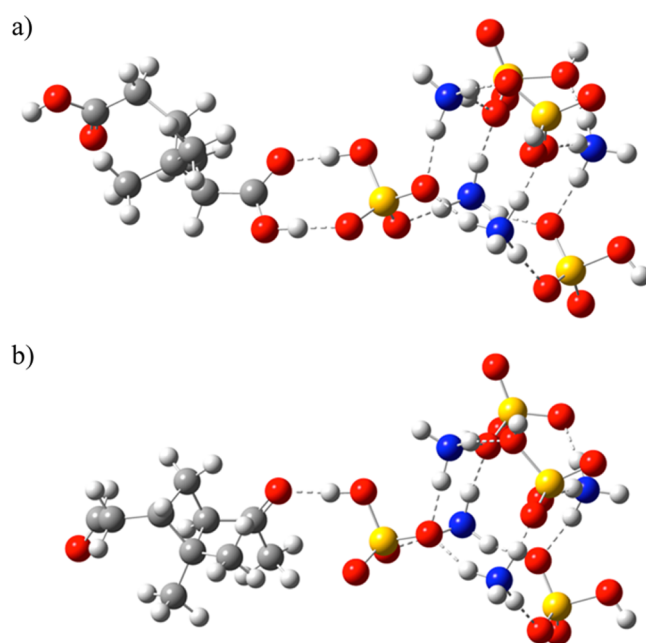

Figure 1. (a) A single *cis*-pinic molecule acid interacting with the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster. (b) A single pinonaldehyde molecule acid interacting with the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster. Nitrogen atoms are blue, oxygen atoms are red, sulfur atoms are yellow, hydrogen atoms are white, and carbon atoms are gray, with hydrogen bonds indicated by dashed lines.

proton and the oxygen atom of the aldehyde. The structure in Figure 1b is characteristic of all clusters studied in this work which involve the interaction of a bisulfate ion with either an aldehyde or a ketone.

Table 1. Thermodynamic Potentials (in kJ/mol) for Adsorption of Various α-Pinene Oxidation Products to the $[(NH_4^+)_4(HSO_4^-)_4]$ Cluster[a]

organic molecule	ΔH_{ads}	$T\Delta S_{ads}$	ΔG_{ads}
cis-pinic acid (α)	−117.4	−47.0	−70.4
cis-pinic acid (β)	−118.2	−46.3	−71.8
cis-pinonic acid	−118.2	−45.6	−72.6
terpenylic acid	−118.8	−47.0	−71.8
2,2-dimethyl-3-formylcyclobutylmethanoic acid	−119.2	−46.9	−72.3
norpinic acid	−117.6	−47.0	−70.6
pinalic-4 acid (α, acid)	−109.8	−40.0	−71.1
pinalic-4 acid (β, aldehyde)	−92.4	−44.1	−48.3
pinonaldehyde (aldehyde)	−91.3	−40.6	−50.7
pinonaldehyde (alkyl carboxy)	−88.6	−41.8	−46.8

[a]Values are computed for the gas phase standard state of 1 atm and 298 K.

Table 1 gives the free energies of adsorption for several organic molecules with the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster as defined by the equation

$$[(NH_4^+)_4(HSO_4^-)_4] + M \rightarrow [(NH_4^+)_4(HSO_4^-)_4(M)] \quad (1)$$
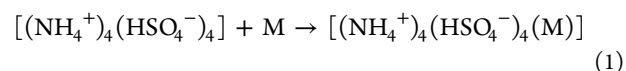
where M = organic molecule. The free energies of adsorption for the bisulfate ion with a carboxylic acid group fall within the

range of −70 to −73 kJ/mol, whereas the free energies of adsorption with a carbonyl (aldehyde or ketone) fall within the range −46 to −50 kJ/mol. The weaker interaction of a carbonyl relative to a carboxylic acid is consistent with one fewer O−H--O hydrogen bond, as illustrated by Figure 1. For a dicarboxylic acid, there is very little difference in the adsorption free energy between the α- and β-positions. The interaction between a bisulfate ion and a carboxylic acid or carbonyl functionality (−46 to −73 kJ/mol) is much more favorable than between two carboxylic acid functionalities (for the molecules of interest here, on the order of −27 to −33 kJ/mol[39]) and most likely reflects the strong electrostatic interaction between a bisulfate ion and an oxygenated molecule relative to the hydrogen bonding interaction between two carboxylic acids. In this regard, we note that hydrogen bonding between the bisulfate ion and *cis*-pinic acid molecule in Figure 1a is not that different from that in a *cis*-pinic acid dimer. In both types of interaction, O−H bond lengths are on the order of 1.03 Å and O−H--O hydrogen bond lengths are on the order of 1.5−1.6 Å. Electrostatics rather than hydrogen bonding configuration appear to drive the energetics.

The free energies in Table 1 suggest it is highly likely that a $[(NH_4^+)_4(HSO_4^-)_4]$ cluster will contain one adsorbed organic molecule under ambient conditions. Oxidation products such as *cis*-pinic acid and *cis*-pinonic acid typically have ambient concentrations in the low parts-per-trillion range.[78−80] Using a gas phase concentration of 10^8 molecules/cm^3 as a guide and the standard state free energies from Table 1, at equilibrium the vast majority of $[(NH_4^+)_4(HSO_4^-)_4]$ clusters have adsorbed one of these carboxylic acid molecules. Even for pinonaldeyde, the least favorable carbonyl studied, ~3% of the clusters have one adsorbed molecule at standard temperature and pressure. Strong interaction of an organic molecule with ammonia and sulfuric acid has been noted previously for much smaller clusters.[42,53−59]

Adsorption of Multiple Molecules and Layers. *cis*-Pinic acid alone makes up approximately 10% of the oxidation products formed from the reaction of α-pinene and ozone.[78−80] As such, it was chosen to investigate the adsorption of additional molecules to the $[(NH_4^+)_4(HSO_4^-)_4(cis\text{-}PA)]$ cluster. Table 2 gives the adsorption free energies (and other relevant thermodynamic potentials) for addition of successive *cis*-pinic acid molecules to the $[(NH_4^+)_4(HSO_4^-)_4(cis\text{-}PA)]$ cluster. These values are computed stepwise, i.e., the free energy changes associated with the general reaction

$$[(NH_4^+)_4(HSO_4^-)_4(cis\text{-}PA)_n] + cis\text{-}PA$$
$$\rightarrow [(NH_4^+)_4(HSO_4^-)_4(cis\text{-}PA)_{n+1}] \quad (2)$$
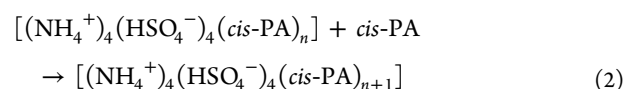
In all, the adsorption of eight successive *cis*-pinic acid molecules were studied, enough to complete two monolayers of adsorption above the bisulfate ions in the original $[(NH_4^+)_4(HSO_4^-)_4]$ salt cluster. We note the values for the free energy in Table 2 do not include a correction for the configurational entropy of the system. The configurational entropy is a function of the number of distinct ways the *cis*-pinic acid molecules can be arranged on the bisulfate ions while maintaining a fixed minimum energy; in this case, it would be a correction term to the entropy calculated via the simulation. For the cluster systems here, the configurational entropy has a value between 3.44 and 4.44 kJ/mol at 298 K (depending on the number of ways to arrange the multiple molecules) and would serve to lower the overall adsorption free energy by that amount. Not including the configurational entropy does not impact the operative conclusions of this work given the order of magnitude of the calculated free energies in Tables 1 and 2.

Figure 2 shows the structure of the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster containing four adsorbed *cis*-pinic acid molecules. Each
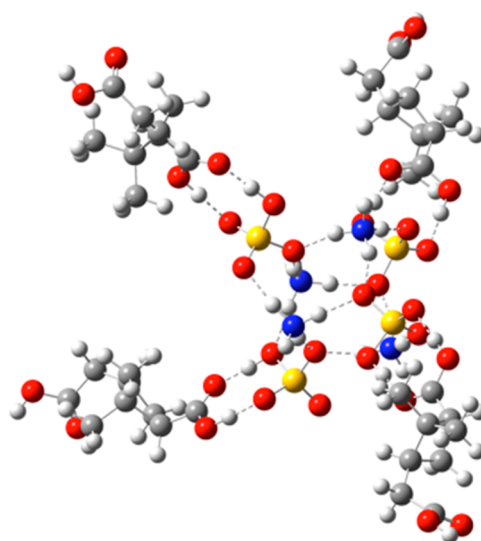

Figure 2. Four *cis*-pinic acid molecules interacting with the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster. Hydrogen bonds indicated by dashed lines. The color scheme is identical to Figure 1. The approximate end-to-end dimension of this structure is 2.7 nm.

molecule interacts with a different bisulfate ion via the α-carboxylic acid functionality in a similar manner to that shown in Figure 1a. The bisulfate ions in the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster adopt a distorted tetrahedral-like structure, which is propagated by the four *cis*-pinic acid molecules in the first adsorption layer. The clusters containing two and three adsorbed molecules are intermediate between the structures in Figures 1a and 2 and are provided in Figure S1 of the Supporting Information. Figure 3 shows the structure of the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster containing eight adsorbed *cis*-pinic acid molecules. Relative to the cluster containing four adsorbed molecules, the addition of molecules 5 through 8 occurs through formation of a second layer via hydrogen bonding of the free carboxylic acid group of a molecule in the first layer with a carboxylic acid group of a molecule in the second layer. There is no evidence for intermolecular hydrogen bonding or

Table 2. Thermodynamic Potentials (kJ/mol) for Adsorption of Successive *cis*-Pinic Acid Molecules (α-Carboxylic Acid) to the $[(NH_4^+)_4(HSO_4^-)_4]$ Cluster^a

$[(NH_4^+)_4(HSO_4^-)_4M_x] + M \rightarrow$	ΔH_{ads}	$T\Delta S_{ads}$	ΔG_{ads}
$[(NH_4^+)_4(HSO_4^-)_4M_1]$	−117.4	−47.0	−70.4
$[(NH_4^+)_4(HSO_4^-)_4M_2]$	−80.0	−42.3	−37.7
$[(NH_4^+)_4(HSO_4^-)_4M_3]$	−86.3	−51.6	−34.7
$[(NH_4^+)_4(HSO_4^-)_4M_4]$	−73.5	−42.8	−30.7
$[(NH_4^+)_4(HSO_4^-)_4M_5]$	−75.8	−51.3	−24.5
$[(NH_4^+)_4(HSO_4^-)_4M_6]$	−75.9	−53.2	−22.7
$[(NH_4^+)_4(HSO_4^-)_4M_7]$	−84.2	−58.0	−26.2

^{a}The data in the first columns correspond to the product of eq 2. Data are computed for the gas phase standard state of 1 atm and 298 K.
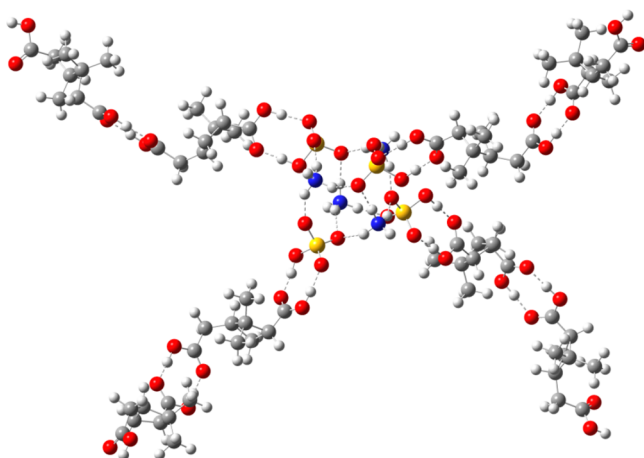
Figure 3. AM1 structure of the largest cluster system studied in this work—the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster interacting with eight *cis*-pinic acid molecules. Hydrogen bonds indicated by dashed lines. The color scheme identical to Figures 1 and 2. The approximate end-to-end dimension of this structure is 3.5 nm.

σ-stacking interaction among the cyclobutane rings or methyl groups of different molecules within the same layer. As discussed previously, the structure in Figure 3 has been optimized only at the AM1 level owing to computational limitations. Clusters containing 5 to 7 adsorbed molecules have structures intermediate between Figures 2 and 3, but with fewer molecules in the second layer. These clusters were optimized at the PW91 level and are provided in Figure S2 of the Supporting Information.

Figure 4, which plots the free energy data listed in Table 2 graphically, shows that the adsorption free energy becomes less favorable for each successive addition of a *cis*-pinic acid molecule in the first layer and then levels off around −25 kJ/mol for each successive addition in the second layer. The horizontal line in Figure 4 corresponds to the free energy change for eq 2 (−59 kJ/mol) that gives a ratio of the product
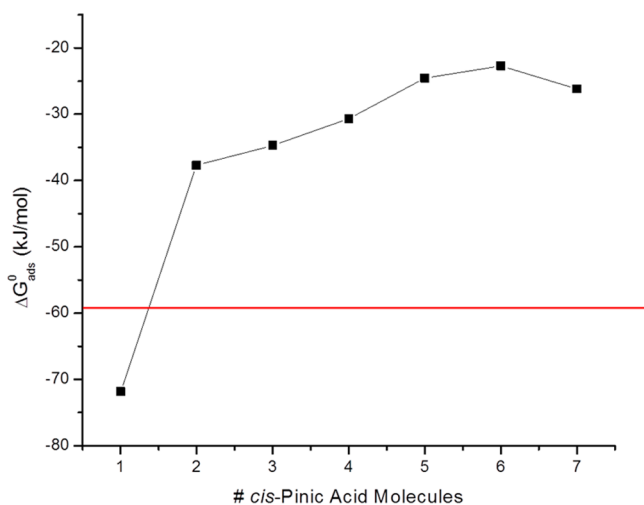

Figure 4. Plot of the free energy of adsorption (kJ/mol) for successive *cis*-pinic acid molecules as a function of total molecules adsorbed, as given by eq 2. The red line gives the free energy of adsorption (−59.3 kJ/mol) where the product cluster concentration is equal to the reactant cluster concentration at equilibrium, assuming a gas phase concentration of 10^8 molecules/cm^3 for *cis*-pinic acid.

cluster to the reactant cluster of 1 at equilibrium when the gas phase concentration of *cis*-pinic acid is 10^8 molecules/cm^3. The difference in free energy between adsorption of the first molecule and subsequent molecules is caused mostly by enthalpy rather than entropy (these values are tabulated in Table 2 along with the free energies). Furthermore, there is no obvious structural change of the $[(NH_4^+)_4(HSO_4^-)_4]$ salt cluster induced by molecular adsorption. Atomic distances in the hydrogen-bonding network between a bisulfate ion and *cis*-pinic acid molecule appears unaffected by number of molecules adsorbed. As noted before, the atomic distances associated with the bisulfate−pinic acid hydrogen bonding interaction are approximately the same as in the *cis*-pinic acid dimer.

The decreasing favorability of adsorption with increasing number of molecules adsorbed in the first (surface) layer is most likely caused by a weakening of the electrostatic interaction between the bisulfate ion and *cis*-pinic acid molecule as successive molecules are adsorbed. The lower favorability of adsorption for these molecules may be thought of as a molecular-scale manifestation of the dependence of surface free energy on particle size, which strongly disfavors adsorption onto small particles. For the second layer of *cis*-pinic acid molecules, the adsorption free energy is similar in magnitude to the formation free energy of a *cis*-pinic acid dimer, −27 kJ/mol.[39]

Atmospheric Implications. Wang and Wexler[63] have suggested that adsorption of organic molecules on the surface of a salt cluster may assist the growth of ambient nuclei. Their classical free energy calculations noted the greatest reduction of the critical saturation ratio of organics over a growing particle at adsorption free energies less than −1 to −8 kJ/mol.[63] While those free energies are higher (less favorable) than those reported here, they suggest that organics must be interacting strongly with the core particle in order to facilitate growth. The molecule-specific results presented here show that the interaction between the bisulfate ion in an ammonium bisulfate cluster and an organic molecule containing a carbonyl functionality is quite strong and able to promote adsorption under typical ambient conditions, even for molecules that from a macroscopic viewpoint, are volatile, i.e., possess a high saturation partial pressure. While carboxylic acids interact most strongly with the bisulfate ion, the interactions of aldehyde and ketone functionalities are also strong enough for adsorption to occur. For the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster studied here, adsorption appears to be confined to a single organic molecule, since the free energies for adsorption of subsequent molecules are much less favorable. Therefore, cluster growth by the sustained uptake of organic molecules is unlikely to occur.

Ambient measurements show that particles smaller than about 1 nm grow slowly at a rate explained by collisions of gas phase sulfuric acid molecules with the particle. It is only above about 1 nm where the growth rate begins to increase sharply with increasing particle size, presumably due to sustained uptake of organic molecules.[22,23] The $[(NH_4^+)_4(HSO_4^-)_4]$ cluster studied here has an effective diameter of about 0.6 nm and appears capable of adsorbing only one organic molecule to produce a cluster of about 1.4 nm in size. The inability of a cluster of this size to uptake additional organic molecules is consistent with an ambient growth rate limited by sulfuric acid uptake.

In the $[(NH_4^+)_4(HSO_4^-)_4]$ cluster, all bisulfate ions reside on the surface, and there is no apparent steric barrier to interaction with an incoming molecule. The largest cluster we

have studied in our previous work is $[(NH_4^+)_{11}(SO_4^-)_{10}]^+$, which has an approximate diameter of ~1.3 nm and contains a fully encapsulated ammonium ion within the particle volume.[26] Smaller charged clusters with 6−10 ammonium bisulfate units have partially encapsulated ions.[26] Therefore, the size at which the growth rate of ambient particles increases rapidly approximately coincides with the onset of ion encapsulation in the computationally derived salt cluster structures. It is possible that salt clusters with encapsulated ion(s) are needed for the strong electrostatic interaction between bisulfate ions and oxygenated organic molecules to extend beyond the adsorption of a single molecule. Alternatively, it may be that the flatter surface of a larger salt cluster permits multifunctional molecules to adopt a configuration on the surface having multiple points of interaction with the surface. Distinguishing these possibilities will require additional calculations with larger ammonium bisulfate salt clusters than was possible in this work.

Sustained uptake of organic molecules onto a multilayer presents a somewhat different challenge at the molecular level. The hydrogen bonding interaction between two carboxylic acid functionalities, one from a molecule in the surface layer and one from a molecule in the multilayer, appears insufficient to grow the multilayer. Multiple points of interaction are needed between the surface layer and incoming molecule, which provides a possible explanation why extremely low volatility organic compounds (ELVOC), which have relatively large molecular sizes and multiple functional groups, are implicated as key growth species for small ambient particles.[9,28] In the work presented here, the $[(NH_4^+)_4(HSO_4^-)_4]$ salt cluster with a complete surface layer of four *cis*-pinic acid molecules is approximately 2.7 nm in diameter and proved too constrained to support multiple points of interaction with a *cis*-pinic acid molecule adding to the multilayer. A larger cluster size and/or incoming organic molecule (e.g., ELVOC) would appear to be needed for multilayer growth.

CONCLUSIONS

Quantum chemical calculations were employed to model the interactions of an ~0.6 nm ammonium bisulfate salt cluster with one or more molecular products of monoterpene oxidation. The interaction between a bisulfate ion in the cluster and a carbonyl functionality of the incoming molecule is sufficient for the molecule to adsorb to the cluster under typical ambient conditions. However, the interaction becomes less favorable for adsorption of additional molecules, suggesting that sustained growth by adsorption of additional organic molecules does not occur for a cluster of this size. Conditions needed for sustained growth are discussed within the context of these calculations and experimental measurements of ambient particle growth. This work provides molecular level insight into particle growth on the scale of nanometers where macroscopic principles and parameters may not apply.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b07744.

Cartesian coordinates, comparisons to experimental free energies, and additional structural comparisons (PDF)

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The authors declare no competing financial interest.

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