

Can Highly Oxidized Organics Contribute to Atmospheric New Particle Formation?

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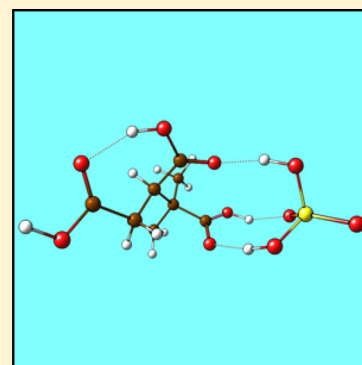
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S Supporting Information

ABSTRACT: Highly oxidized organic molecules may play a critical role in new-particle formation within Earth's atmosphere along with sulfuric acid, which has long been considered as a key compound in this process. Here we explore the interactions of these two partners, using quantum chemistry to find the formation free energies of heterodimers and trimers as well as the fastest evaporation rates of (2,2) tetramers. We find that the heterodimers are more strongly bound than pure sulfuric acid dimers. Their stability correlates well with the oxygen to carbon ratio of the organics, their volatility, and the number of hydrogen bonds formed. Most of the stable trimers contain one sulfuric acid and two organics (1,2), whereas many (2,2) tetramers evaporate quickly, probably due to the stability of (1,2) clusters. This finding agrees with recent experimental studies that show how new-particle formation involving oxidized organics and sulfuric acid may be rate-limited by activation of (1,2) trimers, confirming the importance of this process in the atmosphere.



INTRODUCTION

Atmospheric new-particle formation is an important source of aerosols and cloud condensation nuclei,¹ and there is compelling evidence that sulfuric acid often plays a key role in new-particle formation.^{2,3} On the contrary, sulfuric acid alone cannot explain the new-particle formation rates observed in ambient measurements; binary homogeneous nucleation of sulfuric acid and water is many orders of magnitude too slow over the range of sulfuric acid vapor observed in the atmosphere during new-particle formation events.^{4,5} This indicates that in addition to sulfuric acid some other compounds must be involved in atmospheric new-particle formation.

The identity of these stabilizing compounds has been the subject of several studies recently. Because sulfuric acid is such a strong acid, ternary new-particle formation involving base molecules has been one of the most studied alternatives to sulfuric acid–water binary mechanism.^{6–9} Ammonia is the base most often considered because of its ubiquity in the atmosphere and prevalence in fine particles,^{10,11} but even ternary nucleation involving ammonia is about 2 orders of magnitude too slow to explain observed new-particle formation rates at temperatures and concentrations typical of the planetary boundary layer.^{4,5} Stronger bases such as dimethylamine can drive ternary nucleation rapidly enough to explain rates observed in the atmosphere,¹² but ambient observations of cluster composition show that oxidized organics can dominate the cluster

composition¹³ especially when considering that the gaseous concentration of amines in the atmosphere is typically several orders of magnitude lower than that of oxidized organic compounds.

Highly oxidized organic molecules produced by oxidation of volatile organic compounds (VOCs) have also been proposed to be central compounds in new-particle formation. Some studies have suggested that these oxidized VOCs are only involved in particle growth,¹⁴ whereas others have indicated that they are involved only in the very first steps of new-particle formation but not in subsequent growth.¹⁵ Some studies suggest that oxidized organics are involved in both formation and growth.¹⁶ It is important to note that “organics” constitutes potentially thousands, or even tens of thousands of molecules with an array of properties;¹⁷ it is thus possible that studies relying on one or a few surrogate molecules may miss the full range of behaviors displayed by oxidized organics as a family.

An additional challenge to describing the potential role of oxidized organics in new-particle formation is the evident ubiquity of sulfuric acid in the process.¹⁸ Bases such as ammonia and dimethylamine are extremely volatile and nowhere near saturation in the atmosphere; it is their chemical

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interaction with sulfuric acid via acid–base chemistry that allows them to play a role in particle formation. However, that clearly requires a very strong acid. For example, there is no evidence that nitric acid participates in ambient new-particle formation. The oxidized organics, on the contrary, presumably interact with sulfuric acid by forming strong hydrogen bonds. That same hydrogen bonding ability will also cause the organics themselves to have very low vapor pressures.^{19,20} The oxidized organics would thus be likely to form particles by themselves, without involving sulfuric acid. A successful description thus has to explain not only the ability of oxidized organics to stabilize sulfuric-acid clusters but also the apparent absence (or at least rareness) of pure organic clustering in the present-day atmosphere.

Here we report quantum chemical results on clustering of sulfuric acid and oxidized organic compounds (OxOrg) molecules. We have chosen six oxidation products of α -pinene with increasing oxygen to carbon ratios (O:C): pinanediol ($C_{10}H_{18}O_2$), pinonic acid ($C_{10}H_{16}O_3$), 10-hydroxypinonic acid ($C_{10}H_{16}O_4$), pinic acid ($C_9H_{14}O_4$), diketodicarboxylic acid (DKDCA) ($C_{10}H_{14}O_6$), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) ($C_8H_{12}O_6$). The products span a wide range of volatility, with two (pinanediol and pinonic acid) qualifying as intermediate volatility (IVOC) with saturation concentration (C^*) $\gtrsim 300 \mu\text{g}/\text{m}^3$, two (pinic acid and 10-hydroxypinonic acid) qualifying as semivolatile (SVOC) with $C^* \approx 3 \mu\text{g}/\text{m}^3$, and two (diketodicarboxylic acid and MBTCA) qualifying as low volatility (LVOC)²¹ with $C^* \lesssim 0.3 \mu\text{g}/\text{m}^3$.

THEORETICAL METHODS

We have used the methodology described in Ortega et al.²² to calculate the formation Gibbs free energies of different sulfuric acid–OxOrg clusters. This methodology combines a geometry optimization and frequency calculation with the B3LYP hybrid functional²³ and the CBSB7 basis set²⁴ using the Gaussian09 program,²⁵ with a single-point electronic energy calculation using the RI-CC2 method²⁶ and the aug-cc-pV(T+d)Z basis set²⁷ using the TURBOMOLE program.²⁸ The results obtained with this methodology for pure sulfuric acid clusters are in good agreement with the experimental values reported.²⁹ On the contrary, the method tends to overestimate the stability of sulfuric acid clusters involving base molecules.³⁰ The results obtained in this work for pinic acid are in good agreement with other recent theoretical studies.³¹ In any case, this methodology has been used successfully to interpret different experimental studies.^{12,32,33} It should be noted as well that the final aim of this work is to compare the behavior of different organic compounds rather than to provide absolute formation energies.

In the case of heterodimers, we have used their formation Gibbs free energies to evaluate their stability. In the case of trimers, we have used the formation Gibbs free energies to calculate the addition energy of a sulfuric acid or an OxOrg monomer to the heterodimer to evaluate the most favorable path. Tetramers containing 2 sulfuric acids and 2 identical OxOrg molecules (2,2) can be formed via several pathways, so to evaluate their stability, we have calculated the evaporation rate of these clusters through different pathways based on their formation Gibbs free energy.

The evaporation rate, $\gamma(N_{i+j})$, of a certain molecule or cluster, N_i , from the cluster N_{i+j} is linked to the Gibbs formation free energies through eq 1²²

$$\gamma_i(N_{(i+j)}) = \beta_{ij} c_{\text{ref}} \exp((\Delta G(N_{(i+j)}) - \Delta G(N_i) - \Delta G(N_j)) / kT) \quad (1)$$

where β_{ij} is the kinetic gas theory collision rate of N_i with N_j ; $\Delta G(N_{i+j})$, $\Delta G(N_i)$, and $\Delta G(N_j)$ are the Gibbs free energies of formation of clusters N_{i+j} , N_i , and N_j from monomers at the reference vapor concentration c_{ref} (in this case c_{ref} is equal to 101 325 Pa); k is the Boltzmann constant and T is the temperature (298 K). It must be noted that in the case where either N_i or N_j is a monomer (or both are), $\Delta G(N_i)$ or $\Delta G(N_j)$ is by definition zero. In the specific case of the (2,2) cluster, we have considered all possible pathways for its evaporation: (2,1) + (0,1), (2,0) + (0,2), (1,1) + (1,1), and (1,2) + (1,0).

The collision rate, β_{ij} , depends on the cluster volume. To calculate this volume, we have assumed an ideal solution in which partial molecular volumes of each substance are independent of the liquid composition. The volume is then calculated using the mass and density of each compound forming the cluster. The density of most of the organic compounds studied in this work is unknown, so as an approximation, we have used the density of pinonic acid (1220 kg m^{-3}) for all OxOrg compounds. In any case, the error induced by this choice is minor.²²

RESULTS AND DISCUSSION

We have calculated the formation free energy of each heterodimer formed by one sulfuric acid molecule and one oxidized organic molecule. Figure 1 shows the most stable conformer for each heterodimer.

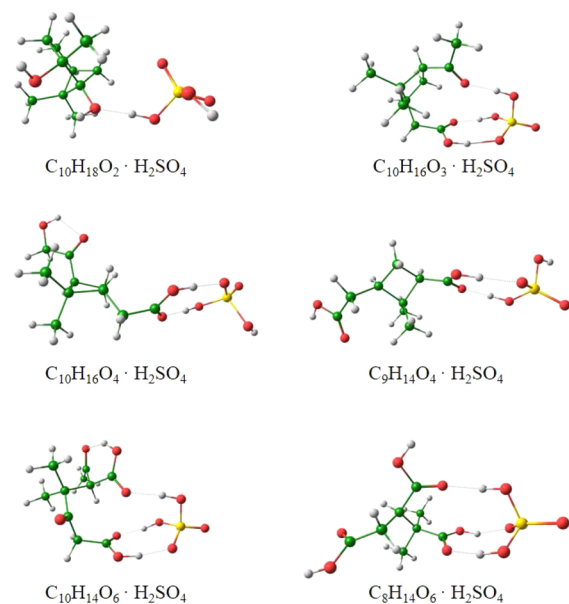


Figure 1. Most stable conformer for each of the sulfuric acid–OxOrg heterodimers studied. Red spheres represent oxygen atoms, yellow spheres represent sulfur atoms, white spheres represent hydrogen atoms, and green spheres represent carbon atoms.

Simplified atmospheric models employ either the oxygen to carbon ratio (O:C), defined as the number of oxygen atoms divided by number of carbon atoms in the compound,^{19,20} or the average carbon oxidation state, defined as 2 times O:C minus the hydrogen to carbon ratio (H:C),¹¹ as a rough measure to track the oxidation behavior of thousands of organic

compounds comprising organic aerosols in the atmosphere. Our calculations show that, in general, when the O:C of the OxOrg increases, the formation of an OxOrg–sulfuric acid heterodimer is favored (Figure 2). The only exception to a very

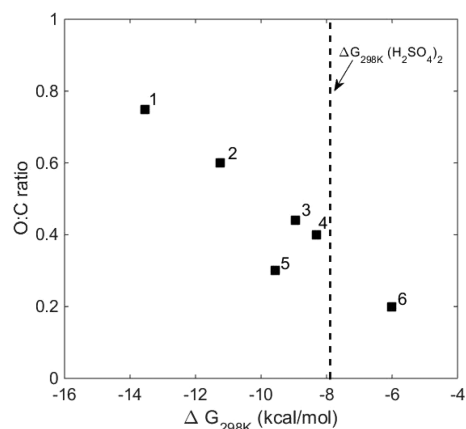


Figure 2. Formation free energies of different heterodimers of oxidized organics with sulfuric acid versus O:C for the oxidized organics: (1) MBTCA, (2) DKDCA, (3) pinic acid, (4) 10-hydroxypinonic acid, (5) pinonic acid, and (6) pinanediol. The dotted line indicates the formation free energy for the sulfuric acid dimer as reference.

tight trend is pinonic acid, which can form more stable heterodimers than pinic and 10-hydroxypinonic acids, though it has a lower O:C. Most OxOrg heterodimers are more stable than the sulfuric acid homodimer, though the latter is for practically all atmospheric conditions stabilized by a few kcal/mol due to hydration.³⁴ DKDCA and MBTCA heterodimers are significantly more stable than even hydrated sulfuric acid dimers. The pinanediol heterodimer is the only one in the group that is less stable than the sulfuric acid homodimer. This is not surprising because pinanediol can only form one hydrogen bond with the sulfuric acid molecule.

In Figure 3 we plot the formation free energy of the heterodimers versus the volatility of each oxidized organic, calculated using the SIMPOL group contribution method that also underlies the volatility basis set.²⁰ There is a correlation between decreasing volatility and increasing cluster stability, again with the exception of pinonic acid. We also include the pure sulfuric acid homodimer, assuming a H_2SO_4 saturation vapor pressure (in the absence of water) of 5.1×10^{-4} Pa.³⁵ Sulfuric acid has an extremely low effective volatility because H_2SO_4 almost always dissociates in bulk solutions, unless the water activity is very low. The results indicate that highly oxidized organic compounds can indeed form strongly bound clusters with sulfuric acid, and also that volatility is a reasonable surrogate for this capability when specific chemical identities of the clustering molecules are unknown.

One of the most important driving forces for the formation of heterodimers is the ability of different organic compounds to form hydrogen bonds with the sulfuric acid molecule. Figure 4 shows how the number of H-bonds formed in the heterodimers is related to the heterodimer formation free energy. This explains the special behavior of pinonic acid, because despite a relatively low O:C it is able to form three hydrogen bonds with sulfuric acid.

As can be seen in Figure 1, the MBTCA heterodimer can form three hydrogen bonds whereas the DKD heterodimer can form four (including one intramolecular H-bond). Despite this,

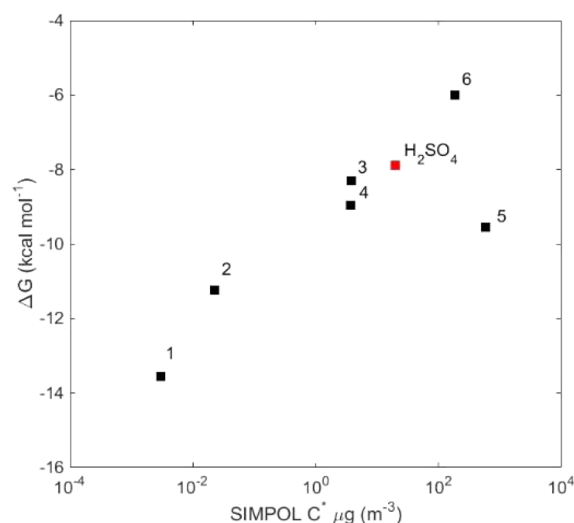


Figure 3. Formation free energies of different oxidized organic-sulfuric acid heterodimers studied versus volatility of the oxidized organic: (1) MBTCA, (2) DKDCA, (3) pinic acid, (4) 10-hydroxypinonic acid, (5) pinonic acid, and (6) pinanediol. The H_2SO_4 dimer is included as a reference (red square).

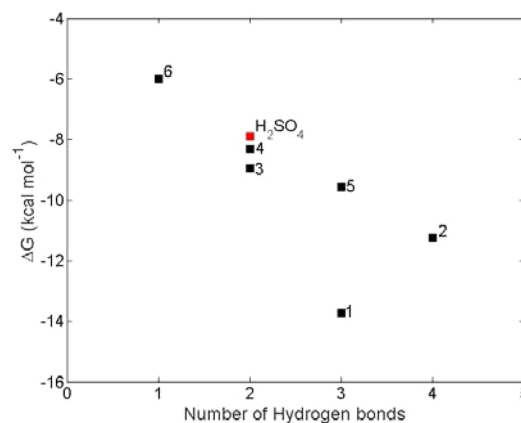


Figure 4. Formation free energies of different heterodimers versus number of hydrogen bonds formed: (1) MBTCA, (2) DKDCA, (3) pinic acid, (4) 10-hydroxy-pinonic acid, (5) pinonic acid, and (6) pinanediol. H_2SO_4 dimer is included as a reference (red square).

the MBTCA heterodimer is 2.5 kcal/mol more stable than the DKDCA heterodimer. The electronic energies and enthalpies for the formation of the DKDCA heterodimers are both more negative than those of the MBTCA, consistent with the number of hydrogen bonds. The difference in ΔG comes from the much higher formation entropy contribution for the DKDCA heterodimer (-49.99 cal/mol), presumably caused by the strained structure. In comparison, the formation entropy for the MBTCA heterodimer is only -36.63 cal/mol. This implies that formation of DKDCA heterodimers will be more favorable than the formation of MBTCA heterodimers at lower temperatures. Nevertheless, the temperature needed for the DKDCA heterodimer to become more stable than the MBTCA heterodimer is 112 K, far below atmospheric conditions.

It is clear that highly oxidized organics can form strongly bound clusters with sulfuric acid, but we also need to understand why sulfuric acid is required at all for atmospheric new-particle formation; many but not all of the molecules studied here have an extremely low vapor pressure, and so in

some circumstances should nucleate on their own. To address this, we calculated the excess free energy of the heterodimers (Table 1). The excess free energy (eq 2) is defined as the

Table 1. Excess Free Energies (kcal/mol) Calculated for Different Compounds Included in This Study

compound	O:C	heterodimer $\Delta G_{298\text{ K}}$	(OxOrg) ₂ $\Delta G_{298\text{ K}}$	excess free energy
MBTCA	0.75	-13.72	-6.17	-6.59
DKDCA	0.6	-11.24	-3.66	-5.47
pinic acid	0.44	-8.96	-8.55	-0.74
10-hydroxypinonic acid	0.4	-8.31	-4.57	-2.08
pinonic acid	0.3	-9.56	-2.51	-4.36
pinanediol	0.2	-6.01	-1.63	-1.24

difference between the formation free energy of the heterodimer and the average of the formation free energy of oxidized organics and pure sulfuric acid homodimers³⁶ (7.89 kcal/mol²²).

$$\Delta G_{\text{xs}} = \Delta G_{(1,1)} - ((\Delta G_{(2,0)} + \Delta G_{(0,2)})/2) \quad (2)$$

A negative excess free energy indicates that the mixture is more stable than either of the pure substances (the activity coefficient, $\exp^{(-\Delta G_{\text{xs}}/RT)} < 1$). The excess free energies of the heterodimers are strongly negative. It is worth noting that for all of the systems studied here, the formation free energy of the pure oxidized organic dimer is lower (less negative) than the formation free energy of sulfuric acid dimer, and for all systems except pinanediol, the formation free energy of the heterodimers is higher (more negative) than either the pure sulfuric acid or the pure oxidized organic clusters. Thus, formation of the heterodimers is very strongly favored.

A stable dimer does not make a particle unless it can continue to grow. To study the subsequent growth of the heterodimers, we use a combination of approaches. In Table 2 we compare the addition free energies of sulfuric acid and a second OxOrg to the heterodimers.

Table 2. Addition Energies (kcal/mol) of H₂SO₄ or OxOrg to the Different Heterodimers Studied^a

compound in the heterodimer	O:C	$\Delta G_{\text{addition OxOrg}}$	$\Delta G_{\text{addition H}_2\text{SO}_4}$
MBTCA	0.75	-9.48	-7.68
DKDCA	0.6	-12.08	-7.33
Pinic acid	0.44	-11.78	-8.39
10-hydroxypinonic acid	0.4	-6.26	-8.10
pinonic acid	0.3	-7.36	-6.62
pinanediol	0.2	-7.88	-6.07

^aThe most favorable addition for each compound is marked in bold.

The addition of a second molecule of OxOrg is more favorable than addition of sulfuric acid for all heterodimers except for those formed by 10-hydroxypinonic acid. Most probably the reason for this difference is the presence of an internal hydrogen bond in the monomers of 10-hydroxypinonic acid that is broken in the case of (1,2) cluster but not in the (2,1) cluster. In reality, the path followed by a growing heterodimer will be determined not only by the energetics of the process but also by the concentration of sulfuric acid compared to the concentration of OxOrg. Even if the addition energy favors one of the compounds, the concentration ratio

can favor the other, thus dictating the clustering path. Furthermore, it is extremely unlikely that the same OxOrg molecule would add to a heterodimer in the atmosphere, but rather a multicomponent structure would result. Determining the actual clustering pathways would require running a cluster kinetic model under a wide range of conditions, which is beyond the scope of this work. However, our finding that clusters with two OxOrg molecules and one sulfuric acid molecule are favored over other types of trimers is consistent with observations reported from the CLOUD chamber involving oxidation products of pinanediol in the presence of sulfuric acid.^{13,33}

As can be seen from Table 2, the addition energies of sulfuric acid to various heterodimers are very similar. Moreover, they are comparable to the formation energy of the pure sulfuric acid dimer. In other words, the presence of the OxOrg molecule does not enhance the addition of two sulfuric acid molecules. There is also not a clear correlation between the addition energies of the second OxOrg molecule to the heterodimer and O:C. However, the compounds studied are divided in two groups when it comes to the second OxOrg addition energy: one group formed by 10-hydroxypinonic acid, pinonic acid, and pinanediol, with addition energies between -6.26 and -7.86 kcal/mol, and a second group formed by MBTCA, DKDCA, and pinic acid, with addition energies between -9.65 and -12.08 kcal/mol. The reason for this separation into two groups is likely the number of carboxylic acid moieties present in the OxOrg forming the heterodimer. The first group of compounds has either zero or one carboxylic acid moiety whereas the second group of compounds has two or three carboxylic acid moieties. For example, pinic acid and 10-hydroxypinonic acid have the same O:C but the addition energy of the second OxOrg molecule to the heterodimer for pinic acid is almost 2 times larger than for 10-hydroxypinonic acid. On the contrary, if we compare the addition energies of the different compounds in the second group, the heterodimer formed by MBTCA has the least favorable addition energy among them, despite having three carboxylic acid moieties and the highest O:C. This is probably because of the high stability of the heterodimer formed by MBTCA. Combined, these results suggest that for continued growth, the oxidized organic molecule forming the cluster must have a sufficient number of hydrogen-bonding moieties to enable strong bonding with multiple molecules.

In the case of tetramers containing 2 sulfuric acids and 2 identical OxOrg molecules (2,2), we calculated the evaporation rate of these clusters through different pathways. Table 3 shows the highest evaporation rate for each (2,2) cluster studied.

The results are surprising. In the case of MBTCA the 2,2 cluster is relatively stable as expected by its high O:C, suggesting that continued growth of sulfuric acid-MBTCA

Table 3. Evaporation Rates at 298 K for Different (2,2) Clusters Studied

compound in the (2,2) cluster	O:C	evaporation rate (s ⁻¹)	evaporating molecule/cluster
MBTCA	0.75	1.2 × 10 ¹	H ₂ SO ₄ -OxOrg
DKDCA	0.6	3.9 × 10 ⁶	H ₂ SO ₄
pinic acid	0.44	5.8 × 10 ¹	H ₂ SO ₄
10-hydroxypinonic acid	0.4	2.8 × 10 ⁵	OxOrg
pinonic acid	0.3	6.4 × 10 ⁵	H ₂ SO ₄ -OxOrg
pinanediol	0.2	0.71	H ₂ SO ₄

clusters will be favorable. On the contrary, the (2,2) cluster formed by DKDCA is extremely unstable. This is because the (1,2) $\text{H}_2\text{SO}_4 \cdot (\text{OxOrg})_2$ cluster is exceptionally stable. To fully assess the implication of this to overall growth process would require a cluster kinetic study, but we expect a high concentration of (1,2) clusters in a steady state. Another surprise is the high stability of the (2,2) cluster formed by pinanediol. In this case, pinanediol acts as a base. When only a few molecules are present in the cluster, there is no proton transfer and the cluster is not stable. However, for larger clusters, starting from size (2,2), a proton can transfer from sulfuric acid to pinanediol (Figure 5).

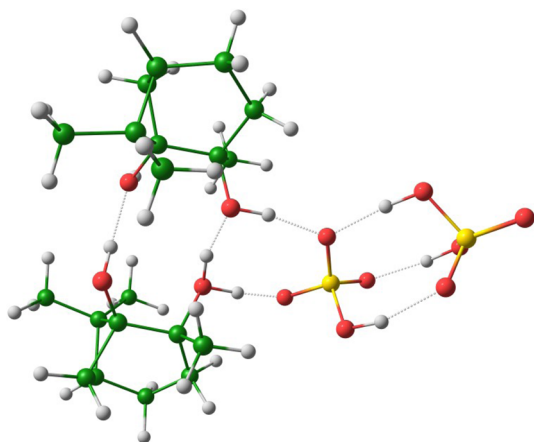


Figure 5. Most stable conformer for $(\text{C}_{10}\text{H}_{18}\text{O}_2)_2 \cdot (\text{H}_2\text{SO}_4)_2$, where a proton from sulfuric acid has been transferred to the OH group in one of the pinanediol molecules. Red spheres represent Oxygen atoms, yellow spheres represent Sulfur atoms, White spheres represent Hydrogen atoms and Green spheres represent carbon atoms.

Something similar happens in the case of $\text{H}_2\text{SO}_4\text{--NH}_3$; a cluster requires at least two sulfuric acid molecules to undergo proton transfer. But when the cluster reaches size (2,1), the proton transfer leads to a large stabilization of the cluster. The absence of proton transfer in the smallest clusters is why sulfuric acid–ammonia ternary nucleation is much slower than suggested by parametrizations based on bulk thermodynamics.³⁷ It seems unlikely that pinanediol concentrations would reach sufficient levels in the atmosphere for this unusual acid–base chemistry to be important—it is much more likely that stronger bases like ammonia or amines play this role—but it does indicate a need for caution and careful analysis under laboratory conditions.

CONCLUSIONS

We have shown that oxidized organic compounds with a high O:C are able to form stable clusters with sulfuric acid. This implies that they can be involved in new-particle formation. The presence of carboxylic acid groups favors the formation of a heterodimer over either pure sulfuric acid or pure organic dimers. The most stable heterodimer for the set of compounds examined here is formed between sulfuric acid and MBTCA, a tricarboxylic acid. There is a clear correlation between the number of hydrogen bonds formed and the stability of the clusters. To confirm the possible participation of oxidized organics in new-particle formation in the future, we will extend the calculations to larger clusters and conduct dynamic calculations of cluster formation and evaporation.

In the atmosphere and even in laboratory experiments where OxOrg formation is driven by oxidation chemistry, it is likely that clusters beyond the (1,1) heterodimers contain multiple different OxOrg molecules. Comprehensive treatment of these systems for even a small number of OxOrg molecules is still prohibitively expensive computationally, and so simplified treatments remain necessary. The results presented here show that although individual OxOrg molecules behave in unique ways, the general features required for formation of stable heterodimers and subsequent cluster growth are related to a sufficiency of hydrogen bonding sites.

The OxOrg species considered here constitute a set of molecules conventionally associated with α -pinene SOA,³⁸ and the least volatile of them, MBTCA, falls at the volatile end of the ELVOC range.¹⁶ Recent field and laboratory observations have identified a novel “auto oxidation” pathway associated with isomerization of peroxy radicals that produces ELVOC with multiple peroxide groups.^{39–41} This new class of organic oxidation products is likely to display the same general behavior as described here, including strong hydrogen bonding with sulfuric acid, which explain the correlation between observed new-particle formation rates and both sulfuric acid and organics in both the laboratory^{13,33} and the atmosphere.⁴²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b07427.

Cluster energies and coordinates (PDF)

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