Ion-induced nucleation of pure biogenic particles

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Atmospheric aerosols and their effect on clouds are thought to be important for anthropogenic radiative forcing of the climate, yet remain poorly understood1. Globally, around half of cloud condensation nuclei originate from nucleation of atmospheric vapours2. It is thought that sulfuric acid is essential to initiate most particle formation in the atmosphere3,4, and that ions have a relatively minor role5. Some laboratory studies, however, have reported organic particle formation without the intentional addition of sulfuric acid, although contamination could not be excluded6-7. Here we present evidence for the formation of aerosol particles from highly oxidized biogenic vapours in the absence of sulfuric acid in a large chamber under atmospheric conditions. The highly oxygenated molecules (HOMs) are produced by ozonolysis of α-pinene. We find that ions from Galactic cosmic rays increase the nucleation rate by one to two orders of magnitude compared with neutral nucleation. Our experimental findings are supported by quantum chemical calculations of the cluster binding energies of representative HOMs. Ion-induced nucleation of pure organic particles constitutes a potentially widespread source of aerosol particles in terrestrial environments with low sulfuric acid pollution. It is thought that aerosol particles rarely form in the atmosphere without sulfuric acid3,4, except in certain coastal regions where iodine oxides are involved8. Furthermore, ions are thought to be relatively unimportant in the continental boundary layer, accounting for only around 10% of particle formation9. Sulfuric acid derives from anthropogenic and volcanic sulfur dioxide emissions as well as dimethyl sulfide from marine biota. However, typical daytime sulfuric acid concentrations (105–107 cm−3, or 0.004–0.4 parts per trillion by volume (pptv) at standard conditions) are too low for sulfuric acid and water alone to account for the particle formation rates observed in the lower atmosphere9, so additional vapours are required to stabilize any embryonic sulfuric acid clusters against evaporation. Base species such as amines can do this and can explain part of atmospheric particle nucleation10. It is well established that oxidation products of volatile organic compounds (VOCs) are important for particle growth11, but whether their role in the smallest particles is in nucleation or growth alone has remained ambiguous12,13. Recently, it has been shown that oxidized organic compounds do indeed help to stabilize sulfuric acid clusters and probably play a major role in atmospheric particle nucleation14,15. We refer to these compounds as HOMs (highly oxygenated molecules) rather than ELVOCs (extremely low-volatility organic compounds)16 because the measured compounds span a wide range of low volatilities. Here we report atmospheric particle formation solely from biogenic vapours. The data were obtained at the CERN CLOUD chamber (Cosmics Leaving OUtdoor Droplets; see Methods for experimental details) between October 2012 and November 2013. In contrast with other works that have reported organic particle formation without intentional addition of sulfuric acid17, here we measure the cluster chemistry and the role of ions, and rule out contamination. Precursor VOCs in the atmosphere arise predominantly from natural sources such as vegetation and largely comprise isoprene (C9H16), monoterpenes (C10H16), sesquiterpenes (C15H24) and diterpenes (C20H32). Here we have studied α-pinene (C10H18) because it is the most abundant monoterpane, often exceeding 50 p.p.t.v in the continental boundary layer17. We oxidized α-pinene by exposure to ozone and also to hydroxyl radicals (OH·) produced from ozone photolysis and secondary reactions. To measure the relative importance of these oxidants we also performed a few pure ozonolysis experiments (in which we removed OH· with a 0.1% H2 scavenger) and a few pure hydroxyl experiments (in which we generated OH· by photolysis of gas-phase nitrous acid, HONO). Two nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometers measured neutral gas-phase compounds in the chamber (H2SO4 and HOMs). Therefore, for this study, HOMs are implicitly defined as oxidized organic compounds that can be detected by a nitrate CI-API-TOF; related molecules with a lower oxidation state

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or different functional groups could be present in the chamber, but undetected by our nitrate chemical ionization set-up.

Before starting measurements, we carefully cleaned the CLOUD chamber (see Methods) and established extremely low contaminant concentrations: at 38% relative humidity and 278 K, the contaminants were below the detection limit for SO2 (<15 p.p.t.v.) and H2SO4 (<5 x 10^4 cm^-3), and total organics (largely comprising high volatility C1–C3 compounds) were below 150 p.p.t.v. Contaminants with a high proton affinity or a high gas-phase acidity can be detected as ions by the API-TOF operating in positive or negative mode, respectively, even at neutral molecule concentrations as low as 10^3 cm^-3. The API-TOF measured contaminant C6H5NH+ (protonated pyridine) and contaminant NO3 to be the dominant positive and negative ions, respectively, before we added any trace gases to the chamber other than water vapour and ozone (Extended Data Fig. 1a, b). Despite its higher gas-phase acidity, we detected contaminant HSO4 at only 1% of the NO3 signal (Extended Data Fig. 1b), ruling out any contribution of sulfuric acid to the nucleation measurements. From previous studies and molecular analysis of the charged clusters (see below), the most abundant positive ion is likely to be contaminant ammonium (NH4+), but its mass is below the acceptance cut-off of the API-TOF as operated in this study.

Within a few minutes of the initial exposure of α-pinene to O3 in the chamber, we detected gas-phase HOM monomers and dimers (Fig. 1a). Particles appeared shortly afterwards (Fig. 1b). HOM monomers (denoted E1) broadly comprise highly oxidized C6–10H14O6–12 species with an oxygen-to-carbon ratio (O/C) above about 0.6. HOM dimers (E2) are two covalently bound monomers (see below), which generally have lower oxygen-to-carbon ratios, but, almost certainly, a lower volatility. For the present study we define E1 (E2) to be the summed monomers (denoted E1.E1) is expected to be unstable (see below).

We measure high HOM molar yields (Extended Data Fig. 2): approximately 1.2% per hydroxyl radical (OH) reaction with α-pinene, 3.2% per ozone reaction with α-pinene, and 2.9% from pure ozonolysis. We find a high E2 yield from ozonolysis (10%–20% of total HOMs), but negligible E2 yield from hydroxyl-initiated oxidation. Neutral trimers are close to the detection limit of the CI-APi-TOF (below 0.1% of total HOMs). High yields of these same HOMs have previously been reported, although our ozonolysis yields are less than half those of ref. 16. For our experiments, α-pinene was in the range 0.1–2 parts per billion by volume (p.p.b.v.), with 20–40 p.p.b.v. of O3. The OH-concentrations were (0.5–0.8) x 10^5 cm^-3 during ozonolysis experiments, and (0.4–2) x 10^5 cm^-3 during pure hydroxyl experiments with 0.5–3 p.p.b.v. of HONO.

This remarkably fast production of HOMs is likely to proceed via an autoxidation mechanism involving peroxy radicals,16,18–20 (Extended Data Fig. 3). There is simply insufficient time for oxidation to proceed in multiple steps through stable intermediate molecules. Here, initial ozonolysis of an α-pinene molecule proceeds via a Criegee intermediate and further steps to form an RO2· radical, followed by several repeated cycles of intramolecular H abstraction and O2 addition to re-form a new RO2· radical. We measure an RO2· fraction of total HOMs between 15% and 1% for HOMs from 0.1 p.p.t.v. to 10 p.p.t.v., respectively. A combination reaction of differently oxidized peroxy radicals explains the rapid high yield of covalently bound E2. The negligible E2 yield from hydroxyl-initiated oxidation could result from additional NOx chemistry that terminates the peroxy radicals before they can combine. Our theoretical calculations further indicate that E2 must be covalently bound because the neutral molecular cluster formed from two monomers (denoted E1.E1) is expected to be unstable (see below).

Figure 1 | Evolution of HOMs and particles during a typical run. a, Evolution of selected HOM monomers (E1), dimers (E2) and peroxy radicals (RO2·) at 300 p.p.t.v. α-pinene, 33 p.p.b.v. O3, zero H2 or HONO, 38% relative humidity, 278 K and [H2SO4] < 5 x 10^4 cm^-3 (the same run as shown in Extended Data Fig. 4). The HOMs start to appear soon after the first injection of α-pinene into the chamber at 21:22, 23 October 2013. A HOM monomer is a highly oxygenated molecule derived from α-pinene (C10H16), and a HOM dimer is a covalently bound pair of monomers. Peroxy radicals are identified by an odd H number. The HOMs are charged with an oxygen-to-carbon ratio (O/C) above about 0.6. HOM dimers (E2) are two covalently bound monomers (see below), which generally have lower oxygen-to-carbon ratios, but, almost certainly, a lower volatility. For the present study we define E1 (E2) to be the summed monomers (denoted E1.E1) is expected to be unstable (see below).

We measured nucleation rates under neutral (Jn), Galactic cosmic ray (GCR; fgr) and π+ beam (Jπ) conditions, corresponding to ion-pair concentrations of around 0 cm^-3, 700 cm^-3 and 3,000 cm^-3, respectively. This range spans atmospheric ion concentrations between ground level and 15-km altitude. The nucleation rate Jn describes the neutral rate alone, whereas Jgr and Jπ describe the sum of the neutral and ion-induced rates, Jn + Jion. We determine the nucleation rates at
Figure 2 | Molecular composition and mass spectra of charged clusters during GCR nucleation events without sulfuric acid. a, b. Cluster mass defect (difference from integer mass) versus m/z of negatively (a) and positively (b) charged clusters measured with the API-TOF at 240 p.p.t.v. α-pinene, 34 p.p.b.v. O₃, zero H₂ or HONO, 38% relative humidity, 278 K and [H₂SO₄] below the detection limit (5 × 10⁻⁴ cm⁻³). The values of \( J_{\text{gcr}} \) and total HOMs concentration are, respectively, 3.4 cm⁻³ s⁻¹ and 1.7 × 10⁴ cm⁻³ s⁻¹ and 3.3 cm⁻³ s⁻¹ and 2.4 × 10⁴ cm⁻³ s⁻¹ (b). The mass bands are labelled according to the number of HOM monomer units in the cluster, \( E_n \). Each circle represents a distinct molecular composition and its area represents the counts per second. The most highly oxidized compounds are located at the lower right-hand edge of each band.

The dark blue circle represents NO₃⁻ ions; the light blue circle represents ClO₄⁻ ions. Clusters with fully identified molecular composition are coloured according to their core ion: purple (NO₃⁻), green (E⁻) or orange (NH₄⁺). Grey circles are unidentified clusters. c, d. Mass spectra from the same events for negative (c) and positive (d) clusters up to m/z = 3,000 Th. A particle of 1.7-nm mobility diameter has a mass of about 1.200 Th. The ‘Nessie’ plot (d) shows that positive-ion-induced nucleation involves HOM dimers alone (\( E_2 \) NH₄⁺ clusters are not seen owing to instrument tuning). The decreasing signal amplitude at larger masses is due to the lower concentration and decreasing detection efficiency of the API-TOF mass spectrometer (the efficiency versus m/z depends on the instrument tune and polarity).

A typical run sequence (Extended Data Fig. 4) begins by establishing ion-free conditions with a high-voltage clearing field and introducing α-pinene to the chamber, where it mixes with ozone. Particles then start to form and, after measuring \( J_n \) at steady-state α-pinene concentration, we turn off the high voltage and measure \( J_{\text{gcr}} \) under otherwise identical chamber conditions. A sharp enhancement of particle formation is seen when the high voltage was turned off (Extended Data Fig. 4b, e), due to ion-induced nucleation of both charge signs (Extended Data Figs 4c, d and 5).

Figure 2 shows the molecular composition and mass spectra of negatively and positively charged ions, monomers, dimers and clusters during ion-induced nucleation events. The dominant core ions in the clusters are identified as NH₄⁺, NO₃⁻ and E⁻. Here E⁻ is inferred for negatively charged ions or clusters that contain only C, H and O; the E⁻ ion corresponds to a HOM of high gas-phase acidity. In contrast to negative clusters, the positive clusters nucleate only with dimers, producing distinct mass bands that are detected up to \( E_{10} \) in the API-TOF (Fig. 2c, d). This indicates the importance of dimers for pure biogenic nucleation. Dimers are expected to be less volatile than monomers, owing primarily to higher molecular weight, but also to additional functional groups. Our previously described definition for neutral gas-phase HOMs encompasses compounds with a wide range of low volatilities, of which only a subset drive nucleation (ELVOCs, which comprise about 36% of measured total HOMs). From the strong ion enhancement of nucleation we conclude that the API-TOF mass peaks above the dimer in Fig. 2 are clusters of ELVOC monomers and dimers. Although we can precisely determine their molecular composition (CₓHᵧOₚ), we can only infer their specific structure and functional groups.

We show the experimental neutral and GCR nucleation rates in Fig. 3 over the total HOMs range 0.1–10 p.p.t.v., which spans the range of atmospheric interest. Below 1 p.p.t.v. HOM, ionization at ground-level GCR intensities enhances the nucleation rate by between one and two orders of magnitude compared with neutral nucleation. At higher concentrations, the neutral and GCR nucleation rates converge because the ion-induced rate, \( J_n \), reaches the limit set by the GCR total ion production rate (3.4 cm⁻³ s⁻¹). Positive and negative clusters nucleate at comparable rates (an example is shown in Extended Data Fig. 5). Relative humidity has little effect on \( J_{\text{gcr}} \) over the range 6%–80% relative humidity, whereas \( J_n \) increases substantially at higher relative humidity (Extended Data Fig. 6).

The large GCR enhancement indicates that biogenic molecular clusters are relatively unstable unless an ion is present. A charged cluster is also likely to experience higher collision rates with HOMs because they are expected to have high electric polarizability and, depending on their structure, large dipole moments. We further investigated the dependence on ion species by adding small amounts of SO₂ to the chamber, up to around 1,000 p.p.t.v. When [H₂SO₄] exceeds about 1 × 10⁵ cm⁻³, the major negative ion species shift to HSO₄⁻, SO₄²⁻ and ClO₄⁻ (Extended Data Fig. 1c), owing to their lower proton affinity (higher gas-phase
acidity) than contaminant compounds. However, the nucleation rates with sulfur ion species remain unchanged (Fig. 3). Taken together, our observations therefore show that ubiquitous ion species can stabilize embryonic biogenic clusters. However, we do not observe chlorine in nucleating clusters, even though contaminant chlorine ion species are present (Fig. 2 and Extended Data Fig. 1), which indicates that not all ions have a suitable chemical structure to bond strongly with the oxidized organic compounds.

Figure 4 shows the CLOUD biogenic nucleation rates extended to \([\text{H}_2\text{SO}_4] = 6 \times 10^6 \text{ cm}^{-3}\) and compared with atmospheric boundary-layer observations\(^{3,4,23,24}\). Biogenic nucleation rates show no significant dependence on sulfuric acid concentration over this range (that is, within the experimental measurement errors, the nucleation rate is consistent with zero dependency on sulfuric acid concentration). This finding sharply contrasts with base-stabilized nucleation of sulfuric acid in the presence of ammonia\(^{8}\) or amines\(^{10}\), where nucleation rates at 1.7 nm show a steep dependency on [\(\text{H}_2\text{SO}_4\)] above \(10^5 \text{ cm}^{-3}\). Comparison of the atmospheric observations (Fig. 4) with our measurements therefore suggests that nucleation in the lower atmosphere may involve a mixture of two distinct mechanisms. The first, which is more important in polluted environments, involves nucleation of sulfuric acid and water together with a combination of amines or ammonia with oxidized organics, and has a strong dependence on sulfuric acid. The second, which is more important in pristine environments, involves nucleation of pure organic particles and depends on only oxidized organics and ions.

To gain further insight into the stability of initial neutral and charged clusters of highly oxidized biogenic molecules, we calculated their Gibbs free energies of formation, \(\Delta G\), using quantum chemical methods (see Methods). For this study we chose \(\text{C}_8\text{H}_{14}\text{O}_7\) and \(\text{C}_8\text{H}_{30}\text{O}_{14}\) as \(\text{E}_1\) and \(\text{E}_2\) surrogates, respectively (Extended Data Fig. 7). We observe these compounds both in the gas (Fig. 1) and particle phases in the CLOUD chamber. We show proposed formation mechanisms and structures\(^{9,20}\) in Extended Data Fig. 3. Our calculations, summarized in Extended Data Table 1 and Extended Data Fig. 8, confirm that ELVOC clusters formed with an \(\text{E}_1\), \(\text{HSO}_4^–\), \(\text{NO}_3^–\) or \(\text{NH}_4^+\) ion are expected to be stable (that is, their growth rate exceeds the evaporation rate) at around 0.1 p.p.t.v. ELVOC, or below. In contrast, the initial neutral clusters are weakly bound and so neutral nucleation is expected to be weaker. Although limited to a single surrogate pair, our theoretical calculations thus provide independent support for the experimental measurements.

Comparisons with atmospheric observations should be considered as preliminary because our measurements were made at only one temperature, with a single monoterpane, in the absence of isoprene and mostly in the absence of \(\text{NO}_x\), which can influence HOM yields. Nevertheless, our results may provide fresh insights into several seemingly disparate
phenomena associated with low atmospheric concentrations of sulfuric acid. First, pure HOM nucleation could provide a mechanism to account for nucleation-mode particles observed at night-time, under low-[H₂SO₄] conditions. Second, although observations are rare, nucleation-mode particles are seen in the Amazon, where SO₂ levels are extremely low (20–30 pptv). Peak particle concentrations often occur at sunrise and sunset, and appear to be associated with rain, which reduces the aerosol condensation sink and may generate high ion concentrations by evaporation of charged droplets at the Rayleigh limit. Third, pure biogenic nucleation could explain new particle formation observed in the upper troposphere in cloud outflows depleted of SO₃, such as over the Amazon. Low-solubility biogenic precursor vapours can be efficiently convected inside clouds to high altitudes where HOMs will form in the cloud outflows on exposure to oxidants, and nucleation is likely to be enhanced by the low temperatures. Since, high HOM yields are also found from other organic compounds with an endocyclic double bond such as cyclohexene, pure HOM nucleation involving anthropogenic organic precursors could be expected when [H₂SO₄] is low. Finally, ion-induced pure biogenic nucleation might shed new light on the long-standing question of a physical mechanism for solar-climate variability in the pristine pre-industrial climate.

Direct observational evidence of pure biogenic nucleation has not been reported so far, owing to atmospheric pollution or lack of suitable instrumentation. The pure biogenic mechanism is likely to dominate nucleation in pristine terrestrial regions such as tropical rainforests or at higher altitudes above forests in convective cloud outflows. Pure biogenic nucleation might also take place over forested areas at high northern latitudes during periods of especially low pollution. Identification of pure biogenic nucleation in the atmosphere will require simultaneous measurements with several newly developed mass spectrometers, API-TOF (for molecular composition of ions and nucleating charged clusters) and CI-API-TOF (gas-phase HOMs and H₂SO₄), together with standard instruments such as low-threshold particle counters, PTD-TOF (precursor organic vapours) and NAIS (spectrum of ions and charged particles).

In summary, we find that highly oxidized organic compounds play a role in atmospheric particle nucleation comparable to that of sulfuric acid; together with a suitable stabilizing agent, each has sufficiently low volatility to form new particles in the lower atmosphere at vapour concentrations near 10⁻⁷ cm⁻³. The stabilizing agent for pure biogenic particles is a suitable ion, whereas for sulfuric acid particles the stabilizing agents are amines, or ammonia with oxidized organics. Ion-induced nucleation of pure biogenic particles may have important consequences for pristine climates because it provides a mechanism by which nature produces particles without pollution. This could raise the baseline aerosol state of the pristine pre-industrial atmosphere and so could reduce the estimated anthropogenic radiative forcing from increased aerosol-cloud albedo over the industrial period.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to Online Content Methods, along with any additional Extended Data display items and aeroil-cloud albedo over the industrial period.

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Author Contributions
J.A., H.G., A.K., T.N., J.T. and C.W. analysed the nucleation rates; C.Fr. analysed the APi-TOF charged clusters; M.H., M.Sim. and C.Y. performed the CI-APi-TOF HOM and H2SO4 analyses; A.-K.B. analysed the PTR-TOF α-pinene; J.H.S. and X.Z. analysed the ELVOC structures and formation mechanisms; I.K.O. performed the quantum chemical calculations; A.Ad., J.A., A.Am., A.-K.B., F.B., M.B., S.B., J.Cu., J.Cr., A.D., J.Do., J.Du., S.E., C.Fr., C.Fu., H.G., M.H., C.R.H., T.J., J.Ka., J.Kim, J.Kir., M.Kr., A.K., K.L., V.M., U.M., T.N., F.P., T.P., A.PP., M.PR., N.S., K.S., M.Sim., M.Sip., G.S., A.T., J.T., A.W., D.W., R.W., C.W., C.Y. and P.Y. collected the data and contributed to the analysis; K.S.C., H.G., K.P., A.R., N.A.D.R., K.S. and C.E.S. evaluated the atmospheric relevance; J.Kir. wrote the manuscript; J.A., J.Do., N.M.D., C.Fr., H.G., M.H., J.H.S., M.Sim., C.W., R.W., C.Y. and X.Z. contributed to Methods and Extended Data; and U.B., K.S.C., J.Cu., J.Do., N.M.D., R.C.F., A.H., J.Kir., M.Ku., J.H.S. and D.R.W. contributed to data interpretation and editing of manuscript. All authors contributed to the development of the CLOUD facility and analysis instruments, and commented on the manuscript.

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METHODS

Overview of the CLOUD facility. The CLOUD experiment at CERN is designed to study the effects of cosmic rays on aerosols, cloud droplets and ice particles, under precisely controlled laboratory conditions. The 3-m-diameter stainless-steel CLOUD chamber and its gas system have been built to the highest technical standards of cleanliness and performance. The CLOUD chamber is periodically cleaned by rinsing the walls with ultra-pure water, followed by heating to 373 K and flushing at a high rate with humidified synthetic air and elevated ozone (several parts per million by volume). Contaminant levels of condensable vapours are in the sub-p.p.t.v. range. The high cleanliness of the chamber, together with its large volume (26.1 m³) and highly stable operating conditions, allows particle formation to be studied under atmospheric conditions at nucleation rates between about 0.001 cm⁻³ s⁻¹ and 100 cm⁻³ s⁻¹. The loss rate of condensable vapours and particles onto the chamber walls is comparable to the ambient condensation sink of the pristine boundary layer.

Ion production in the chamber can be controlled using an internal electric clearing field (which creates an ion-free environment), GCRs or an adjustable π⁺ beam from the CERN Proton Synchrotron. The π⁺ beam is de-focused to a transverse size of about 1.5 m × 1.5 m when it passes through the CLOUD chamber. With the electric field set to zero, the equilibrium ion-pair concentration in the chamber due to GCRs is around 700 cm⁻³. With the π⁺ beam, this can be increased to any value up to about 3,000 cm⁻³. Hence, ion concentrations corresponding to any altitude in the troposphere can be generated in the CLOUD chamber.

The experiment has precise control of the trace vapours inside the chamber and also of the environmental temperature between 300 K and 205 K. Uniform mixing is achieved with magnetically coupled stainless-steel fans mounted at the top and bottom of the chamber. The characteristic gas mixing time in the chamber is a few minutes, depending on the fan speeds. Photochemical processes are initiated by illumination with an ultraviolet fibre-optic system, providing highly stable gas-phase reactions with a precise start time. The contents of the chamber are continuously analysed by instruments connected to sampling probes that project into the chamber. The sampling analysers are tailored for each experimental campaign, but typically comprise around 30–35 instruments, of which up to 10 are mass spectrometers.

Summary of analysing instruments. For the results reported here, the analysing instruments attached to the chamber included a chemical ionization mass spectrometer (CIMS) for H₂SO₄ concentration; an atmospheric pressure interface time-of-flight (API-TOF; Aerodyne Research Inc. and Tofwerk AG) mass spectrometer for molecular composition of positively or negatively charged ions and clusters; two chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF; Aerodyne Research Inc. and Tofwerk AG) mass spectrometers for molecular composition and concentration of neutral gas-phase H₂SO₄ and HOMs; a proton transfer reaction time-of-flight (PTR-TOF; Ionicon Analytik Gmbh) mass spectrometer for organic vapours; a neutral cluster and air ion spectrometer (NAIS; Airel Ltd) for concentrations of positive, negative ions and charged clusters in the range 1–40 nm; a nano-radiial differential mobility analyser (nRDMA) and a nano scanning mobility particle sizer (CPCs) with 50% detection efficiency thresholds between 1 nm and 4 nm: two Airmodus A09 particle size magnifiers, PSM; one fixed-threshold and the other scanning, two diethylene glycol CPCs, DEG-CPC; a butanol TSI 3776 CPC and a water TSI 3786 CPC (TSI Inc.).

Additional gas analysers included dew-point sensors (EdgeTech), sulfur dioxide (Thermo Fisher Scientific, Inc. 421-TLE) and ozone (Thermo Environmental Instruments TEI 49C). For certain tests, HONO vapour was supplied to the chamber. The HONO analyser involved a specially designed probe that involves a gaseous HONO being generated by continual mixing of H₂SO₄ with NaNO₂ and photolysed with ultraviolet light to produce OH· in the absence of O₃. The gaseous HONO was generated by continual mixing of H₂SO₄ with NaNO₂ and photolysed with ultraviolet light to produce OH· in the absence of O₃.

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In the model essentially as kinetically limited growth by particle coagulation plus gas-phase reactions with a precise start time. The contents of the chamber are continuously analysed by instruments connected to sampling probes that project into the chamber. The sampling analysers are tailored for each experimental campaign, but typically comprise around 30–35 instruments, of which up to 10 are mass spectrometers.

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The neutral–neutral collision kernel, \( K_{nn} \), in equation (1) is the Fuchs form of the Brownian coagulation coefficient \(^{47,48}\). The van der Waals enhancement factor is the modification to Fuchs theory due to Scoats \(^4\), as described in ref. 50, for a Knudsen number in the kinetic (free molecular) regime. The enhancement factor is:

\[
V_{21} = 1 + \frac{\sqrt{\frac{\pi}{3}}}{1 + b_0 A'} + b_1 \ln(1 + A') + b_2 \ln(1 + A')^3
\]

where the reduced Hamaker constant, \( A' \), is:

\[
A' = \frac{A}{kT} \left( r + \frac{2}{r} \right)^2
\]

where \( r \) and \( A \) are the particle radii, \( A = 6.4 \times 10^{-20} \) (the Hamaker constant for sulfuric acid \(^{46}\)), \( b_0 = 0.0151, b_1 = -0.186, b_2 = -0.0163 \), is the Boltzmann constant and \( T \) is temperature. The same Hamaker constant is used for both sulfuric acid and HOMs because it does not noticeably change the model predictions.

Ions and charged clusters collide according to a similar expression as equation (1):

\[
n_{i2} = (E \times K_{20}) S' n_{i1} \Delta t
\]

where \( E \) is an enhancement factor to obtain the charged collision kernels (described below). The sticking probability for collisions between a neutral particle and a charged particle, \( S_{b+0} \), is:

\[
S_{b0} = \exp[ -0.693 (C/m_{b0})^{f_{b0,0}} ]
\]

where \( S_{b0} \) is a free parameter and \( C = C_b \) or \( C_a \) for biogenic or acid particles, respectively. Ion–ion recombination results in a neutral particle, which may evaporate at small sizes. The model allows partial evaporation of such recombination products; in this case the cluster divides into monomers and the mass is conserved. The probability of cluster survival after ion–ion recombination, \( S'_{b+} \), is:

\[
S'_{b+} = \exp[ -0.693 (C_{b+} / m_{b+})^{f_{b+0}} ]
\]

where \( C_{b+} \) is a free parameter. A power of unity (\( S_{b+0} = 1 \)) is used because the data do not constrain this parameter well.

To obtain the charged collision kernels, the neutral–neutral collision kernel is multiplied by size-dependent enhancement factors, \( E \):

\[
E_{b0,0} = K_{b0,0} / K_{20} \quad E_{b+,+} = K_{b+,+} / K_{20} \quad E_{b+,0} = K_{b+,0} / K_{20}
\]

where \( K \) are the collision kernels and the subscripts refer to the charge of the colliding particles. The charged collision kernels in equation (2) are obtained from ref. 51, which refers to sulfuric acid particles. Because biogenic particles may have different neutral–charged collision kernels, their enhancement factor is left free in the fit:

\[
E_{b0,0} = E_{b0,0} - 1 + \frac{1}{fo_{b0,0}}
\]

where \( f_{b0,0} \) is a free parameter.

Ions, monomers, clusters and larger particles are continually lost by diffusion to the walls and by dilution of the chamber contents with fresh gas mixture. The dilution lifetime is near 3 h (10 \(^{-3} \) s), depending on the total sampling rate of all instruments attached to the chamber. The wall loss rate is 1.8 \( \times 10^{-11} \) s\(^{-1} \) for \( H_2SO_4 \) monomers, and decreases with increasing cluster or molecule diameter as 1/d. The same scaling law is used to obtain the wall loss rate for HOMs that is, it is assumed that HOMs and particles that collide with the walls are irreversibly lost. For experimental runs for which there is a pre-existing population of particles in the chamber at the start of a run due to incomplete cleaning of the chamber, losses to this coagulation sink are accounted for by inserting the initial size distribution into the size bins of the model.

To determine the nucleation rates, the five free parameters of the model (\( S_{b0}, S_{b+,0}, f_{b0,0} \), and \( S_{b+} \)) are fitted to the experimental particle concentrations in the PSM1.8 and CPC2.5 versus time. For example, for neutral pure biogenic runs, only one free parameter (\( S_{b0} \)) is involved in the fit. The value of \( S_{b0} \) ranges from 12 to 14. \( S_{b+} \) from 4 to 6, \( S_{b+,0} \) from 0.1 to 1.0, \( f_{b0,0} \) is near 4 and \( S_{b+} \) is near 10,000 Th. The parameters \( C_b, C_a, S_{b+} \) and \( f_i \) were determined by a global fit to all runs in the dataset and then subsequently fitted at these values. The fitted threshold masses for \( C_b \) and \( C_a \) are around 1,300 Th and 700 Th, respectively. The parameter \( S_{b+} \) is set to 1.0 and \( f_i \) is set to 0.52. The time development of the particle number concentrations in both counters throughout all of the nucleation events in our dataset is well reproduced by the model (an example is shown in Extended Data Fig. 4b).

After fitting the data with the model, the nucleation rate \( f_j \) is determined as the number of particles that grow to a mobility diameter of 1.7 nm or larger in any time-step, divided by the time increment. In each nucleation run at fixed conditions, the time \( t_{\text{max}} \) is determined at which \( f_j \) is maximum; the value of \( f_j \) for that run is then calculated as the mean measurement over the interval (\( t_{\text{max}} \leq 300 \) s).

There are three major advantages of using a data-driven kinetic model to determine nucleation rates rather than making direct measurements with the PSM1.8 or CPC2.5 data. First, it avoids the need for time derivatives of the data, which are subject to large errors at low counting rates. Second, particle growth rates are determined by kinetics and properly account for growth due to collisions with both monomers and with other particles. The model treatment of the data therefore avoids the exponential sensitivity on experimental growth rates that occurs with other methods \(^{52,53}\). Experimental growth rates are determined from particle counter rise times and have relatively large uncertainties in the 1–3 nm size range. Finally, the model requires consistency between the PSM1.8 and CPC2.5 so that the formation rates are experimentally constrained both near the 1.7-nm threshold size and near 3 nm.

**Verification of the model nucleation rates.** We performed extensive cross-checks of the nucleation rates obtained with the model by calculating the nucleation rates independently in two additional ways: (1) direct measurements at 1.8 nm using the scanning PSM and (2) CPC2.5 measurements that are stepwise-corrected to 1.7-nm threshold size. Within their experimental uncertainties, the nucleation rates obtained by both these methods agree well with the values obtained with the AEROCLOUD kinetic model.

The stepwise-corrected method is described in detail in ref. 55, but a brief summary is provided here. The nucleation rates are derived from the rate of change of the formation rates, \( dN_{\text{CPC}}/dt \), where \( N_{\text{CPC}} \) is the particle number concentration measured with the CPC2.5 above its detection threshold, \( d_o \). The formation rate is corrected in two sequential steps for particle losses to chamber walls, dilution and coagulation: (1) particle losses above \( d_o \) and (2) particle losses during growth from 1.7 nm to \( d_o \). The dilution and wall loss rates are the same as in the kinetic model. To calculate the coagulation rate, the particles are divided into size bins and then the loss rate in each bin \( i \) is computed by summing the size-dependent collision (coagulation-loss) rate of the particles in bin \( i \) with those in all other bins. The total coagulation loss rate is then the sum of the particle loss rates in each bin \( i \).

Correcting for particle losses during growth from 1.7 nm to \( d_o \), the model requires knowledge of the particle growth rate. This is experimentally determined with several instruments, for example, from the appearance times measured in the scanning PSM \(^{56}\), which detects particles over a range of threshold diameters between 1 and 2.5 nm. The growth rates were also measured over different size ranges with several other instruments, including a fixed-threshold PSM, two DEG-CPCs, a TSI 3776 CPC, an API-TOF, an NAIS, an rNMDA and a nano-SMPS. The experimental growth rates are parameterized because they cannot be measured sufficiently precisely at each point in time during all events. To determine the nucleation rate at 1.7 nm from the corrected formation rate at \( d_o \), the size interval is divided into \( n \) log-normally spaced bins, \( \log(D_i) \), chosen to match the spacing of the SMPS bins at larger sizes. The residence time of a particle in each bin is \( t_b = \log(D_i) / (\text{growth rate}) \), where \( \log(D) \) is the size of bin \( i \). Starting with the measured particle distribution above \( d_o \), the size distribution and formation rate is then extended towards 1.7 nm in a stepwise process. In the first step, using the known loss rates due to the chamber walls, dilution and coagulation, as well as the time \( t_b \), the concentration in the largest new bin is calculated, as well as the formation rate into this bin. Using this concentration, the size distribution is updated and the process is repeated until, after \( m \) steps, the smallest size bin at 1.7 nm is reached, where the nucleation rate is determined.

**The NAIS.** The neutral cluster and air ion spectrometer (NAIS) \(^{57}\) measures the size distributions of positively and negatively charged particles, and also of total (charged plus neutral) particles, between mobility-equivalent diameters of 0.75 nm and 45 nm. Because the instrument includes two mobility analysers operating in parallel, positive and negative spectra are obtained simultaneously, each with 21 electrometers. Taking into account the internal diffusion losses, the mobility distribution is then calculated in 28 size bins from the measured electrometer currents.

The instrument operates sequentially in three modes: ion, particle and offset mode (one cycle takes 150 s). The aerosol sample first passes through a preconditioning section containing a discharger, an electric filter, a charger and a second electric filter (post-filter). The charger and discharger are corona needles of opposite polarities. In ion mode, the preconditioning unit is switched off and the sample passes through unaffected. In this way, the mobility analysers...
measure only ions and charged particles from the CLOUD chamber. In particle mode—which was not used for the results reported here—both chargers are switched on and so neutral particles from the CLOUD chamber can be classified. The post-filters improve the measurements by removing residual ions from the charger. In offset mode, the dischargers and corresponding filters are switched on. The sample is charged to the opposite polarity as the subsequent analyser and so no detectable particles can enter. In this way, the noise levels and possible parasitic currents are measured to provide corrections for the preceding ion and particle measurement.

After preconditioning, the aerosol sample is classified in two cylindrical mobility analysers. The central electrode consists of several sections, each at a different fixed electric potential. The particles enter the analysers through a circular slit near the central electrode and are collected at the 21 outer electrodes where they transfer their charge to the connected electrometer and the resulting current is measured. The analysers operate at a sheath flow rate of 601 min⁻¹. Filtered excess air serves as sheath gas to ensure conditions similar to the sample flow. The data inversion that converts the measured electrometer currents to particle concentrations is based on model calculations simulating trajectories of particles with different mobilities, and on calibration measurements of the internal losses. The performance of the NAIS for ion-mobility (size) and concentration measurements is described in refs 58, 59.

The APi-TOF mass spectrometer. The atmospheric pressure interface time-of-flight (APi-TOF) mass spectrometer²⁴ measures the mass-to-charge ratio of positive or negative ions with an inlet at atmospheric pressure. The first stage of the instrument consists of an atmospheric pressure interface (API) section where ions are focused and guided by two quadrupoles and an ion lens through three chambers at progressively lower pressures down to 10⁻⁷ mbar. The second stage of the instrument is a time-of-flight (TOF) mass spectrometer at 10⁻¹⁰ mbar.

The APi-TOF is connected to the CLOUD chamber via a 1" (21.7-mm-inner diameter) sampling probe shared with the NAIS. A Y-splitter divided the total flow of 201 min⁻¹ equally between the two instruments. The sample flow for the APi-TOF was 0.81 min⁻¹, with the remainder being discarded.

The APi-TOF measurements were made during GCR and π⁺ beam runs; that is, the ions were charged by GCRs or charged pions traversing the CLOUD chamber. Because the APi-TOF can measure only one polarity at a time, positive and negative ions were measured in different runs. Different instrument settings were used during the campaigns to optimize detection in the low- or high-mass regions of the spectrum. The data were analysed with tofTools²⁵, developed by the University of Helsinki. The tool is implemented in MATLAB and allows complete processing of TOF data: averaging, mass calibration, baseline detection, peak fitting and high-resolution analysis.

The CI-APi-TOF mass spectrometer. Two nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometers were used to measure neutral sulfuric acid and HOMs. The instruments were operated by the University of Frankfurt (UFRA-CI) and the University of Helsinki (UHEL-CI); differences between the two instruments are indicated in this section by adding the UHEL-CI characteristics in parentheses after those of the UFRA-CI. The CI-APi-TOF has been described previously³⁶,³⁷. The sample air from the CLOUD chamber was drawn in through a 1/2"-inner-diameter (300 μm) sampling probe shared with the NAIS. A Y-splitter divided the total flow of 201 min⁻¹ equally between the two instruments. The sample flow for the APi-TOF was 0.81 min⁻¹, with the remainder being discarded.

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The SO₂-CIMS. The SO₂ chemical ionization mass spectrometer (SO₂-CIMS) uses CO₃⁺ primary ions to convert SO₂ to SO₄²⁻ which is then measured in a quadrupole mass spectrometer with an API interface (Georgia Tech). The general design of the ion source is shown in ref. 60, but the primary ions are generated with a corona discharge³⁸. The corona needle holder was modified so that CO₂, O₃ and Ar are fed directly over the corona discharge. In this way, direct contact between the N₂ sheath flow and the discharge needle is avoided, which leads to a reduced
contamination by NO$_3$ and maximizes the ratio of CO$_2$ to NO$_2$. The reaction scheme for the ionization of SO$_2$ to SO$_3$ can be found in ref. 63. The use of a dry N$_2$ buffer flow in front of the pinhole of the mass spectrometer evacuates associated water molecules from SO$_3^+$ ions, and so sulfur dioxide is detected in the mass spectrum at m/z = 112 Th (SO$_3^+$).

The SO$_2$ concentration (in p.p.t.v.) is calculated from the ion count rates, R$_{HOM}$, as follows:

$$SO_2 = C_0 \ln(1 + R_{112}/R_{0})$$

where R$_{112}$ corresponds to the background-corrected ion count rate of SO$_2$ and R$_{0}$ is the ion count rate of the primary ion CO$_2$. The calibration factor C$_0$ was obtained by periodically calibrating the instrument with a SO$_2$ gas standard (Carbagas AG) during the campaign. During a calibration, the gas standard was diluted with ultraclean humidified air at 38% relative humidity (the same as that supplied to the CLOUD chamber) to achieve a range of different SO$_2$ mixing ratios between 12 p.p.t.v. and 11 p.p.b.v. The calibration factor was found to be 1.3 $\times$ 10$^3$ p.p.t.v., with an estimated uncertainty of ±11%. The error includes uncertainties in the flow rates during a calibration and in the gas standard concentration, as well as statistical uncertainties. However, we also observed that temperature changes in the experimental hall where the experiments were conducted led to a drift in the SO$_2$ background signal when no SO$_2$ was applied to the CIMS. This effect contributes to the overall uncertainty and mainly affects the measurement at low SO$_2$ levels (<100 p.p.t.v.), with lower precision in this concentration range. For example, at 30 p.p.t.v. SO$_2$, the estimated uncertainty is ±23%, but it becomes progressively smaller with higher SO$_2$ levels, reaching ±13% above 100 p.p.t.v. SO$_2$.

The detection limit of the instrument is 15 p.p.t.v. SO$_2$.

**Experimental errors.** To determine J$_{1,3}$, the measured particle concentrations in the PSIM1.8 and CPCI2.5 versus time are fitted with the AEROCLOUD model (see above). The nucleation rate error, $\sigma_J$, has three main components. The dominant error at slow growth rates is due to uncertainties in the PSIM1.8 and CPCI2.5 detection thresholds for HOM particles$^{24}$. The threshold error components are first determined numerically for each nucleation measurement by performing additional AEROCLOUD fits after shifting the PSIM1.8 particle detection threshold by +0.2–0.1 nm and the CPCI2.5 threshold by ±0.4 nm. This provides four fractional J$_{1,3}$ errors which are then averaged for each counter to provide a mean fractional uncertainty, $\sigma_{\text{dthr}}$ and $\sigma_{\text{dexp}}$, respectively. The total error due to detection threshold uncertainties, $\sigma_{\text{dth}}$, for the combined fit to the PSIM1.8 and CPCI2.5 data is then:

$$\sigma_{\text{dth}} = \frac{1}{2} \sigma_{\text{dthr}} + \sigma_{\text{dexp}}$$

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The total fractional J$_{1,3}$ error, $\sigma_J$, is then obtained by adding $\sigma_{\text{dth}}$ in quadrature with an experimental error due to run-to-run reproducibility under nominally identical chamber conditions, $\sigma_{\text{exp}}$ and $\sigma_{\text{mod}}$, respectively.

$$\sigma_J = \sigma_{\text{dth}} + \sigma_{\text{exp}} + \sigma_{\text{mod}}$$

The concentration of O$_3$ is measured with a calibrated instrument and is known to ±10%. The α-pinene concentration in the PTR-TOF is known to ±10%. As discussed above, the uncertainty on SO$_3$ is ±13% above 150 p.p.t.v., increasing at lower values to ±23% at 30 p.p.t.v.

For CI-API-TOF measurements, the run-to-run experimental uncertainties are ±10% for [H$_2$SO$_4$] and ±20% for [HOM]. However, there is a larger overall systematic error that scales all measurements by the same amount. The systematic scale uncertainty is 5% to 33%, with the largest effect being a 15%–33% systematic error due to run-to-run reproducibility under nominally identical chamber conditions. The systematic uncertainties for [HOM] have the following sources and fractional errors ($\sigma_J$): sulfuric acid calibration (50%), efficiency of MO62X/6-31$^+$ G(d) basis set66 of different molecular clusters of E1 and E2 that are either neutral or else include an ion of the ELVOC dimer, E2. Their formation is studied in ref. 68 for calculating the formation free energy of different clusters. Ref. 70 has shown reducing the basis set from large to small (STO-3G) leads to differences in the calculated formation free energies below 1 kcal mol$^{-1}$. The MO62X functional has been shown to be well suited to the study of atmospheric clusters$^{23}$. The neutral and ion-induced pure biogenic nucleation rates (in cm$^{-3}$ s$^{-1}$) are parameterized as:

$$J_a = \frac{2n[HOM][HOM] \alpha_{HOMO \rightarrow HOM}}{[HOM]_a}$$

where $[HOM]$ is the small-ion concentration of either sign. Expressions for [HOM] and $[HOM]$ are given in equations (7) and (10) below, respectively. The parameters $\alpha_a$ are determined from fits to the data in Fig. 3 and have the values $\alpha_a = 0.40001, \alpha_2 = 1.848, \alpha_3 = 0.001366, \alpha_4 = 1.566$ and $\alpha_5 = 0.1863$, with [HOM] expressed in units of 10$^9$ molecules cm$^{-3}$. The parameterized rates are shown by the curves in Fig. 3. The $R^2$ value of the fit is 0.97. The terms $\alpha_1$–$\alpha_4$ describe simple power laws, whereas the term $\alpha_5$ accounts for the steepening of the nucleation rate at low HOM concentrations. The nucleation rates are assumed to be independent of temperature, except for the effect of rate constants (equation (6) below), because the experimental measurements exist at only a single temperature.

The HOM concentration in equation (4) is determined from its production and loss rates:

$$\frac{d[HOM]}{dt} = Y_{HOM-\text{O}_2}J_{MT-O_2}[MT][O_2] + Y_{HOM-\text{OH}}J_{MT-OH}[MT][OH] - k_{HOM}[HOM]$$

where $T$ (in K) is the temperature (the α-pinene + O$_3$ rate constant is updated on the IUPAC website at http://iupac.pole-ether.fr/htdocs/datasheets/pdf/Ox_VOC8. O3_spine.pdf). The HOM yields in each of ozone–monoterpenes and hydroxyl–monoterpenes reaction are $Y_{HOM-O_2}$ and $Y_{HOM-OH}$, respectively. The parameter $k_{HOM}$ is the HOM loss rate or, equivalently, the atmospheric condensation sink, CS (in s$^{-1}$). The condensation sink is determined assuming the diffusion characteristics of a typical α-pinene oxidation product (see appendix A1 of ref. 71). Assuming steady-state in equation (5), the HOM concentration becomes:

$$[HOM] = Y_{HOM-O_2}J_{MT-O_2}[MT][O_2] + Y_{HOM-OH}J_{MT-OH}[MT][OH] - k_{HOM}[HOM]$$

where the HOM yield from ozonolysis is $Y_{HOM-O_2} = 2.9\%$, and from reaction with the hydroxyl radical is $k_{HOM} = 1.2 \times 10^{-11}$ exp(−440/T). The HOM yield from ozonolysis is determined from CLOUD measurements in the presence of a hydroxyl scavenger (0.1% H$_2$). The HOM yield from reaction with hydroxyl radicals is determined from CLOUD measurements in the absence of ozone, and where photolyzed HONO provides the OH source. Therefore, the experimental measurement of hydroxyl-initiated oxidation is made in the presence of NO$_x$, as occurs in the atmosphere.
The small-ion concentration in equation (4) is calculated from the steady-state solution of the ion balance equation:

$$\frac{dn_i}{dt} = q - \alpha n_i^2 - k_i n_i$$

(8)

where \( q \) (in cm \(^{-3} \cdot s^{-1} \)) is the ion-pair production rate and \( \alpha \) is the ion–ion recombination coefficient (in cm \(^{3} \cdot s^{-1} \)). The factor of 2 in equation (4) accounts for nucleation from positive and negative ions. For the CLOUD GCR data, \( q = 1.7 \) cm \(^{-3} \cdot s^{-1} \). Terrestrial radioactivity such as radon contributes additional ionization in the boundary layer over land masses \(^{31} \). The ion loss rate, \( k_i \), is due to the condensation sink, CS, and ion-induced nucleation:

$$k_i = CS + \frac{J_{\text{ion}}}{2n_i}$$

(9)

where \( J_{\text{ion}}/(2n_i) \) is given by equation (4) and the steady-state concentration of small ions is, from equation (8):

$$n_i = \frac{(K_2 + 4\alpha q)^{1/2}}{2\alpha}$$

(10)

From equations (8) and (9), \( J_{\text{ion}} \) saturates at 2\( q \) at high nucleation rates (see Fig. 3).

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Extended Data Figure 1 | Small-ion mass spectra. a, b, Composition of positive (a) and negative (b) small ions measured by the API-TOF under GCR conditions and before adding any SO\textsubscript{2} to the chamber. The experimental conditions are zero α-pinene, 35 p.p.b.v. O\textsubscript{3}, zero H\textsubscript{2} or HONO, 38% relative humidity, 278 K and [H\textsubscript{2}SO\textsubscript{4}] < 5 × 10\textsuperscript{4} cm\textsuperscript{−3}. Collisions will transfer positive charge to contaminant molecules having the highest proton affinity (a), and negative charge to contaminant molecules with the lowest proton affinity, that is, highest gas-phase acidity (b). From molecular cluster measurements, the positive ions also include ammonium (NH\textsubscript{4}\textsuperscript{+}), but its mass is below the set acceptance cut-off of the API-TOF. c, The negative small-ion spectrum at [H\textsubscript{2}SO\textsubscript{4}] = 1.2 × 10\textsuperscript{5} cm\textsuperscript{−3}, after adding 32 p.p.t.v. SO\textsubscript{2} to the chamber, showing that the dominant ions species shift from nitrate to sulfur-containing. The experimental conditions are 340 p.p.t.v. α-pinene, 35 p.p.b.v. O\textsubscript{3}, zero H\textsubscript{2} or HONO, 38% relative humidity and 278 K. Water molecules evaporate rapidly from most hydrated ions in the API-TOF and so are not detected.
Extended Data Figure 2 | HOM yields versus α-pinene oxidation rates with O₃ and OH. Total HOM mixing ratios versus α-pinene reaction rate with (i) O₃ plus OH· (ozone without H₂ scavenger; circles and solid line), (ii) O₃ alone (ozone with 0.1% H₂ scavenger; triangles and dashed line) and (iii) OH· alone (produced by ultraviolet photolysis of nitrous acid, HONO, in the absence of O₃; squares and dotted line). The yields are shown for total HOMs = RO₂ + E₁ + E₂. The experimental conditions are 38% relative humidity, 278 K and (i) 70–440 p.p.t.v. α-pinene, 21–35 p.p.b.v. O₃, zero H₂ or HONO, 0%–100% ultraviolet, (ii) 80–1,230 p.p.t.v. α-pinene, 21–35 p.p.b.v. O₃, 0.1% H₂, zero HONO, 0%–100% ultraviolet, and (iii) 840–910 p.p.t.v. α-pinene, zero O₃ or H₂, 0.5–3 p.p.b.v. HONO, 0%–100% ultraviolet. The bars indicate 1σ point-to-point errors. Overall systematic scale uncertainties of ±40% for the reaction rates and +80%−45% for the HOM mixing ratios are not shown. The combined errors on the HOM molar yields for either ozonolysis or hydroxyl chemistry are +100%−60% (±1σ).
Extended Data Figure 3 | Proposed mechanism for the formation of the E1 and E2 surrogates via peroxy radical formation. The proposed scheme for the formation of the ELVOC monomer (C_{10}H_{14}O_7) and dimer (C_{20}H_{30}O_{14}) surrogates selected for quantum chemical calculations (Extended Data Fig. 7) is based on recently established autoxidation mechanisms for a series of cycloalkane + O_3 systems. Peroxy radicals in the figure are indicated by a green label, E1 by a red label and E2 by a blue label. Addition of ozone to the double bond of α-pinene produces two carbonyl-substituted Criegee biradicals. The energy-rich Criegee biradical is either collisionally stabilized, or isomerizes via 1,4-H-shift to a vinylhydroperoxide (VHP), which then decomposes to yield an OH- and an alkeno radical. The alkeno radical reacts with O_3, leading to a peroxy radical, which is the potential precursor to a sequence of autoxidation reactions leading to the formation of HOMs. Here the peroxy radical C_{10}H_{15}O_5· is chosen as the starting point for HOM formation. The first intramolecular hydrogen abstraction is likely to take place at the aldehydic carbon from the opposite side of the peroxy group, although the rigid four-carbon-atom ring could hinder bending of the structure. The cis configuration where the peroxy group and the aldehydic hydrogen are on the opposite side of the cyclobutyl ring, the 1,7-H-shift is calculated to be 0.14 s^{-1}, which initiates the autoxidation chemistry on a fast timescale compared to the HOM lifetime resulting from loss to the CLOUD chamber walls (about 900 s). The resultant acyclic radical undergoes rapid O_3 addition, leading to an -OOH functionalized peroxy radical (C_{10}H_{15}O_6·). The second intramolecular hydrogen abstraction is expected to proceed at the carbon atom in the α position of the peroxy group via 1,4-H isomerization. The resultant C_{10}H_{15}O_8· terminates by known reactions of peroxy radicals (HO_2· or RO_2· under the present experimental conditions), producing a spectrum of HOM monomers that includes the E1 surrogate, C_{10}H_{15}O_7. The homogeneous recombination of two peroxy radicals via elimination of O_3 produces the covalently bound dimer C_{20}H_{30}O_{14} chosen as the E2 surrogate. Alternatively, C_{10}H_{15}O_8· can undergo further autoxidation, if sufficiently labile hydrogen atoms are available, leading to the observed closed-shell monomers with ≥9 O (Fig. 1). The self/cross-reaction of the C_{10}H_{15}O_7 peroxy radical produces an alkoxo radical, which decomposes rapidly, leading to a carbonyl-functionalized peroxy radical (C_{10}H_{15}O_5·). This peroxy radical is another potential starting structure for HOM formation. The carbon-ring-opening reaction pathway, while increasing the steric availability of the H atom, might be a slow step. The effective formation rate of the C=O-functionalized peroxy radical is calculated to be less than about 10^{-3} s^{-1}, which is comparable to its wall deposition rate. The timescale with respect to the subsequent autoxidation reaction, on the other hand, is expected to be of the order of seconds, by analogy with that for branched-chain peroxy radicals. The unbalanced sources and sinks potentially account for the low signals of peroxy radicals with odd oxygen numbers (for example, C_{10}H_{15}O_5, C_{10}H_{15}O_7 and C_{10}H_{15}O_9). The autoxidation process of C_{10}H_{15}O_5· is presumed to proceed by an α-pinene peroxy radical is another potential starting structure for HOM formation.
Extended Data Figure 4 | Typical nucleation run sequence. Example of a typical measurement sequence of the neutral and GCR nucleation rates as a function of coordinated universal time (utc), at zero H$_2$ or HONO, 38% relative humidity and 278 K. a, The run began at 21:22, 23 October 2013, by starting the α-pinene flow into the chamber to reach a chosen equilibrium value near 300 p.p.t.v., which produced an equilibrium total HOMs concentration near $2 \times 10^7$ cm$^{-3}$ (0.8 p.p.t.v.). b, Particles (red curve) formed at a slow rate in the chamber without ions present ('neutral' conditions). The clearing field high voltage (HV) was turned off at 05:16, 24 October 2013, and the subsequent presence of ions in the chamber from GCRs caused a sharp increase in the particle formation rate by about one order of magnitude (as seen by the increase in the gradient of the red curve). The nucleation rates are measured under constant gas conditions in the period before ($J_n = 0.14$ cm$^{-3}$ s$^{-1}$) and after ($J_{gcr} = 3.3$ cm$^{-3}$ s$^{-1}$) turning off the clearing field high voltage. c, d, Ion-induced nucleation is observed both for positive (c) and negative (d) charged particles, followed by rapid particle growth to sizes above 10 nm. e, The nucleated particles grew over a period of several hours to diameters approaching 50 nm, where they begin to constitute cloud condensation nuclei. A sharp increase in the formation rate of particles above the SMPS detection threshold of 5 nm can be seen when GCR ions are present. The colour scale in c–e indicates $dN/d\log(D_p)$, where $N$ (in cm$^{-3}$) is the particle number concentration and $D_p$ (in nm) is the particle diameter. The concentrations of ozone and contaminant H$_2$SO$_4$ were essentially constant during the run, which ended at 09:30 when the α-pinene flow to the chamber was turned off. The H$_2$SO$_4$ measurement near $5 \times 10^4$ cm$^{-3}$ corresponds to the instrumental background level of the CI-API-TOF mass spectrometer and so represents an upper limit on the actual concentration. Further characteristics of this run can be seen in Fig. 1.
Extended Data Figure 5 | Ion-induced nucleation event without $\text{H}_2\text{SO}_4$, measured in the NAIS. a, b. Example of a nucleation event showing the growth versus time of positive (a) and negative (b) charged particles at 530 p.p.t.v. $\alpha$-pinene, 35 p.p.b.v. $\text{O}_3$, zero $\text{H}_2$ or HONO, $3.4 \times 10^7 \text{ cm}^{-3}$ HOM, 38% relative humidity, 278 K and $[\text{H}_2\text{SO}_4] < 5 \times 10^4 \text{ cm}^{-3}$. The colour scale shows the concentration of ions and charged particles. The clearing field high voltage was turned off at 06:48, marking the start of GCR ionization conditions in the chamber, and the $\alpha$-pinene flow into the chamber was stopped at 10:52. Ion-induced nucleation can be seen for positive and negative charged particles, followed by rapid growth to sizes above 10 nm. Ion–ion recombination progressively neutralizes the charged particles as they grow, but some reappear at larger sizes, owing to diffusion charging.
Extended Data Figure 6 | Nucleation rates versus relative humidity.
Neutral ($J_n$; circles) and GCR ($J_{gcr}$; triangles) nucleation rates versus relative humidity. The experimental conditions are 250–800 p.p.t.v. α-pinene, 30–35 p.p.b.v. O₃, zero H₂ or HONO, (1.1−2.9) × 10⁷ cm⁻³ HOM, 278 K and (0.5−1.5) × 10⁵ cm⁻³ H₂SO₄. All measurements have been corrected to the same total HOMs concentration (2.05 × 10⁷ cm⁻³) using the curves shown in Fig. 3. The bars indicate 1σ total errors, although these are not shown in the x direction because they are smaller than the symbols.
Extended Data Figure 7 | Surrogate molecules chosen for quantum chemical calculations. a, b. Structures of the surrogate molecules chosen for quantum chemical calculations to represent the ELVOC monomer, E1, C10H14O7 (a) and the covalently bound dimer, E2, C20H30O14 (b).

Grey spheres represent carbon atoms, red are oxygen atoms and white are hydrogen atoms. We show their proposed formation mechanisms in Extended Data Fig. 3.
Extended Data Figure 8 | Relationship between cluster formation energies and equilibrium evaporation/condensation rates.

Estimated ELVOC vapour mixing ratios versus the ΔG_{278K} at which the condensation and evaporation rates of the cluster at 278 K are in equilibrium. For example, a formation free energy of −15.3 kcal mol$^{-1}$ corresponds to equal rates for particle evaporation and vapour condensation at 278 K and 1 p.p.t.v. ELVOC vapour mixing ratio ($2.6 \times 10^7$ cm$^{-3}$). The evaporation rate increases by a factor of 10 for each 1.27 kcal mol$^{-1}$ reduction of the cluster formation energy.
Extended Data Table 1 | Quantum chemical calculations of ELVOC cluster formation energies

| Cluster process | \( \Delta G_{278\,K} \) (kcal/mol) | Cluster process | \( \Delta G_{278\,K} \) (kcal/mol) | Cluster process | \( \Delta G_{278\,K} \) (kcal/mol) |
|-----------------|---------------------------------|-----------------|---------------------------------|-----------------|---------------------------------|
| \( E_1 + E_1 \) | -5.76                           | \( E_1 + E_1^- \) | -20.95                          | \( E_1 + NH_4^+ \) | -22.46                          |
| \( E_2 + E_1 \) | -2.15                           | \( E_2 + E_1^- \) | -19.90                          | \( E_2 + NH_4^+ \) | -30.87                          |
|                 |                                 |                 |                                 | \( E_1 + E_1\cdot NH_4^+ \) | -11.71                          |
|                 |                                 |                 |                                 | \( E_2 + E_1\cdot NH_4^+ \) | -24.35                          |
|                 |                                 |                 |                                 | \( E_1 + E_2\cdot NH_4^+ \) | -15.94                          |
| \( E_1 + H_2SO_4 \) | -9.90                           | \( E_1 + HSO_4^- \) | -26.97                          | \( E_1 + NO_3^- \) | -25.99                          |
| \( E_2 + H_2SO_4 \) | -12.04                          | \( E_2 + HSO_4^- \) | -30.30                          | \( E_2 + NO_3^- \) | -25.65                          |
| \( E_1 + E_1\cdot H_2SO_4 \) | +2.49                            | \( E_1 + HSO_4^- \) | -15.28                          | \( E_1 + E_1\cdot NO_3^- \) | -10.09                          |
| \( E_2 + E_1\cdot H_2SO_4 \) | +3.13                            |                 |                                 |                 |                                 |
| \( E_1 + E_2\cdot H_2SO_4 \) | -5.69                            |                 |                                 |                 |                                 |

Formation Gibbs free energies at 278 K, \( \Delta G_{278\,K} \), for neutral, negatively charged and positively charged ELVOC clusters. The cluster processes indicate the incident \( E_1/E_2 \) vapour molecule + the target cluster. Quantum chemical calculations made at other temperatures (not shown) indicate that the binding energies strengthen by \( \sim 1.0 \text{ kcal mol}^{-1} \) per 20 K reduction in temperature. The uncertainty in the calculated energies is less than 2 kcal mol\(^{-1}\). Our calculations indicate the following approximate order for different functional groups to contribute to the cluster binding energies involving HSO\(_4^-\) or H\(_2\)SO\(_4\) (starting with the strongest): (i) carboxylic acids, \( R\cdot-C(=O)\cdot-OH \); (ii) hydroxyls, \( R\cdot-OH \); (iii) hydroperoxy acids, \( R\cdot-C(=O)\cdot-O-\cdot OH \); (iv) hydroperoxides, \( R\cdot-O-\cdot OH \); and (v) carbonyls, \( R\cdot(C(=O))\cdot C=O \). In the case of \( NH_4^+ \), the main interacting group is carbonyl, independently of which other groups are attached to it; therefore ammonium will form stronger clusters with carboxylic acids, hydroperoxy acids or carbonyls than it will with hydroxyls or hydroperoxides.