Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere

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Nucleation of aerosol particles from trace atmospheric vapours is thought to provide up to half of global cloud condensation nuclei¹. Aerosols can cause a net cooling of climate by scattering sunlight and by leading to smaller but more numerous cloud droplets, which makes clouds brighter and extends their lifetimes². Atmospheric aerosols derived from human activities are thought to have compensated for a large fraction of the warming caused by greenhouse gases³. However, despite its importance for climate, atmospheric nucleation is poorly understood. Recently, it has been shown that sulphuric acid and ammonia cannot explain particle formation rates observed in the lower atmosphere³. It is thought that amines may enhance nucleation⁴–¹⁶, but until now there has been no direct evidence for amine ternary nucleation under atmospheric conditions. Here we use the CLOUD (Cosmics Leaving OUtdoor Droplets) chamber at CERN and find that dimethylamine above three parts per trillion by volume can enhance particle formation rates more than 1,000-fold compared with ammonia, sufficient to account for the particle formation rates observed in the atmosphere. Molecular analysis of the clusters reveals that the faster nucleation is explained by a base-stabilization mechanism involving acid–amine pairs, which strongly decrease evaporation. The ion-induced contribution is generally small, reflecting the high stability of sulphuric acid–dimethylamine clusters and indicating that galactic cosmic rays exert only a small influence on their formation, except at low overall formation rates. Our experimental measurements are well reproduced by a dynamical model based on quantum chemical calculations of binding energies of molecular clusters, without any fitted parameters. These results show that, in regions of the atmosphere near amine sources, both amines and sulphur dioxide should be considered when assessing the impact of anthropogenic activities on particle formation. The primary vapour responsible for atmospheric nucleation is thought to be sulphuric acid (H₂SO₄), derived from the oxidation of sulphur dioxide. However, peak daytime H₂SO₄ concentrations in the atmospheric boundary layer are about 10⁶ to 3 x 10⁷ cm⁻³ (0.04–1.2 parts per trillion by volume (p.p.t.v.)), which results in negligible binary homogeneous nucleation of H₂SO₄–H₂O (ref. 3). Additional species such as ammonia or amines⁴–⁵ are therefore necessary to stabilize the embryonic clusters and decrease evaporation. However, ammonia cannot account for particle formation rates observed in the boundary layer and, despite numerous field and laboratory studies⁶–¹⁰, amine ternary nucleation has not yet been observed under atmospheric conditions. Amine emissions are dominated by anthropogenic activities (mainly animal husbandry), but about 30% of emissions are thought to arise from the breakdown of organic matter in the oceans, and 20% from biomass burning and soil¹¹–¹⁴. Atmospheric measurements of gas-phase amines are sparse, but typical values range between negligible and a few tens of p.p.t.v. per amine species¹⁵–¹⁸.

Here we report results from the CLOUD experiment at CERN (for experimental details see Methods, Extended Data Fig. 1 and Supplementary Information). The data were obtained during three campaigns at the CERN Proton Synchrotron between October 2010 and November 2012, and comprise measurements of sulphuric acid–amine nucleation at atmospheric concentrations. Dimethylamine (DMA; CH₃NH₂) was selected for this study because it is expected to have cluster binding energies representative of other light alkyl amines. Nucleation rates J were measured under neutral (J₀), galactic cosmic ray (J_gcr) and n° beam (J_e) conditions, corresponding to ion-pair concentrations of about 0, 560 and 3,000 cm⁻³, respectively. Both J_gcr and J_e comprise the sum of neutral and ion-induced nucleation rates, whereas J₀ measures the neutral rate alone. Figure 1 shows the nucleation rates at 1.7 nm mobility diameter (1.4 nm mass diameter) as a function of [H₂SO₄] for ‘binary’ (H₂SO₄–H₂O), ammonia ternary (H₂SO₄–NH₃–H₂O) and amine ternary (H₂SO₄–DMA–H₂O) nucleation at 278 K and 38% relative humidity (RH). Here ‘binary’ includes previous measurements made in the presence of NH₃ and DMA contaminants¹⁹, estimated from earlier campaigns to be <2 p.p.t.v. and <0.1 p.p.t.v., respectively, for the conditions of ref. 3. Nucleation rates
with amine nucleation. However, the atmospheric data show considerable variability, probably resulting from variations in ternary vapour concentrations and particle coagulation sinks. When growth rates are low, the measured nucleation rates are highly sensitive to particle coagulation sinks, which influence particle losses both above and below the quoted formation threshold sizes. Losses below the threshold size are uncorrected, implying higher variability in the atmosphere, where conditions are less well defined than in the laboratory.

Figure 1 shows the theoretical expectations for NH₃ (blue band) and DMA ternary nucleation (orange band), obtained with the Atmospheric Cluster Dynamics Code model (ACDC)²⁴ (see Methods and Supplementary Information for further details). The model uses cluster evaporation and fragmentation rates calculated from quantum chemistry, with no fitted parameters²⁵. The agreement is quite good, although the model predicts somewhat higher DMA ternary nucleation rates than measured experimentally. Part of this discrepancy is due to the smaller size—and hence higher formation rate—of the modelled clusters (up to four acid and four base molecules per cluster, corresponding to mobility diameters of 1.2–1.4 nm). Computational studies (see Supplementary Information and Extended Data Figs 2 and 3) indicate that DMA ternary nucleation is rather insensitive to RH or temperature, reflecting the strong acid–base binding. The experimental measurements obtained at 38% RH and 278 K may therefore be considered representative of a wide range of boundary layer conditions.

Plots of the nucleation rates Jₑ, Jₐcr, and Jₐ against DMA mixing ratio are shown in Fig. 2a. Here, all measurements have been scaled to [H₂SO₄] = 2.0 × 10⁶ cm⁻³ using the fitted slopes, n, from Fig. 1. The addition of only 5 p.p.t.v. DMA enhances the nucleation rate of sulphuric acid particles by more than six orders of magnitude, but the addition of further DMA up to 140 p.p.t.v. produces a negligible further increase. The measured neutral, galactic cosmic ray (GCR) and beam nucleation rates are indistinguishable, within experimental uncertainties. However, a more sensitive determination of the ion-induced nucleation rate, J_{ion} = J_{ion}^+ + J_{ion}^−, is obtained from direct ion measurements with the neutral cluster and air ion spectrometer. The ion-induced fractions, J_{ion}/J_{tot} or J_{ion}/Jₐ (Fig. 2b), are found to average about 20% at 0.5 cm⁻³ s⁻¹ but grow in relative importance as the total nucleation rate decreases. This indicates that the influence of galactic cosmic rays on the nucleation of sulphuric acid–amine particles is only significant at low overall formation rates. No difference is measured for the ion-induced fraction under GCR or beam conditions (Fig. 2b). This follows, because the ion–ion recombination lifetimes are below 10 min and are comparable to the monomer arrival rate on the cluster (one molecule per 12 min for H₂SO₄·HSO₄⁻ at 10⁶ cm⁻³ [H₂SO₄]). Consequently, although the ion pair concentration is larger for beam conditions, it is compensated for by a shorter ion lifetime, which decreases the time available for nucleation before the ion cluster is neutralized.

Figure 3 shows the molecular composition of nucleated charged clusters in the presence of DMA for negative ions (Fig. 3a) and positive ions (Fig. 3b), measured with atmospheric-pressure interface time-of-flight mass spectrometers (APi-TOFs). The predominant negatively charged clusters include an HSO₄⁻ or HSO₅⁻ ion. The latter is deprotonated peroxysulphuric acid, whose presence varies with the ozone concentration in the chamber (it is absent when no ozone is present). We found no indication that the nucleation rates are sensitive to the relative contribution of these ion species. Contaminant NO₃⁻ ions are also detected, but at much lower concentrations. The predominant positively charged clusters contain a protonated DMA ion, DMA•H⁺ (C₅H₇•NH⁺), in association with H₂SO₄ and DMA. The remaining positive ions are largely protonated light organic contaminants, mostly also nitrogen-containing.

Amine ternary nucleation is observed to proceed by the same base-stabilization mechanism as that found previously for ammonia ternary nucleation²⁶. We will use the label (n, m) to indicate the number of sulphuric acid (nSA) and DMA (mDMA) molecules in pure
SA·DMA clusters, where \( n \) and \( m \) include both neutral and charged species. Negatively charged nucleation (Fig. 3a) proceeds as follows. The first step is dimer (2, 0) formation: HSO\(_4^−\) bound to form an acid–base pair is the acid trimer. The most abundant acid trimer contains two DMA molecules (3, 2). Thereafter, each additional acid molecule is stabilized by one additional DMA molecule, following a sequence of acid–base pairs: (3, 2) → (4, 3) → (5, 4) → \( \ldots \), \( n, \quad n = 1 \). Our calculations suggest that the process involves mainly the accretion of SA·DMA (dimethylaminium bisulphate) clusters, but it may also involve the stepwise addition of an SA molecule followed by a DMA molecule. Beyond (7, 6) clusters, there is evidence for further neutralization of the acid by additional DMA (partial formation of dimethylammonium sulphate).  

Positively charged nucleation (Fig. 3b) proceeds similarly. Here DMA·H\(^+\) is a Lewis acid and so binds only weakly with H\(_2\)SO\(_4\). Hence the first positively charged cluster is a DMA·H\(^+\) ion together with a single SA·DMA acid–base pair (1, 2). Thereafter, the cluster grows by the accretion of SA·DMA pairs, exactly as seen for negatively charged clusters. No DMA·H\(^+\) monomer is detected because its mass-to-charge ratio \((m/z)\) is below the API-TOF cutoff, as configured for these experiments.

Because both HSO\(_4^−\) and DMA are Lewis bases, each can form an acid–base pair with H\(_2\)SO\(_4\). In fact HSO\(_4^−\) is the stronger base, as demonstrated by its much stronger binding energy with H\(_2\)SO\(_4\) (Supplementary Table 1)\(^b\). The only fundamental difference is that not more than one HSO\(_4^−\) ion can be present in the cluster because of electrostatic repulsion. So, although the API-TOF measures only charged clusters in the CLOUD chamber, this suggests that neutral nucleation proceeds by the same mechanism, namely the initial formation of an acid–base pair (SA·DMA)—equivalent to the acid–base pair (SA·HSO\(_4^−\)) seen in charged nucleation (Fig. 3a)—and subsequently the accretion of additional SA·DMA pairs. This is also indicated by the Atmospheric Cluster Dynamics Code (ACDC) model (see Supplementary Information and Extended Data Fig. 4).

There is direct experimental evidence to support this picture of the neutral nucleation mechanism. Figure 4 shows a plot of the concentration...
of the neutral acid dimer against that of the neutral acid monomer, measured with the chemical ionization mass spectrometer (CIMS) before and after the addition of DMA, when the clearing field was present (implying that there were only neutral clusters in the CLOUD chamber). We infer from the observed absence of DMA on the negatively charged monomer or dimer (Fig. 3a) that, after charging in the CIMS, clusters containing one H$_2$SO$_4$ molecule will be detected as DMA-free charged monomers, and clusters containing two H$_2$SO$_4$ molecules will be detected as DMA-free charged dimers—regardless of whether or not they were originally clustered with DMA. Before adding any DMA, the dimer concentrations are consistent with the expected production in the CIMS ion source. However, with 5 p.p.t.v. DMA or more, the dimer concentrations are about six orders of magnitude higher than those measured with the CIMS before and 10 p.p.t.v. DMA in the ACDC model, assuming 0.5 sticking probability (dashed red line). The orange band shows the model uncertainty range (sticking probabilities between 0.1 and 1.0). The brown curve indicates the upper limit of the dimer concentration calculated with the ACDC model, which is close to the kinetic limit (unit sticking probability and negligible evaporation).

The results reported here show that nucleation in the atmospheric boundary layer is highly sensitive to trace amine levels of only a few p.p.t.v. Sulphuric acid–amine nucleation is found to proceed by the same base-stabilization mechanism as that previously observed for ammonia, in which each additional acid molecule in the cluster is stabilized by one (or occasionally, two) base molecules\(^5\). However, the acid–base pairs that sulphuric acid forms with amines are more tightly bound than with ammonia, resulting in cluster formation rates that approach the kinetic limit. Little increase is seen above 5 p.p.t.v. DMA, indicating that nucleation at atmospheric H$_2$SO$_4$ concentrations (below $3 \times 10^7$ cm$^{-3}$ or 1.2 p.p.t.v.) is then limited by the availability of H$_2$SO$_4$ and not that of DMA. Our experimental rate and molecular measurements are well reproduced by a dynamical model based on quantum chemical calculations of binding energies of molecular clusters.

Although measurements of ambient gas-phase amines are rare, mixing ratios of a few p.p.t.v. in the continental boundary layer have been reported\(^{17,19,20}\), suggesting that sulphuric acid–amine nucleation is likely to be an important atmospheric process. However, atmospheric observations indicate both the presence\(^{10,11,16}\) and the absence\(^{22}\) of a significant amine fraction in newly formed particles, which suggests considerable variability of ambient amine levels. Although amines are volatile vapours, our measurements show that sulphate particles constitute an almost perfect sink (negligible evaporation). However, unlike H$_2$SO$_4$, amine vapours are directly emitted from sources in their chemically active form and so they will be localized to source regions, with highly variable concentrations that depend on ambient sulphate particle sinks and OH radical levels (the DMA oxidation lifetime is about 4 h at $10^6$ cm$^{-3}$ (OH)). Amines can therefore explain only a part of atmospheric nucleation. Indeed, our measurements leave open the possibility that nucleation may also proceed with other atmospheric vapours, such as highly oxidized organic species of very low volatility. In such cases, extremely low amine concentrations may still enhance nucleation by forming stable acid–base pairs with some fraction of the sulphuric acid molecules in an embryonic cluster (constituting at least four-component nucleation). The ion-induced contribution to amine ternary nucleation is generally small, except at low overall formation rates. Ions can enhance nucleation either by an increased collision rate between a charged cluster and polar molecules (such as H$_2$SO$_4$ or H$_2$SO$_4$•••DMA) or by an increased cluster binding energy (and hence decreased evaporation rate). Because neutral clusters of H$_2$SO$_4$ and DMA are highly stable, charge offers little competitive advantage. Taken together with previous CLOUD measurements\(^1\), this suggests that ions can be significant in atmospheric particle formation provided that the associated neutral particles have appreciable evaporation and provided that the overall nucleation rates are low and below the ion-pair production rate.

The Intergovernmental Panel on Climate Change (IPCC) considers that the increased amount of aerosol in the atmosphere from human activities constitutes the largest present uncertainty in climate radiative forcing\(^7\) and projected climate change this century\(^8\). The results reported here show that the uncertainty is even greater than previously thought, because extremely low amine emissions—which have substantial anthropogenic sources and have not hitherto been considered by the IPCC—have a large influence on the nucleation of sulphuric acid particles. Moreover, amine scrubbing is likely to become the dominant technology for CO$_2$ capture from fossil-fuelled power plants, so anthropogenic amine emissions are expected to increase in the future\(^8\). If amine emissions were to spread into pristine regions of the boundary layer where they could switch on nucleation, substantial increases in regional and global cloud condensation nuclei could occur. This underscores the importance of monitoring amine emissions—as well as those of sulphur dioxide—when assessing the impact of anthropogenic activities on the radiative forcing of regional and global climate by aerosols.

**METHODS SUMMARY**

CLOUD is designed to study the effects of cosmic rays on aerosols, cloud droplets and ice particles, under precisely controlled laboratory conditions. The CLOUD chamber and gas system have been built to the highest technical standards of cleanliness and performance. Owing to its large volume (26 m$^3$) and highly stable...
operating conditions, the chamber allows nucleation rates to be measured reliably over a wide range from 0.001 cm$^{-3}$ s$^{-1}$ to well above 100 cm$^{-3}$ s$^{-1}$. The loss rate of condensable vapours onto the walls of the chamber is comparable to the condensation sink rate onto ambient aerosols under pristine atmospheric boundary layer conditions. The experiment has several unique aspects, including precise control of the ‘cosmic ray’ beam intensity from the CERN Proton Synchrotron, the capability to create an ion-free environment with an internal electric clearing field, precise and uniform adjustment of the H$_2$SO$_4$ concentration by means of ultraviolet illumination from a fibre-optic system, and highly stable operation at any temperature between 203 and 300 K. The contents of the chamber are continuously analysed by a suite of instruments connected to sampling probes that project into the chamber.

The experimental measurements are compared with theoretical expectations based on a dynamical model in which collision and coagulation rates are computed from kinetic gas theory. Equilibrium constants are computed from quantum chemical calculations of binding energies of molecular clusters, and evaporation and cluster fission rates are then obtained from detailed balance. All possible ionic-molecule collisions is calculated by using dipole moments and polarizabilities obtained from quantum chemistry. The model has no fitted parameters.

Online Content Any additional Methods, Extended Data display items and Source Data are available in the online version of the paper; references unique to these sections appear only in the online paper.

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METHODS

The key features of the CLOUD experiment (Extended Data Fig. 1) are a large-volume (26 m³) stainless steel chamber; precise (±0.1 K) temperature control at any tropospheric temperature; precise delivery of selected trace gases and ultrapure humidified air; precise and uniform adjustment of the H₂SO₄ concentration by means of ultraviolet illumination from a fibre-optic system; suppression of contaminant vapours at the technological limit; an adjustable π beam from the CERN Proton Synchrotron to simulate cosmic rays; and the ability to simulate an ion-free environment by applying an electric field to sweep ions from the chamber.

A comprehensive array of state-of-the-art instruments continuously samples and analyses the contents of the chamber. For the results reported here, the instruments included a chemical ionization mass spectrometer for H₂SO₄ concentration, two API-TOFs (TOPWERK AG and Aerodyne Research, Inc.) for the molecular composition of positive and negative charged clusters, several on-line condensation particle counters (CPCs) with 50% detection efficiency thresholds near 2 nm (two Airmondo A09 particle size magnifiers (PSMs)) , two diethyleneglycol CPCs (DEG-CPCs)), a TSI 3776 CPC and a TSI 3786 CPC), a scanning mobility particle sizer (SMPS), a neutral cluster and air ion spectrometer (NAIS) , a proton transfer reaction time-of-flight mass spectrometer for organic vapours, and an ion chromatograph for measurements of NH₃ and DMA concentrations.

Two particle counters were operated in a continuously stepped scanning mode to provide measurements of particle growth rates at small sizes: first, a PSM whose detection threshold was varied between about 1 and 2.5 nm, and second, the TSI 3786 with a variable laminar flow rate through its sampling probe, leading to a cutoff size between about 2.5 and 5 nm. The H₂SO₄ concentration is derived from the AIS measurement of sulphuric acid monomer signal after charging in the CIMS ion source. The sulphuric acid dimer concentration measured by the CIMS is derived assuming the same calibration factor as for monomers.

Nucleation rates \( J_{\text{nucl}} \), ion-induced nucleation rates \( J_{\text{ind}} \), and \( J_{\text{gcr}} \) cm² s⁻¹ were measured as follows. Neutral nucleation rates are measured with no pion beam and with the field cage electrodes set to ±30 kV, which establishes an electric field of about 20 kV m⁻¹ in the chamber. This completely suppresses ion-induced nucleation because, under these conditions, small ions or molecular clusters are swept from the chamber in about 0.1 ms. This completely suppresses ion-induced nucleation because, under these conditions, boundary-layer conditions, the reported formation rates at 1.7 nm size should correlate with the detection size threshold. The overall measurement error on \([\text{H}_2\text{SO}_4]\) measured by the CIMS is estimated to be ±100%/±50%, on the basis of three independent measurements: particle growth rate under binary nucleation conditions, the depletion rate of [SO₂] by photo-oxidation, and an external calibration source. However, the run-to-run relative experimental uncertainty on \([\text{H}_2\text{SO}_4]\) is smaller, typically ±10%. In deriving the sulphuric acid dimer concentrations measured by the CIMS (Fig. 4), we assumed the same charging efficiency by the ion source as for monomers. The concentrations of SO₂ and O₃ are measured with calibrated instruments and are known to ±10%. The overall uncertainty on the NH₃ mixing ratio is estimated to be ±100%/±50%. The point-to-point uncertainty on the DMA mixing ratio is estimated to be ±11% [±12% (p.p.t.v.)]. With an overall scan uncertainty of ±50%/±33%. The minimum directly measurable values are 2 p.p.t.v. for NH₃ and 0.2 p.p.t.v. for DMA. However, lower values can be estimated from the precise calibration of the APi-TOF mass spectrometer, the removal of clusters of neutral mass 101, and the progression of the mass spectrum with molecular analysis of the nucleating clusters in the APi-TOFs.

To compare the CLOUD measurements with theoretical expectations, all possible collision, coagulation, evaporation and fragmentation reactions have been explicitly simulated for a certain set of clusters. Collision and coagulation rates are computed from kinetic gas theory, while evaporation and fragmentation rates are obtained from quantum chemistry. Dynamical simulations were performed with the ACDC model to calculate the formation of neutral, positively charged and negatively charged clusters containing sulphuric acid, ammonia and DMA. The electrostatic enhancement of ion-molecule collisions is calculated using dipole moments and polarizabilities as obtained from quantum chemistry. The model has no free fitting parameters. As a result of computing limitations, the formation and evaporation of clusters containing up to four sulphuric acid and four base molecules (mobility diameters 1.2–1.4 nm) have been modelled so far. The diameters of the largest computed clusters are smaller than the 1.7 nm size at which the experimental formation rates \( J_{\text{nucl}} \) are determined. The modelled formation rates can therefore be expected to overestimate the CLOUD measurements somewhat. Further description of the ACDC model is provided in Supplementary Information.

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Extended Data Figure 1 | Schematic diagram of the CLOUD experiment at the CERN Proton Synchrotron.
Extended Data Figure 2 | Theoretical dependence of amine ternary nucleation rates on RH. Modelled neutral nucleation rates as a function of RH (left-hand scale) at $2.0 \times 10^6$ cm$^{-3}$ [H$_2$SO$_4$] and 278 K, and either 0.1 p.p.t.v. DMA (purple curve) or 10 p.p.t.v. DMA (red curve). The nucleation rates relative to their value at 38% RH are shown on the right-hand scale (dashed purple and red curves).
Extended Data Figure 3 | Theoretical dependence of ammonia ternary and amine ternary nucleation rates on temperature. Modelled GCR nucleation rates as a function of temperature (left-hand scale) at $2.0 \times 10^8 \text{ cm}^{-3} \text{[H}_2\text{SO}_4\text{]}$ and either $2.0 \times 10^8 \text{ cm}^{-3} \text{[NH}_3\text{]}$ (blue curve) or $2.0 \times 10^8 \text{ cm}^{-3} \text{[DMA]}$ (red curve). (A concentration of $2.0 \times 10^8 \text{ cm}^{-3}$ is equivalent to mixing ratios between 7.0 p.p.t.v. at 255 K and 8.2 p.p.t.v. at 300 K.) The sulphuric acid–DMA nucleation rate relative to the value at $T = 278 \text{ K}$ is shown on the right-hand scale (dashed red line). In the sulphuric acid–DMA system a sticking probability of 0.5 is assumed for all neutral–neutral collisions, and 1.0 for all charged–neutral collisions.
Extended Data Figure 4 | Theoretical concentrations of negative, positive and neutral clusters during DMA ternary nucleation. Modeled steady-state concentrations (mDMA versus nSA) at $4.0 \times 10^6$ cm$^{-3}$ [H$_2$SO$_4$], 10 p.p.t.v. DMA, 4 ion pairs cm$^{-3}$ s$^{-1}$ and 278 K. a, Negative clusters. b, Positive clusters. c, Neutral clusters. A sticking probability of 0.5 is assumed for all neutral–neutral collisions and 1.0 for all charged–neutral collisions. The numbers below the centre of each circle show log$_{10} C$, where $C$ (cm$^{-3}$) is the cluster concentration (the threshold is 0.01 cm$^{-3}$). The circle areas within each panel are proportional to $C$ (with the exception of the DMA monomer in c).