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Methane sulfonic acid enhanced formation of molecular clusters of sulfuric acid and dimethyl amine

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Abstract. Over oceans and in coastal regions methane sulfonic acid (MSA) is present in substantial concentrations in aerosols and in the gas phase. We present an investigation of the effect of MSA on sulfuric acid and dimethyl amine (DMA) based cluster formation rates. From systematic conformational scans and well tested ab initio methods, we optimize structures of all MSA_x $(H_2SO_4)_yDMA_z$ clusters where $x+y \leq 3$ and $z \leq 2$. The resulting thermodynamic data is used in the Atmospheric Cluster Dynamics Code and the effect of MSA is evaluated by comparing ternary MSA-H_2SO_4-DMA cluster formation rates to binary H_2SO_4-DMA cluster formation rates. Within the range of atmospherically relevant MSA concentrations, we find that MSA may increase cluster formation rates by up to one order of magnitude, although typically, the increase will be less than 300 % at 258 K, less than 100 % at 278 K and less than 15 % at 298 K. The results are rationalized by a detailed analysis of the the main growth paths of the clusters. We find that MSA enhanced clustering involves clusters containing one MSA molecule, while clusters containing more than one MSA molecule do not contribute significantly to the growth.

1 Introduction

One of the least understood micro-physical processes in the atmosphere is the conversion of low volatile gaseous molecules into an aerosol particle. Aerosol particles are a major source of cloud condensation nuclei and aerosol formation represents one of the largest uncertainties in climate and cloud models (Solomon et al., 2007; Kazil et al., 2010; Pierce and Adams, 2009). Despite recent advances in theory and instrumentation, the chemical composition of the molecular clusters forming the seeds for the thermally stable aerosol particles remains highly uncertain in most locations.

The decisive importance of sulfuric acid for atmospheric aerosol formation is well established, but within the last decades it has become evident that at least one, but probably more stabilizing species participate as well (Weber et al., 1996; Almeida et al., 2013). Nitrogenous bases, most efficiently dimethyl amine (DMA), and highly oxidized organic compounds are known to enhance sulfuric acid based aerosol formation. However, in locations where these are sparse other species may contribute significantly.

Methane sulfonic acid (MSA) is the simplest organosulfate and is a well known oxidation product of dimethylsulfide. Over oceans and in coastal regions, gaseous MSA is present in concentrations of about 10 to 50 % of the gaseous sulfuric acid (H_2SO_4) concentration, (Berresheim et al., 2002; Huebert et al., 1996) although MSA/H_2SO_4 ratios up to 250 % have been reported (Davis et al., 1998). Similarly, in sub-μm aerosol particles MSA is typically found in concentrations of 5 to 30 % of the sulfate concentrations (Ayers et al., 1991; Huebert et al., 1996; Kerminen et al., 1997) although MSA/sulfate ratios around 100 % have been reported in aerosols smaller than 0.2 μm (Facchini et al., 2008). It is generally accepted that much particulate MSA originate from surface oxidation of dimethyl sulfoxide (DMSO) and methane sulfinic acid (MSIA) (Davis et al., 1998; Barnes et al., 2006). However, in a recent study by Dall'Osto et al. (2012), gaseous MSA concentrations were found to decrease during marine particle formation events, suggesting that MSA may contribute to growth and possibly formation of the initial molecular clusters seeding aerosol formation.

Several laboratory and theoretical studies have attempted to explain these observations and determine at which state MSA enters the aerosol particle. Earlier studies have often used classical nucleation theory to predict or reproduce particle formation rates of various mixtures of H_2SO_4, MSA and water, generally finding that MSA is of minor importance

(Wyslouzil et al., 1991; Napari et al., 2002; Van Dingenen and Raes, 1993). Later studies by Dawson et al. (2012) and Bzdek et al. (2011) combining flow tube experiments and ab initio calculations, found that water and nitrogenous bases enhanced MSA based aerosol formation and that amines are more efficient than ammonia, and recently, Dawson et al. (2014) found that trimethylamine was susceptible for substitution by both methylamine and DMA. Further, Dall'Osto et al. (2012) used quantum chemical calculations, considering the molecular clusters containing up to two acids and one DMA molecule, to support the hypothesis that MSA, H_2SO_4 and DMA could co-exist in newly formed molecular clusters.

These studies have prompted a more rigorous ab initio based evaluation of whether MSA contributes to aerosol formation or mainly enters the aerosol during growth. This study targets the enhancing effect of MSA on sulfuric acid-DMA based cluster formation. Via systematic conformational searches we have obtained minimum free energy structures of clusters of composition MSA_x $(H_2SO_4)_y DMA_z$ where $x+y \leq 3$ and $z \leq 2$. The corresponding thermodynamic data is used in the Atmospheric Cluster Dynamics Code (ACDC) (McGrath et al., 2012; Olenius et al., 2013) whereby the enhancing effect of MSA is obtained by comparing ternary MSA-H_2SO_4-DMA to binary H_2SO_4-DMA based cluster formation rates.

The clusters studied in this work do not contain water molecules due to the considerable additional computational effort required to obtain the necessary thermodynamic data. Hydration can be expected to stabilize weakly bound clusters more than strongly bound clusters and it is therefore conceivable that we will underestimate the contribution from some of the minor growth pathways. However, since DMA is a much stronger base than water, hydration is not likely to have a significant effect on the stability of clusters containing DMA. Therefore, the main growth pathways and growth rates are unlikely to change significantly due to hydration. See e.g. Almeida et al. (2013) and Henschel et al. (2014) for further discussion.

2 Computational details

2.1 Ab initio calculations

The most critical parameters in cluster growth models are the cluster binding free energies since the evaporation rate depends exponentially on these. At present, density functional theory (DFT) and second order Møller–Plesset perturbation theory (MP2) are the most popular ab initio methods for calculating the thermodynamics of molecular clusters. It is often mentioned that average uncertainties are on the order of 1 kcal mol^{-1}, but depending on the specific system and method, uncertainties may be significantly larger. Therefore, careful testing and validation should precede each study, which we will discuss in the following.

Since acid-base clustering is considered one of the fundamental processes driving aerosol formation, we have tested the performance of four commonly used DFT functionals and MP2, comparing these to previously published data. Also, the effect of electronic energy corrections from high level coupled cluster calculations is tested. The basis set effects have previously been found to be much less significant, provided that a basis set of at least triple-ζ quality is used (Bork et al., 2014a). In this study we use the 6-311++G(3df,3pd) (Francl et al., 1982; Clark et al., 1983) basis set in all DFT and MP2 calculations.

From the first and second sections of Table 1, we see that the CCSD(T)-F12/VDZ-F12 electronic energy corrections significantly reduce the scatter of the data. This suggest that the thermal and zero-point vibrational terms are well produced by the four DFT functional and MP2, and that the main errors are associated with the electronic energies. Also, the data reveal that amongst the tested methods the M06-2X, ωB97X-D and PW91 density functionals perform well whereas B3LYP performs poorly on systems representative by clustering of H_2SO_4 and MSA with DMA.

In several recent studies (Bork et al., 2014a,b; Leverentz et al., 2013; Elm et al., 2012, 2013b) the M06-2X functional (Zhao and Truhlar, 2008) has been shown to be amongst the most reliable and accurate density functionals with respect to binding free energies of molecular clusters. Therefore, its performance for the present systems was investigated in greater detail. Table 2 shows the effect of a CCSD(T)-F12a/VDZ-F12 single point electronic energy correction to the M06-2X Gibbs free energy for six relevant reactions. For the formation of the $DMA \cdot H_2SO_4$ and $DMA \cdot MSA$ complexes a slight underestimation is observed in agreement with previous studies of similar systems (Bork et al., 2014a; Elm et al., 2012, 2013b). For the $MSA \cdot H_2SO_4$, $(H_2SO_4)_2$ and MSA_2 complexes the DFT values are seen to overestimate the Gibbs free energies of formation by up to 2.14 $kcal\,mol^{-1}$. No reliable representative experimental data exist for comparison of acid-acid cluster binding energies. However, the binding energy of $(H_2SO_4)_2$ has been investigated by Ortega et al. (2012), using MP2 up to pentruple ζ basis sets including also anharmonic and relativistic effects, arriving at a value of $-7.91\,kcal\,mol^{-1}$. This indicates that the apparent overbinding of the M06-2X functional is less severe than $2\,kcal\,mol^{-1}$ and that M06-2X based errors in binding energies of molecular clusters with both acid-acid and acid-base bonds will tend to cancel out rather than to accumulate.

All DFT and MP2 geometry optimizations and frequency calculations are performed using Gaussian 09 (Revision B.01, http://www.gaussian.com) and all CCSD(T)-F12 calculations are performed using Molpro (Version 2012.1, http://www.molpro.net).

Besides an appropriate computational method, a second pre-requisite for obtaining correct cluster binding free energies is to obtain the global minimum energy structures. In

this study we employ a systematic sampling technique initiated by 1000 auto generated guess structures, pre-optimized using the PM6 semi-empirical method (Stewart, 2007). The up to 100 best guess structures are further refined using M06-2X/6-311++G(3df,3pd). For full detail of the sampling technique we refer to our previous investigations (Elm et al., 2013c,a). Additionally, guess structures for all cluster compositions were manually constructed based on previously published $(H_2SO_4)_x DMA_y$ and $(H_2SO_4)_x\ (NH_3)_y$ structures (Nadykto et al., 2011; Ortega et al., 2012). In several cases this lead to identical structures as the above mentioned systematic sampling, but in no cases did the manual approach lead to improved binding energies compared to the systematic approach.

2.2 Cluster growth model

The resulting thermodynamic data was studied with the kinetic model Atmospheric Cluster Dynamics Code (ACDC) (McGrath et al., 2012; Olenius et al., 2013). The code solves the time evolution of molecular cluster concentrations for a given set of clusters and ambient conditions, considering all possible collision and fragmentation processes. In this study, ACDC is used to find the steady-state of the cluster distribution at given concentrations of MSA, H_2SO_4 and DMA. The collision rate coefficients are calculated as hard-sphere collision rates and the evaporation rate coefficients are calculated from the Gibbs free energies of formation according to detailed balance.

As the vapour-phase concentrations of MSA and H_2SO_4 generally are measured with chemical ionization mass spectrometry (CIMS), the atmospheric concentrations reported in the literature are likely to include contributions from acid molecules clustered with bases, in addition to the bare acid monomer (Kupiainen-Määttä et al., 2013). Therefore the acid concentrations in ACDC (both MSA and H_2SO_4) are defined as the sum of all clusters consisting of one acid molecule and any number of DMA molecules. An external sink with a loss rate coefficient of $2.6 \times 10^{-3}\,\mathrm{s}^{-1}$, corresponding to coagulation onto pre-existing larger particles is used for all clusters (Dal Maso et al., 2008). Testing showed that variations in this value between $10^{-3}\,\mathrm{s}^{-1}$ and $5 \times 10^{-3}\,\mathrm{s}^{-1}$ did not affect the main conclusions of this study (Figure S1).

When a collision leads to a cluster that is larger than the simulated system, the cluster is allowed to grow out if it contains at least three acid and three base molecules since these compositions are assumed to be along the main growth path. The probability of a three acid-three base cluster to grow further vs. to re-evaporate back into the system was investigated by optimizing also the $MSA(H_2SO_4)_2DMA_3$ cluster. At $T = 298\,\mathrm{K}$, for example, the reaction

$$MSA(H_2SO_4)_2DMA_3 \leftrightarrow MSA(H_2SO_4)_2DMA_2 + DMA$$

has $\Delta G^{\circ}_{298\,\mathrm{K}} = 14.5\,\mathrm{kcal\,mol}^{-1}$ corresponding to an evaporation rate of $4.3 \times 10^{-1}\,\mathrm{s}^{-1}$ which can be compared to a collision rate with another DMA or H_2SO_4 molecule of $8.4 \times 10^{-2}\,\mathrm{s}^{-1}$ or $5.7 \times 10^{-4}\,\mathrm{s}^{-1}$, respectively ($[\mathrm{DMA}]=10^8\,\mathrm{molecules\,cm}^{-3}$ and $[H_2SO_4]=10^6\,\mathrm{molecules\,cm}^{-3}$). At $T = 258\,\mathrm{K}$, $\Delta G^{\circ}_{258\,\mathrm{K}} = 16.1\,\mathrm{kcal\,mol}^{-1}$ and the evaporation rate of $4.4 \times 10^{-4}\,\mathrm{s}^{-1}$ is much lower compared to collision rates with DMA or H_2SO_4 of $7.8 \times 10^{-2}\,\mathrm{s}^{-1}$ or $5.3 \times 10^{-4}\,\mathrm{s}^{-1}$. This reveals that, depending on the conditions, evaporation of 3 acid and 3 based clusters can be significant and that larger clusters than considered in this study should be included for quantitative assessments of formation rates of nanometer sized MSA-H_2SO_4-DMA based particles, in particular at higher temperatures. Our analysis is therefore restricted to formation rates of 3 acid-3 base molecular clusters.

Cluster types outside the simulation box not containing at least three acids and at least three base molecules are considered unstable and hence much more likely to shrink by evaporations rather than being stabilized by another collision. Therefore these types of clusters are brought back into the simulation by monomer evaporations. In the case that the evaporating molecules are excess acid, the first evaporating molecule is assumed to be MSA since it is a weaker acid than H_2SO_4. From these simulations we determine the formation rate of clusters that grow out of the system, and track the main growth routes by following the flux through the system (Olenius et al., 2013).

3 Results

3.1 Structures and thermodynamics

Structures and thermodynamic data for all of the most stable $MSA_x\ (H_2SO_4)_y DMA_z$ clusters, where $x + y \leq 3$ and $z \leq 2$, are given as Supplement. These clusters share several structural features. In all cases where the number of base molecules does not exceed the number of acid molecules (MSA or H_2SO_4) the DMA moiety is protonated but in none of the clusters SO_4^{2-} is found. In most clusters containing both H_2SO_4 and MSA, H_2SO_4 is more acidic than MSA. However, in a few cases including the most stable $H_2SO_4 \cdot MSA \cdot DMA$ cluster, deprotonated MSA and doubly protonated H_2SO_4 is seen in the same cluster (Fig. 1a). This is in accordance with the findings of Dall'Osto et al. (2012). Another common feature is the monolayer-like rather than bulk-like structures of even the largest clusters investigated, e.g. $MSA(H_2SO_4)_2DMA_3$ (Fig. 1b). This tendency has been seen in other studies of similar systems, e.g. H_2SO_4-DMA based clusters (Ortega et al., 2012) and HSO_4^--H_2SO_4-NH_3 based clusters (Herb et al., 2012). This is opposite to clusters containing several water molecules where bulk-like H_2O structures tend to be more stable (Bork et al., 2013, 2011).

It is well known that strong acids and strong bases tend to form strong hydrogen bonds and more stable clus-

ters than weaker acids and bases. Since MSA is a weaker acid than H_2SO_4 it is expected that the MSA · DMA binding energy is weaker than the H_2SO_4 · DMA binding energy (Table 2). It is, on the other hand, surprising that the MSA · H_2SO_4 bond is at least 1.5 $\mathrm{kcal\,mol^{-1}}$ stronger than the $H_2SO_4 \cdot H_2SO_4$ bond, and that the MSA · MSA bond is at least 0.5 $\mathrm{kcal\,mol^{-1}}$ stronger than the $H_2SO_4 \cdot H_2SO_4$ bond. In larger clusters, H_2SO_4 is, however, significantly more stabilized compared to MSA, and, besides the MSA dimer, clusters containing more than one MSA molecule are less stable than their corresponding H_2SO_4 containing analogues (Table S1).

3.2 Clustering enhancements

To analyse the clustering abilities of MSA, a series of ACDC simulations based on these thermodynamics were performed at varying conditions. As a first measure, the binary cluster formation rate of MSA and DMA was compared to those of H_2SO_4 and DMA at similar conditions, i.e. the ratio

$$r_1 = \frac{J([H_2SO_4]{=}0,\ [\mathrm{MSA}]{=}x,\ [\mathrm{DMA}]{=}y)}{J([H_2SO_4]{=}x,\ [\mathrm{MSA}]{=}0,\ [\mathrm{DMA}]{=}y)} \quad (1)$$

where J denotes the cluster formation rate at the indicated conditions.

This was calculated for three temperatures (258, 278 and 298 K) spanning the boundary layer to the lower half of the troposphere, and x in the range from 10^5 to 2×10^6 $\mathrm{molecules\,cm^{-3}}$, corresponding to typical H_2SO_4 and MSA concentrations as described in the introduction. We used three DMA concentrations spanning most reported marine values ($y = 10^7$, 10^8 and 10^9 $\mathrm{molecules\,cm^{-3}}$) (see Gibb et al., 1999 and Table 4 in Ge et al., 2011). Only field data from the boundary layer is available and the results presented here may thus not be representative for the free troposphere, if DMA concentrations turn out to be very different from the boundary layer. The resulting values for r_1 are shown in Fig. S2. In all cases, we find that this ratio is less than 10^{-2} and, as expected, we conclude that binary MSA and DMA based cluster formation is of minor importance under normal conditions.

The main objectives of this study is to investigate the errors of neglecting MSA as a source of condensible vapour, as this is the case in most present aerosol formation parametrizations and models. A suitable measure for this is the ratio

$$r_2 = \frac{J([H_2SO_4]{=}10^6,\ [\mathrm{MSA}]{=}x,\ [\mathrm{DMA}]{=}y)}{J([H_2SO_4]{=}10^6,\ [\mathrm{MSA}]{=}0,\ [\mathrm{DMA}]{=}y)} \quad (2)$$

where J denotes the cluster formation rate at the indicated MSA concentration on top of a representative H_2SO_4 concentration, here chosen to be 10^6 $\mathrm{molecules\,cm^{-3}}$. All other parameters are as defined above. r_2 is shown in Fig. 2 as a function of [MSA].

As expected both temperature and DMA concentrations are important parameters for the ratio, r_2. At lower temperatures, entropy effects are decreased and all binding free energies are more negative. In this case, the cluster growth becomes increasingly insensitive to the chemical nature of the colliding species and more dependent on the collision frequency. At high DMA levels, DMA is in large excess compared to H_2SO_4 and cluster growth is thus limited by acid collisions. In this case, having an extra source of acid has a larger effect than at lower DMA concentrations where the DMA excess is less severe. The approximately linear dependence of r_2 on the MSA concentration could indicate that only a single MSA molecule participates at these cluster sizes. This will be further investigated in Sect. 3.3.

Adding a small amount of MSA has a small effect on the cluster formation rate, but in locations where approximately equimolar amounts of MSA and H_2SO_4 are present, this added MSA increases the cluster formation rate by ca. 15 % at 298 K, by ca. 100 % at 278 K, but by more than 300 % at 258 K in the case of $[\mathrm{DMA}]{=}10^9$ $\mathrm{molecules\,cm^{-3}}$. Recalling the discussion in the Sect. 2.1, and taking the latter case as example, this increase may, however, be as small 200 % or as large as 500 % if the binding energies are 1 $\mathrm{kcal\,mol^{-1}}$ over- or underestimated, respectively (Fig. S3).

We consider a final descriptive ratio, indicating the effects of an unknown concentration of MSA compared to a similar deficiency in the H_2SO_4 concentration. This is given as the ratio

$$r_3 = \frac{J([H_2SO_4]{=}10^6,\ [\mathrm{MSA}]{=}x,\ [\mathrm{DMA}]{=}y)}{J([H_2SO_4]{=}10^6 + x,\ [\mathrm{MSA}]{=}0,\ [\mathrm{DMA}]{=}y)} \quad (3)$$

where J represents the cluster formation rate at the given conditions and x represents the added/deficient concentration of MSA or H_2SO_4 in addition to a fixed H_2SO_4 concentration, again chosen to be 10^6 $\mathrm{molecules\,cm^{-3}}$. This ratio is shown in Fig. 3 for $T = 258$ K as function of x with the same conditions as above. This figure confirms that MSA is a less efficient clustering agent than H_2SO_4, but also that the difference is very concentration dependent. Adding a small extra amount of acid, e.g. up to 2×10^5 $\mathrm{molecules\,cm^{-3}}$, MSA is ca. 60–90 % as efficient as a similar amount of added H_2SO_4. However, when the acid concentrations is doubled from the $[H_2SO_4]{=}10^6$ $\mathrm{molecules\,cm^{-3}}$ forming the reference conditions, the added MSA yields an increased cluster formation rate of ca. 20–60 % compared to the same amount of added H_2SO_4. When the acid concentration is tripled the enhancement is ca. 10–40 %. See Figs. S4 and S5 for corresponding plots of $T = 278$ K and $T = 298$ K.

3.3 Growth paths

The ACDC model was used to track the main growth pathways of the clusters growing out of the simulation system. As shown in Fig. 4, the flux through the system proceeds principally via two clustering mechanisms: one that involves pure

H_2SO_4-DMA clusters, and another one where the clusters contain one MSA molecule in addition to H_2SO_4 and DMA. Clusters containing more than one MSA molecule were not found to contribute significantly to the growth. The relative contribution of the two growth mechanisms to the flux out of the system depends on the concentrations of the different species; at a higher MSA concentration the contribution of MSA-containing clusters is more prominent, as can be expected. In the case of $[\mathrm{DMA}]=10^8\,\mathrm{molecules\,cm^{-3}}$ between 11 and ca. 51 % of the clusters growing out of the simulation box contains one MSA at $[\mathrm{MSA}]=10^5\,\mathrm{molecules\,cm^{-3}}$ and $10^6\,\mathrm{molecules\,cm^{-3}}$ (Fig. 4). Since such clusters contain three acid molecules (H_2SO_4 or MSA), this implies overall MSA/H_2SO_4 ratios of 3 % and 17 % at these conditions.

The growth of pure H_2SO_4-DMA clusters begins with the formation of the $H_2SO_4 \cdot \mathrm{DMA}$ heterodimer, whereas the first step on the MSA-H_2SO_4-DMA growth route is the $\mathrm{MSA} \cdot H_2SO_4$ complex or the $\mathrm{MSA} \cdot H_2SO_4 \cdot \mathrm{DMA}$ cluster, formed by collision of MSA and $H_2SO_4 \cdot \mathrm{DMA}$. This is understandable as $H_2SO_4 \cdot \mathrm{DMA}$ and $\mathrm{MSA} \cdot H_2SO_4$ are the two most stable dimers that can form in the system (Table 2). After the formation of the initial complex, the growth proceeds through subsequent collisions with H_2SO_4 and DMA molecules, but also $H_2SO_4 \cdot \mathrm{DMA}$ dimers that are bound strongly enough to exist in notable amounts. In the MSA-H_2SO_4-DMA system, the $H_2SO_4 \cdot \mathrm{DMA}$ dimers contribute up to approximately 15 % of the H_2SO_4 concentration measurable by CIMS (i.e. clusters consisting of one H_2SO_4 and zero or more DMA molecules) in the conditions of Fig. 4, whereas $\mathrm{MSA} \cdot \mathrm{DMA}$ dimer concentrations, on the other hand, are negligible.

4 Conclusions

Methane sulfonic acid (MSA) is found in considerable quantities in the gas and aerosol phase over oceans and in coastal regions. We have investigated the effect and role of MSA in formation of molecular clusters in atmospheres containing various quantities of MSA, H_2SO_4 and dimethyl amine (DMA). We use the kinetic model Atmospheric Cluster Dynamics Code and quantum chemical calculations of clusters containing up to three acids (MSA and/or H_2SO_4) and two DMA molecules.

In accordance with numerous previous studies, we confirm that MSA is a less potent clustering agent than H_2SO_4, but far from negligible at normal conditions. The effect of MSA depends on both temperature and concentrations of MSA and DMA, but we find that enhancements of binary H_2SO_4-DMA based cluster formation between 15 and 300 % are typical in the marine lower to mid-troposphere.

We analyse these findings by tracking the main growth paths. We find that at most a single MSA is present in the growing clusters at the conditions investigated here and, typically, MSA/H_2SO_4 ratios are below ca. 15 % at these cluster sizes. Using this model, we are thus unable to explain MSA/H_2SO_4 ratios up to 30 % observed by Ayers et al. (1991), Huebert et al. (1996) and Kerminen et al. (1997) in small aerosol particles. This strengthen the hypotheses that surface oxidation of DMSO or MSIA is the major source of particulate MSA (Davis et al., 1998; Barnes et al., 2006). However, we have shown that MSA may enter the aerosol particle at the earliest possible stage and significantly assists in cluster formation.

This is a consequence of MSA being a strong acid, binding strongly to DMA and H_2SO_4, and that DMA in most pristine oceanic locations is in large excess compared to acid. For actual predictions of nanometer sized aerosol formation rates, larger clusters than the three acid-two base clusters studied here must be included in the kinetic model.

Supplementary material related to this article is available online at: http://\@journalurl/\@pvol/\@fpage/\@pyear/\@journalnameshortlower-\@pvol-\@fpage-\@pyear-supplement.pdf.

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Table 1. Comparison of various computational approaches for calculating Gibbs free binding energies. Unless otherwise stated, the basis set is 6-311++G(3df,3pd). F12 is shorthand for CCSD(T)-F12/VDZ-F12. Values in $\mathrm{kcal\,mol^{-1}}$.

table

Method	Gibbs free binding energy $H_2SO_4 + DMA$	Gibbs free binding energy $MSA + DMA$
M06-2X	−11.26	−7.42
B3LYP	−8.71	−4.59
PW91	−11.44	−7.75
ωB97X-D	−11.96	−8.98
MP2	−13.70	−10.84
F12//M06-2X	−11.72	−8.19
F12//B3LYP	−11.96	−8.57
F12//PW91	−12.07	−8.74
F12//ωB97X-D	−11.97	−9.33
F12//MP2	−11.99	−9.36
RI-MP2/AV(T+d)Z// RI-MP2/AV(D+d)Z	−12.49[1]	−9.29[1]
RI-MP2/AV(T+d)Z// BLYP/DZP	−15.57 [2]	
RI-CC2/AV(T+d)Z// B3LYP/CBSB7	−15.40 [3]	
PW91	−11.38 [4]	

References: [1] Dall'Osto et al. (2012), [2] Loukonen et al. (2010), [3] Ortega et al. (2012), [4] Nadykto et al. (2011).

Table 2. Testing the effect of CCSD(T)-F12/VDZ-F12 electronic energy corrections to M06-2X/6-311++G(3df,3pd) Gibbs free energy changes of the indicated reactions. Values in $\mathrm{kcal\,mol^{-1}}$.

Reaction	Gibbs free binding energy F12//M06-2X	Gibbs free binding energy M06-2X	$\Delta_{\text{F12-DFT}}$
$DMA + H_2SO_4$	−11.72	−11.26	0.46
$DMA + MSA$	−8.19	−7.42	0.77
$H_2SO_4 + H_2SO_4$	−7.07	−8.38	−1.31
$H_2SO_4 + MSA$	−8.56	−10.70	−2.14
$MSA + MSA$	−7.53	−9.07	−1.54

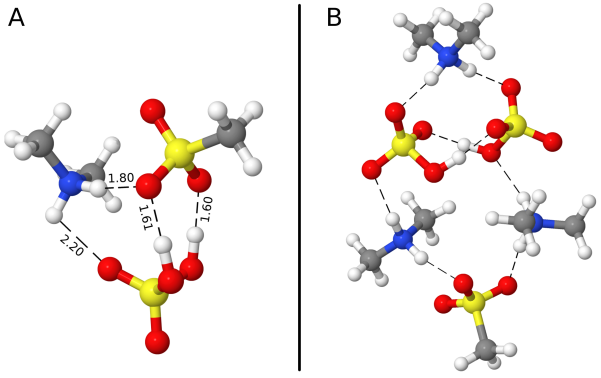

Fig. 1. **(A)** Most stable configuration of the MSA $\cdot$ H_2SO_4 $\cdot$ DMA cluster. The lengths of the hydrogen bonds are given in Å. In this cluster, MSA is a stronger acid than H_2SO_4. **(B)** Configuration of the MSA $\cdot$ $(H_2SO_4)_2$ $\cdot$ DMA_3 cluster. As all investigated clusters, the most stable structure is more monolayer-like than bulk-like. The hydrogen bonds are shown as dashed lines.
figure

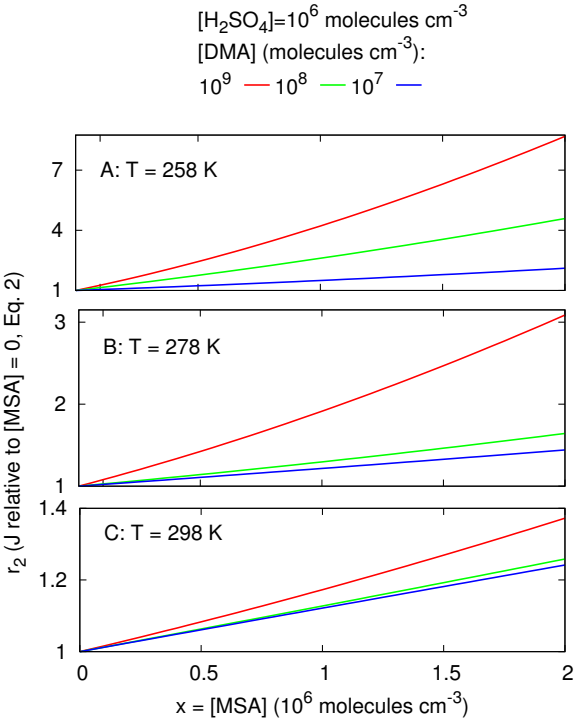

Fig. 2. MSA-H_2SO_4-DMA based particle formation rates at varying MSA concentrations relative to $[\mathrm{MSA}]$=0 (Eq. 2).

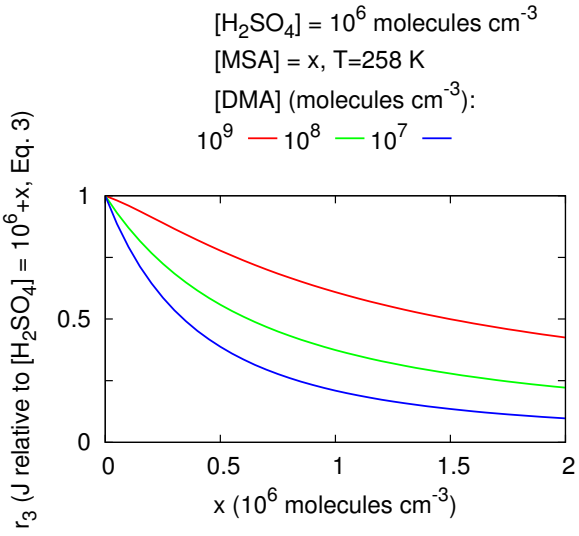

Fig. 3. Cluster formation rate of added MSA relative to the same amount of added H_2SO_4 as defined in Eq. (3).

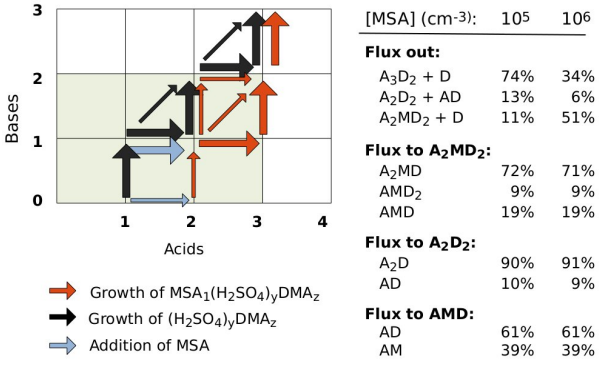

Fig. 4. Main cluster formation pathways at $T = 258\,\mathrm{K}$ and $[\mathrm{H_2SO_4}]{=}10^6\,\mathrm{molecules\,cm^{-3}}$, $[\mathrm{DMA}]{=}10^8\,\mathrm{molecules\,cm^{-3}}$ and two representative MSA concentrations. Dominating growth pathways are represented by thick arrows. Fluxes to clusters formed via several different pathways are indicated in the side table where A, M and D is shorthand for H_2SO_4, MSA and DMA, respectively.