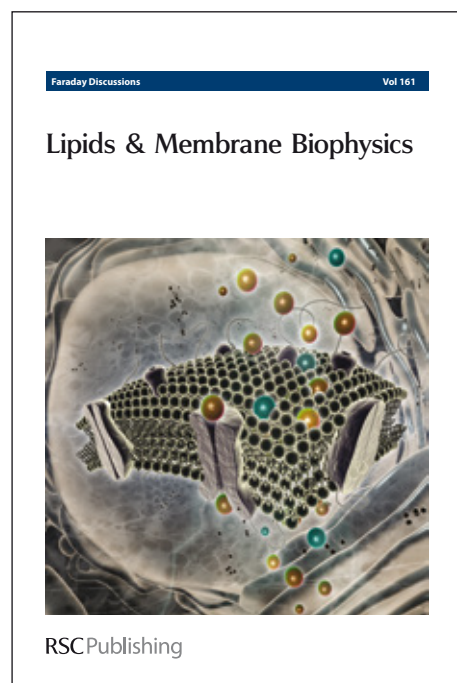


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How Do Organic Vapors Contribute to New-Particle Formation?

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/c000000x

Highly oxidised organic vapors can effectively stabilize sulphuric acid in heteronuclear clusters and drive new-particle formation. We present quantum chemical calculations of cluster stability, showing that multifunctional species can stabilize sulphuric acid and also present additional polar functional groups for subsequent cluster growth. We also model the multi-generation oxidation of vapors associated with secondary organic aerosol formation using a two-dimensional volatility basis set. The steady-state saturation ratios and absolute concentrations of extremely low volatility products are sufficient to drive new-particle formation with sulphuric acid at atmospherically relevant rates.

1 Background

New-particle formation is the dominant source of particle number in the atmosphere,^{1–4} and a sufficient number of nucleated particles survive and grow large enough to make new-particle formation a globally important source of cloud condensation nuclei (CCN).^{5,6} CCN levels and their changes over time in turn constitute a major source of uncertainty in climate forcing.

There is strong evidence that new-particle formation in the atmosphere is associated with sulphuric acid vapor,^{4,7–9} suggesting that sulphuric acid (H₂SO₄, or SA) is almost always present in the smallest molecular clusters. An exception is coastal regions with abundant iodine.¹⁰ Observed new-particle formation rates cover the range $0.1 < J_{1.5} < 1000 \text{ cm}^{-3} \text{ s}^{-1}$ over a sulphuric acid vapor

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concentration $10^6 < [\text{SA}] < 10^8 \text{ molec cm}^{-3}$, where $J_{1.5}$ is the appearance rate of particles at 1.5 nm mobility diameter.^{11,12} The two are highly correlated, with $J_{1.5}$ vs $[\text{H}_2\text{SO}_4]$ showing a log-log slope between 1 and 2, but also showing variability of more than 1 order of magnitude at any given $[\text{SA}]$. Over this same range, the sulphuric acid collision rate (J_{SA}) ranges from $10^2 < J_{\text{SA}} < 10^6 \text{ cm}^{-3} \text{ s}^{-1}$. There are also strong indications that organic compounds may be involved in the nucleation^{13,14} and growth¹⁵ of the smallest clusters. Here we shall explore the role of organics, focusing on the potential for gas-phase oxidation to generate organic compounds that can enhance new-particle formation and growth.

A significant challenge regarding oxidised organic compounds is the huge number of different compounds present in the atmosphere.^{16,17} Thus, if organics are involved in nucleation and/or growth of the smallest molecular clusters, it is important to identify the critical properties of those organics, and probably to understand how the diversity of compounds and properties influences the role of organics.

The diversity of organic properties is also important to the formation and attributes of secondary organic aerosol (SOA). One approach to confronting the diversity of ambient organic compounds is to group them based on their vapor pressure (volatility), using a formalism known as the Volatility Basis Set (VBS).¹⁸ The VBS emerged from a paper in the Atmospheric Chemistry Faraday Discussion (130) that identified the continuous effect of oxidation chemistry on the organic volatility distribution as a potentially critical part of the SOA atmospheric lifecycle.¹⁹ That work also identified multi-generation gas-phase oxidation of organics as a potentially important source of extremely low volatility compounds (ELVOC),¹⁹ which has subsequently been verified in experimental studies designed to isolate later-generation aging effects.^{20,21} Those ELVOC will play a prominent role in this work.

In the VBS, organics are grouped in decadal spaced “volatility bins” for both SOA production^{22,23} and Primary Organic Aerosol (POA) emission,^{24,25} and the chemical evolution can be modeled with simplified mechanisms.²⁶ However, the single dimension of volatility is ill suited to describing progressive oxidation, and so a second dimension describing oxidation has been discussed, using either the mean oxidation state of carbon $\overline{\text{OS}}_C = 2\text{O}:\text{C}-\text{H}:\text{C}$,^{17,27} or the oxygen to carbon ratio (O:C).^{28–30} The 2D-VBS ansatz is that pure-component volatility (C°) and carbon oxidation state ($\overline{\text{OS}}_C$) alone can reasonably describe the properties of the highly complex mixture of organic molecules comprising organic aerosol, though there may be hundreds of thousands of different organic compounds involved. A corollary, however, is that the diversity of properties of the organics (for example the volatility distribution) is itself fundamentally important to organic-aerosol behaviour.

While the VBS was formulated to represent the bulk equilibrium thermodynamics of OA partitioning, it also can be used to represent the dynamics of organic condensation, including the effect of curvature on net condensation for very small particles.³¹ It is not obvious that saturation vapor pressure alone should describe the interactions of oxidised organic compounds and sulphuric acid in the smallest clusters of only a few molecules, where specific hydrogen bonding interactions are likely to dominate. However, here we shall consider the possibility that volatility and oxidation state together are also a reasonable indicator of the

degree to which organics can contribute to new-particle formation.

2 Theory

The essential features of condensation to a bulk phase were presented in the units common to organic-aerosol dynamics by Donahue *et al.*³¹ The net flux of a compound labeled i to unit surface area of a particle is:

$$F_i = v_D \alpha_i [C_i^v - a_i K C_i^o] = v_D C_i^o \alpha_i [S_i - a_i K(D_p)] \quad (1)$$

Where v_D is a characteristic condensation velocity, α_i is the mass accommodation coefficient of the molecule on the surface (typically assumed to be 1), C_i^v is the vapor-phase mass concentration, and C_i^o is the saturation concentration. S_i is the saturation ratio, $S_i = C_i^v/C_i^o$, and a_i is the activity of the species at the condensed-phase surface.

The velocity (for diameter change) in Eq. 1 for a 200 g/mole compound with a density of 1.4 g/cc is: $v_D = 0.226 \text{ (nm hr}^{-1}) / \text{(ng m}^{-3})$. We use units of nm hr^{-1} because growth rates during new-particle formation events are expressed in those units, typically ranging from 1-10 nm hr^{-1} depending on particle size and ambient conditions.^{4,32} In addition, the condensation sink for vapors to particle surfaces ranges from 0.1-100 hr^{-1} under a wide range of conditions in the atmosphere.^{11,33,34} Eq. 1 is fundamentally about evaporation, and an important scaling can be found by assuming that a surface monolayer changes diameter by about 0.8 nm, this means that a species with a concentration of $C^o \sim 4 \text{ ng m}^{-3}$ will cause condensation at a rate of approximately 1 monolayer per hour. If this species is in equilibrium, it also indicates a characteristic molecular evaporation lifetime of 1 hr from a flat surface.

The term $K(D_p)$ describes the Kelvin effect, the increase in the equilibrium saturation concentration, for particles with diameter D_p . This scales with a "Kelvin Diameter", D_K . Assuming a surface tension $\sigma = 0.03 \text{ N m}^{-1}$:

$$K = \exp(D_K/D_p); D_K = (4\sigma M) / (RT\rho) \simeq 7 \text{ nm} \quad (2)$$

Thus, at the bulk limit, 3 nm diameter spheres (containing roughly 64 molecules with a molar weight of 200 g/mole and a density of 1.5 g/cc) will increase volatility by 1 order of magnitude and 1.5 nm spheres (with roughly 8 molecules) would increase volatility by 2 orders of magnitude, were bulk behavior a sensible descriptor for such a tiny object.

The Kelvin term is central to classical nucleation theory,³⁵⁻³⁷ as any sphere in a single-component system with $S_i > K(D_{\text{crit}})$ will grow without limit, and nucleation is governed by the equilibrium distribution of particles with $D_p = D_{\text{crit}}$ at that given S_i . Furthermore, for new-particle formation in the atmosphere, supersaturation is governed in almost all cases by a steady state between chemical production of condensable vapors and condensational loss of those vapors to larger background aerosol particles, which dominate the overall surface area.

While the surface tension $\sigma = 0.03 \text{ N m}^{-1}$ is typical of many organic compounds, independent of polarity,³⁸ its role here is more for illustration than calculation. We do not know the structure of condensing organic compounds, and as we shall argue their interactions with sulphuric acid molecules are of paramount

importance; thus D_K effectively subsumes uncertain properties into a single albeit rough scaling factor. It is more important that accurate quantum chemical calculations are becoming feasible for molecular clusters similar in size to that expected for $K(D_p) \simeq 100$.³⁹ It is thus now possible to probe interactions at the Kelvin scale computationally and to eliminate unphysical extrapolations of bulk properties.

Multi-component nucleation is more complicated, but at the classical limit largely reduces to calculation of the activity coefficient γ_i for small clusters with rapidly changing composition. However, the logical starting point is for a more or less ideal mixture, where $\gamma_i = 1$. This is an especially sensible when considering highly oxidised, low-volatility organic vapors that one might find in the atmosphere. There are thousands of different molecules^{16,17} associated with organic aerosols, and so we must resort to broad average properties to render the problem tractable (and, conversely, if average properties are not valid and instead only a few select molecular types participate in new-particle formation, then the formation rate would be inconsequential).

For bulk organic aerosol conditions, organics with O:C > 0.33 and low volatility ($C^o < 300 \text{ ng m}^{-3}$) will on average have activity coefficients very near 1 in the organic mixture.²⁸ Assuming a very rich mixture of molecules, we can usefully define an *effective* saturation ratio

$$S_i^{\text{eff}} = \frac{1}{C_i^o} \sum_j^{C_j^o \leq C_i^o} C_j^{\text{vap}} \quad (3)$$

To the extent that these compounds do form an ideal mixture, an effective supersaturation over some critical threshold, broadly between 10 and 1000 (a few molecules), would ensure “quasi-homogeneous” nucleation of purely organic particles.

More scaling is in order for these units. A mass concentration of 3 ng m^{-3} is equivalent to a mass fraction of 3 ppt, and if these molecules have a molar weight of order 300 g/mole, that corresponds to a mole fraction of 3×10^{-14} , or a number density of roughly 10^7 molecules cm^{-3} at STP. In this discussion we will assume a collisional rate constant for relatively heavy molecules of order $k_{\text{col}} \simeq 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} = 3.6 \times 10^{-7} \text{ cm}^3 \text{ molec}^{-1} \text{ hr}^{-1}$. Thus molecules and small clusters will collide with condensible molecules that have a concentration of 10^7 molecules cm^{-3} with a frequency of 10^{-3} s^{-1} , or 3.6 hr^{-1} .

If we consider that all compounds likely to be involved in nucleation are of sufficiently low volatility that they stick to background aerosols with nearly unit probability, then the steady-state concentration of these “nucleator” vapors will be given by the simple steady-state relation:

$$C_i^{\text{ss}} = \frac{P_i}{CS}; \quad S_i^{\text{ss}} = \frac{P_i}{CS C_i^o} \quad (4)$$

If we consider an arbitrary threshold of 0.3 ng m^{-3} ($10^6 \text{ molec cm}^{-3}$) for a saturation concentration and $S = 10$ for a critical saturation ratio for organics to participate in new-particle formation, along with a condensation sink of 10 hr^{-1} , condensible organic vapors would need to have a production term $P_i =$

$30\text{ ng m}^{-3}\text{ hr}^{-1}$. This is a small fraction of the secondary organic aerosol formation rate.

Organic vapors will certainly nucleate quasi-homogeneously when S^{eff} rises to some critical value. However, under atmospheric conditions that homogeneous organic nucleation rate may be negligible. Because of the strong indications that sulphuric acid is involved in atmospheric new-particle formation, it is likely that the activity coefficient for mixtures of sulphuric acid and the relevant organics is significantly less than 1, allowing nucleation at much lower values of S^{eff} . It is also almost certain that water molecules are present in the small clusters. However, ambient observations reveal no strong dependence of observed new-particle formation attributable to relative humidity,⁴⁰ nor does bulk SOA show a strong humidity dependence in the laboratory⁴¹ or and the field (below 80% RH).⁴² Consequently, because the treatment here is semi-empirical, we shall overlook the role of water vapor until there is empirical evidence of an important role.

3 New-Particle Formation and sulphuric Acid

Stipulating that sulphuric acid vapors are involved in the formation of nucleating clusters, the variability in observed new-particle formation rates is thus likely driven by varying levels of stabilizing agents for sulphuric acid clusters. Those stabilizing agents may be bases (ammonia or amines)^{3,43} or oxidised organic vapors,^{14,44} among other things, though here we are focused on the potential role of hydrogen bonding oxidised organic vapors. If two sulphuric acid molecules are typically involved in very small clusters, we can define an operational new-particle formation rate:

$$J_{\text{npf}} = f_{\text{npf}} k_{\text{col}} [\text{SA}]^2; \quad 0.0003 \leq f_{\text{npf}} \leq 0.03 \quad (5)$$

where f_{npf} described the fraction of the sulphuric acid dimer formation rate that ends up with new-particle formation (the apparent survival probability of sulphuric acid dimers).³ Consequently, in this discussion we shall explore two related hypotheses: organic vapors are (or can be) intimately involved in each step of new-particle formation and growth; or, inorganic sulphate salts form seeds for heterogeneous nucleation of organic vapors at very small sizes ($D_p \ll 3\text{ nm}$).

New-particle formation rates are typically specified for mobility diameters of 1.5 nm ^{4,14} or 1.7 nm ,² based on a combination of the minimum size cutoff of state-of-the-art particle counters and inference about the “critical cluster” size for nucleation. The mobility diameter is larger than the physical diameter by approximately 0.3 nm due to the finite size of air molecules through which particles move during mobility measurement;⁴⁵ in this discussion we use physical size. Observed growth rates over this size range are of order $1\text{--}2\text{ nm hr}^{-1}$.⁴ Very small clusters thus must remain suspended in air for a long time – tens of minutes or more – before growing via condensation. Thus, the relevant timescales for evaporation and coagulation loss are of that order. Furthermore, clusters with short evaporation lifetimes (minutes or less) have no hope of growing.

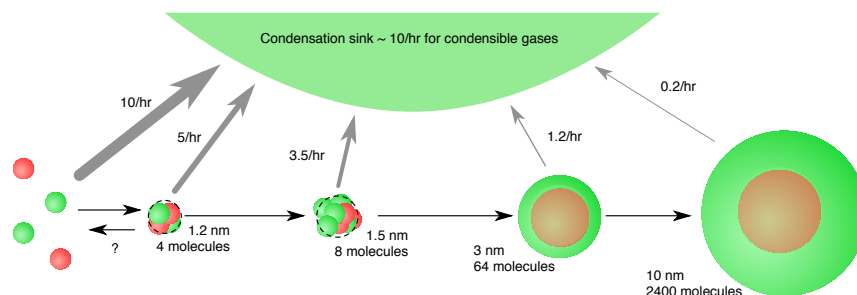


Fig. 1 Nucleation process for organics (green) and sulphuric acid (red). Diameters are physical diameters (mobility diameters are ~ 0.3 nm larger). Typical growth rates, especially for $D_p \leq 3$ nm, are of order $1\text{--}2$ nm hr^{-1} . Coagulative loss is the dominant process below this size; thus, even with no evaporation of small clusters, only a small fraction reach the operational threshold for particle formation (1.2 nm $\lesssim D_p \lesssim 1.5$ nm).

4 Coagulative Loss

Coagulation losses above the operational nucleation threshold but below the minimum size of microphysics modules in chemical transport models are typically treated via the parameterization of Kerminen and Kulmala.⁴⁶ However, coagulation loss below this threshold is thus part of the new-particle formation process leading up to the empirically observed rate at (mobility) diameters of 1.5 or 1.7 nm. Here we shall argue that coagulation is the dominant contributor to f_{npr} and thus that there is very little room for significant evaporation of small clusters.

For this discussion we shall consider an example case with fairly vigorous new-particle formation (for a boreal-forest environment), with $[\text{H}_2\text{SO}_4] = 10^7$ molec cm^{-3} , $\text{CS} = 10$ hr^{-1} , and different levels of condensable organic vapors. New particle formation rates under these conditions span the range $1 < J_{1.5} < 30$ $\text{cm}^{-3} \text{ s}^{-1}$ $\text{cm}^{-3} \text{ s}^{-1}$,^{4,14} while $J_{\text{SA}} = 10^4$ $\text{cm}^{-3} \text{ s}^{-1}$, so $10^{-4} \leq f_{\text{npr}} \leq 3 \times 10^{-3}$, the arrival frequency of sulphuric acid vapors is $10^{-3} \text{ s}^{-1} = 3.6$ hr^{-1} , and the growth rate from sulphuric acid condensation alone is approximately 0.3 nm hr^{-1} . If additional vapors are condensing more rapidly than sulphuric acid (with a ratio $\Gamma \simeq 3$),⁴⁷ the timescale for small cluster growth (doubling of size) via condensational growth is of order $1/3$ hr, so the “loss” term for growth is of order 3 hr^{-1} .

On its face, this would suggest that of order 0.1% of the sulphuric acid collisions result in new-particle formation. However, ambient measurements also indicate that the smallest clusters grow slowly, at roughly 1 nm hr^{-1} or less.⁴ Consequently, one must account for the loss of these smallest clusters to larger particles (i.e. coagulation). As shown in Fig. 1, the loss rate of small clusters is appreciable. If the first nanometer of growth (to particles with a physical diameter of roughly 1.5 nm) takes as much as 2 h, and loss to the condensational sink averages 4 hr^{-1} , then the survival probability of these clusters against loss to larger (accumulation mode) particles is $\exp(-8) = 3.3 \times 10^{-4}$. Thus, if growth of the smallest clusters is governed by sulphuric acid vapor it appears likely that most of the nucleating fraction f_{npr} may be determined by coagulation of the smallest (most diffusive) clusters. This is entirely consistent with the findings from

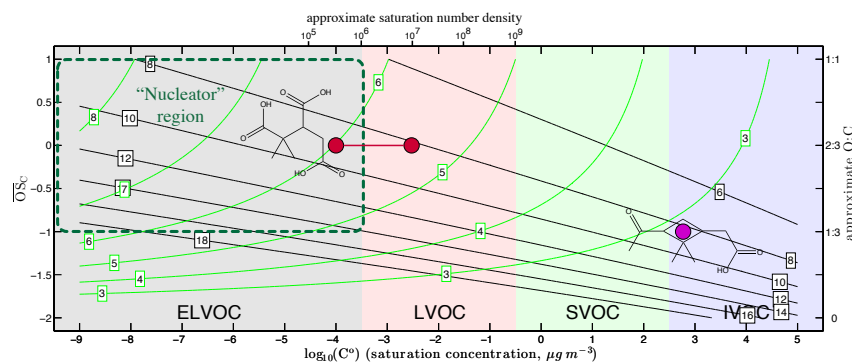


Fig. 2 Two dimensional volatility-oxidation space for organics. The x-axis is saturation concentration (in $\mu\text{g m}^{-3}$) with a secondary axis showing the approximate saturation number density. The y-axis is the average oxidation state of carbon atoms in a molecule ($\overline{\text{OS}}_{\text{C}} = 2\text{O}:\text{C}-\text{H}:\text{C}$), with a secondary axis showing approximate O:C for species with alternating $=\text{O}$ and $-\text{OH}$ functional groups. Contours show average carbon number (n_{C} , black) and average oxygen number (n_{O} , green), while colored regions indicate broad classes. Intermediate volatility organics (IVOC) are entirely in the gas phase under ambient conditions; Semivolatile organics (SVOC) are significantly in both phases, Low volatility organics (LVOC) have small gas-phase fractions, and Extremely low volatility organics (ELVOC) are only in the gas-phase because of steady-state disequilibrium from gas-phase formation. One such process is gas-phase oxidation of cis-pinonic acid by OH radicals to produce the triacid MBTCA, as shown. This oxidised, ELVOC region may be a “nucleator region” where organics can assist sulphuric-acid nucleation; alternatively, organics with $n_{\text{O}} \gtrsim 5-6$ may be needed, but these definitions are similar.

Chen *et al.*³ showing that sulphuric acid forms a semi-stable dimer and a stable heterodimer, and there is evidently no other evaporation loss.

It follows from the preceding argument that evaporation must be negligible for all or almost all of the nucleation process, compared with the condensation timescales. Otherwise the empirical nucleating fraction would be even lower than observed. Pure sulphuric acid nucleation is far too slow to account for observations,² almost certainly because evaporation of the smallest SA clusters is too rapid. Thus for oxidised organics to play a substantial role in nucleation, they must form very stable clusters with sulphuric acid, with evaporation lifetimes of many minutes under standard conditions.

5 Organic Aging and Nucleation

Here we shall consider oxidation of cis-pinonic acid and other first-generation pinene oxidation products by OH in the gas phase to produce second-generation gas-phase products with multiple polar functional groups capable of forming stable heterodimers with sulphuric acid but also capable of continued growth to larger, equally stable clusters. Previous studies have shown that “aging” of α -pinene secondary organic aerosol (SOA) can significantly enhance bulk SOA levels^{21,48,49} and that gas-phase oxidation of specific first-generation tracers such as cis-pinonic acid by OH radicals can lead to rapid formation of highly oxidised

species such as 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA).^{20,50}

In Fig. 2 we place these two species in a two-dimensional volatility oxidation space (2D-VBS) used to describe complex oxidation and phase partitioning of organic systems.^{21,27,28,51} The 2D-VBS is shifted toward very low volatility species, with contours showing a range of carbon and oxygen numbers. Depending on the method used to estimate its vapor pressure, MBTCA falls in the range $0.1 \leq C^o \leq 3 \text{ ng m}^{-3}$.

While MBTCA is a relatively minor product of cis-pinonic acid oxidation,^{20,50} there is strong evidence that aging of SOA species in general produces highly oxidised species,^{45,51} and the tendency of the “oxidised organic aerosol” (OOA) to decarboxylate after vaporization at 600 °C indicates many of the oxygenated functional groups are organic acids or even diacids.⁵² It is not certain that OOA formation occurs wholly via gas-phase oxidation,⁵³ but observational^{54,55} and modeling³⁰ studies suggest that gas-phase oxidation can be a major contributor.

This is potentially a recipe for generating supersaturation of organics that can participate in nucleation; low yields of very low volatility species can still lead to high supersaturations. While the fractional yields of ELVOC products may be low, oxidation may still produce substantial supersaturation. The “bins” in the 2D-VBS are separated by decades in volatility; if the mass yield into a less volatile bin is more than 10% of the yield into its more volatile neighbor, the resulting supersaturation in that bin will be higher. Thus product yields must decrease by more than one order of magnitude per decade for the resulting supersaturations to decrease. However, below some limit, products may be supersaturated, even homogeneously nucleating, but irrelevant. As we shall argue below, a practical lower limit to the organic vapor number density is of order 10^6 cm^{-3} , so species with $S_{\text{eff}} \approx 100$ would have $C^o \approx 3 \times 10^{-6} \mu\text{g m}^{-3}$ – a very small value, but less than halfway through the “nucleator region” shown in Fig. 2.

5.1 quantum chemistry modeling

Quantum chemistry calculations using the method combination B3LYP/CBSB7 // RI-CC2/Aug-cc-pV(T+d)Z³⁹ show that organic compounds with a significant number of polar functional groups can form stable clusters with sulphuric acid, while less oxidised organics are substantially less effective in this capacity. For example, MBTCA and sulphuric acid can form a stable, 302 amu cluster, as shown in Fig. 3, with heterodimer evaporation rates four orders of magnitude lower than pure sulphuric acid dimer clusters (and 5 orders of magnitude lower than pure MBTCA dimer clusters). The key elements to forming stable clusters that can also grow are first and foremost the ability to form strong hydrogen bonds, as shown in Fig. 3, most notably via carboxylic-acid moieties, but also multiple such moieties so that stable heterodimers are not a “dead end” but rather present additional hydrogen-bonding sites for cluster growth via addition of either sulphuric acid or additional organic acids.

While it is not obvious that a low saturation vapor pressure is an essential attribute for stabilization of sulphuric acid clusters, we shall show that for organic vapors, stabilizers that facilitate both clustering and subsequent growth for the most part do have a low saturation vapor pressure as well. Though ammonia is quite effective, this requires a dissociation reaction to make ammonium

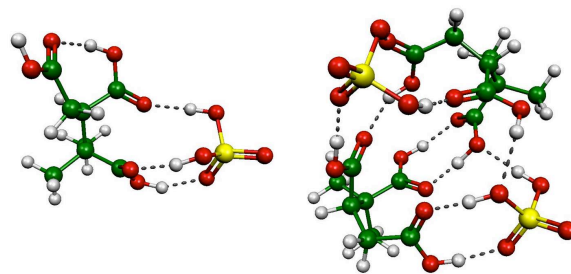


Fig. 3 Stable clusters of MBTCA and sulphuric acid. Both 1:1 and 2:2 MBTCA sulphuric-acid heteromer clusters are substantially more stable than pure clusters of either constituent. Strong hydrogen bonding networks stabilize the clusters, with evaporation rates up to 4 orders of magnitude lower than sulphuric acid dimer evaporation rates, and the large number of hydrogen bonding moieties on the molecules enables continued growth via condensation of similar species.

bisulphate clusters, which only occurs in clusters with a few sulphuric acid and ammonia molecules.^{2,43} Stable clusters involving organic acids and sulphuric acid do not require a chemical reaction; they rely on hydrogen bonds only. Consequently, if three acid moieties are required to form a stable cluster that can also grow, the resulting molecules can hardly avoid having a very low saturation vapor pressure.

It also appears that low volatility organic compounds produced via atmospheric oxidation reactions do have the appropriate attributes for cluster formation and growth. There is strong evidence that oxidised organic aerosol (OOA) comprises a high degree of carboxylic acid functionality, so being in the upper left region of the 2D-VBS may be a necessary and sufficient condition for a vapor to participate in new-particle formation. Thus, while we do not expect a perfect correlation between low volatility and the ability to stabilize sulphuric acid clusters, the region shown as “nucleator region” in Fig. 2 is roughly the region where molecules should have more than 5-6 oxygen atoms, and many should thus form strong hydrogen bonds with multiple bonding partners.

The boundaries of this region are also quite uncertain. The low O:C boundary is motivated by the evident role of polar moieties, but because gas-phase production of less oxidised ELVOC species is unlikely to be significant, that boundary is functionally irrelevant. The boundary at the ELVOC-LVOC demarkation is also vague, and in practice will be treated as adjustable in parameterizations; however, as we shall show below calculations suggest that reasonable conditions can lead to effective supersaturations near 100 at the boundary shown here.

5.2 2D-VBS modeling

A final question to address is whether reasonable gas-phase oxidation chemistry can produce a sufficient quantity of gas-phase vapors in steady state with appropriate properties to participate in atmospheric new-particle formation. Consequently, we implemented an oxidation scheme for cis-pinonic acid vapors in the 2D-VBS model described in Donahue *et al.*, 2012.²¹ Here, we assume that the first-generation oxidation products of cis-pinonic acid all retain 10 carbon

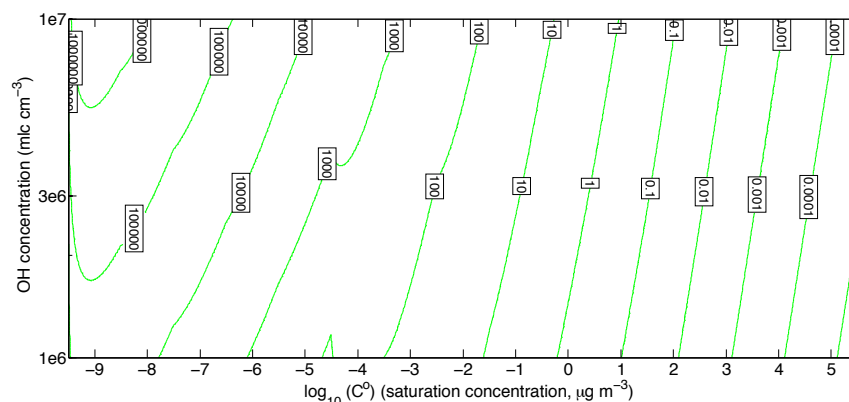


Fig. 4 Modeled effective saturation ratios for products of cis-pinonic acid oxidation as a function of C^o and $[\text{OH}]$ under typical conditions. The ELVOC (“nucleator”) limit is indicated with a dashed vertical line; products in this region have cumulative saturation ratios over 100 for all conditions (the total number density is $> 10^8$ molec cm^{-3}).

atoms (they all fall of the “functionalization” branch of the oxidation chemistry) but later generation products behave as described in previous publications, with a probability of product fragmentation rising with increasing O:C.^{21,51} We consider oxidation of 3–20 ppb of cis-pinonic acid for $10^5 < [\text{OH}] < 10^7$ cm^{-3} . The condensation sink at the Hyytiälä boreal-forest research station ranges between 2 hr^{-1} (10% cumulative probability) and 11 hr^{-1} (90%), with a median value of 6.5 hr^{-1} .^{11,56} Here we assume a condensation sink of 10 hr^{-1} , which is in the range of the Hyytiälä data and also close to the condensation sink of the CLOUD experiment at CERN.²

In Fig. 4 we show the resulting modeled effective organic saturation ratios given in Eq. 3 for different OH levels and cis-pinonic acid = 20 ppbv. For this simulation, organics in the “nucleator region” have a supersaturation above 100 for all $[\text{OH}]$, with supersaturation increasing with increasing OH as expected. This means the total gas-phase number density of species in this region is $> 10^8$ cm^{-3} . Thus, under conditions similar to those encountered in remote environments, gas-phase oxidation of first-generation SOA vapors can produce a sufficient steady-state burden of oxidised condensible products to contribute to new-particle formation.

It is likely important that the oxidised organic vapor concentrations exceed the sulphuric-acid vapor concentrations (for the example case under consideration here, where $[\text{SA}] = 10^7$ cm^{-3}). Quantum calculations show that small clusters with organic:SA > 1 are much less stable than those with 1:1 stoichiometry. However, as there is no chemical reaction taking place but rather formation of an H-bond network, there is no reason to expect a strict stoichiometric equivalence. Thus it seems likely that nucleation involving sulphuric acid and organics under conditions with excess organic vapors will occur with clusters containing more organic species than sulphuric acid, within some range defined by the stability of the small clusters.

The model results shown in Fig. 4 show $S_{\text{eff}} > 100$ for condensible organic

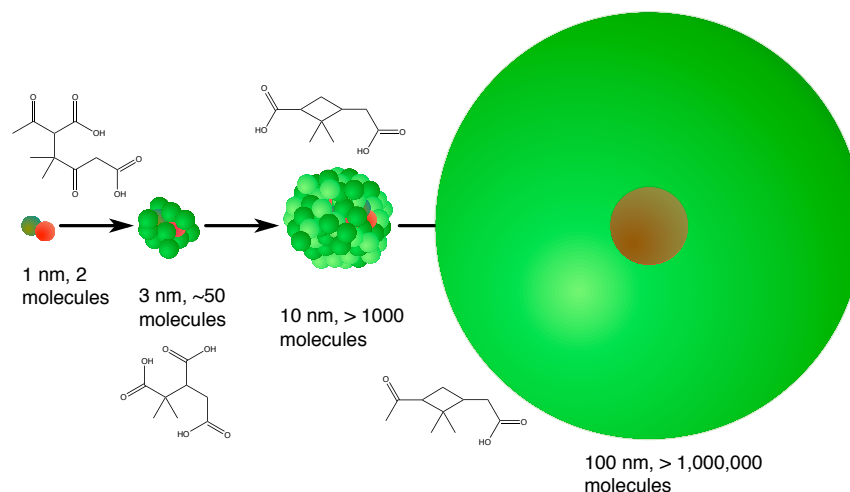


Fig. 5 Overall process of new-particle formation and growth involving association of oxidised organics and sulphuric acid. Initial stable cluster formation requires rare but highly oxidised, extremely low volatility organics. As clusters grow, progressively more common but also more volatile species can contribute to growth, until at some size near 10 nm the particle organic composition begins to resemble bulk organic-aerosol composition. In this illustration, a highly oxidised C_{10} keto-diacid and/or MBTCA (C_8 triacid) may stabilize the smallest clusters (dark green spheres) while more volatile species like pinic acid (C_9 diacid) may contribute to growth below 10 nm. Volatile species such as cis-pinonic acid (C_{10} keto acid) partition only to larger particles, if at all.

vapors (oxidised ELVOC). This also means that, regardless of the composition of the nucleating core, once the cluster reaches approximately 1.5 nm diameter, the core will be an effective heterogeneous nucleus for continued condensation of organic vapors. With increasing particle size, progressively more volatile organic vapors will be able to condense, as described in Donahue *et al.*³¹ As the particles grow, progressively smaller values of S_{eff} will be required to support continued growth, and even more volatile constituents will rapidly reach an equilibrium activity as Raoult law mixing offsets the Kelvin term. Thus, at a relatively small particle size, dependent on conditions, subsequent particle growth is likely to decouple from the sulphuric acid condensation rate; if condensable organic vapor concentrations are larger than sulphuric acid vapor concentrations, the particle composition will thus become progressively more dominated by oxidised organic compounds.

6 Conclusions

Quantum chemical calculations show that highly oxidised polycarboxylic acids can make strong hydrogen bonds with sulphuric acid and form stable molecular clusters, leading to new-particle formation in the atmosphere. In addition, a 2D-VBS model of SOA “aging” – simplified as gas-phase oxidation of cis-pinonic acid by OH radicals – generates a sufficient supersaturation of condensable oxidised organic vapors to support nucleation and growth in this mixed organic-

sulphuric acid system.

Schematically, the wide range of properties exhibited by oxidised organic vapors is a central element governing the behavior of growing particles, as shown in Fig. 5. Rare but strongly binding vapors can stabilize clusters with sulphuric acid down to the 1:1 heterodimer, while progressively more volatile but also more common organics can help drive subsequent growth. While large vapor concentrations of these organics are not required, roughly pptv levels are. Thus, it is unlikely that certain special compounds drive the process but rather that, collectively, a large body of oxidised ELVOC compounds are formed via gas-phase oxidation chemistry at a sufficient rate to drive the process.

Acknowledgements

This work was supported by funding from the U.S. National Science Foundation (grants AGS1136479 and CHE1012293), the Academy of Finland (CoE Project No. 1118615, LASTU Project No. 135054), ERC Project Nos. 257360- MOCA-PAF and 27463-ATMNUCLE, the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), and the Swedish Research Council, Vetenskapsrådet (grant 2011-5120). The authors are indebted to the CLOUD consortium for countless stimulating discussions and to the CSC Centre for Scientific Computing in Espoo, Finland for computer time.

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