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Amine substitution into sulfuric acid – ammonia clusters

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Abstract

The substitution of ammonia by dimethylamine in sulfuric acid – ammonia – dimethylamine clusters was studied using a collision and evaporation dynamics model. Quantum chemical formation free energies were computed using B3LYP/CBSB7 for geometries and frequencies and RI-CC2/aug-cc-pV(T+d)Z for electronic energies. We first demonstrate the good performance of our method by a comparison with an experimental study investigating base substitution in positively charged clusters, and then continue by simulating base exchange in neutral clusters, which cannot be measured directly. Collisions of a dimethylamine molecule with an ammonia containing positively charged cluster result in the instantaneous evaporation of an ammonia molecule, while the dimethylamine molecule remains in the cluster. According to our simulations, a similar base exchange can take place in neutral clusters, although the overall process is more complicated. Neutral sulfuric acid – ammonia clusters are significantly less stable than their positively charged counterparts, resulting in a competition between cluster evaporation and base exchange.

1 Introduction

Atmospheric aerosols are known to affect the climate by absorbing and scattering radiation and acting as cloud condensation nuclei. According to recent estimates (Merikanto et al., 2009) 20–80 % of the aerosol particles are formed in the atmosphere by gas-to-particle nucleation. There remains, however, much uncertainty related to their actual birth-mechanism and composition. Consequently, aerosol forcing forms the largest uncertainty in global climate modeling.

New-particle formation rates have been observed to correlate strongly with sulfuric acid concentrations in a wide range of conditions (Sihto et al., 2006; Kuang et al., 2008), suggesting that sulfuric acid would be involved in the first steps of nucleation. However, particle formation can not be explained by homogeneous nucleation of sulfuric acid and

water alone. Instead, some third compound is needed to stabilize the small sulfuric acid clusters and enable them to grow into particles. Bases such as ammonia that are present in the atmosphere at relevantly high concentrations have been proposed as good candidates since they bind strongly with sulfuric acid (Torpo et al., 2007; Nadykto and Yu, 2007; Ortega et al., 2008). Recent results at the CLOUD experiment in CERN suggest that ammonia does not enhance the growth of sulfuric acid clusters enough to account for the nucleation rates observed in the boundary layer (Kirkby et al., 2011), but it has been seen in earlier modeling studies that amines stabilize sulfuric acid clusters significantly more than ammonia (Kurtén et al., 2008; Loukonen et al., 2010).

Although aerosol measurement techniques have been developing rapidly (Kulmala et al., 2007; Manninen et al., 2009; Junninen et al., 2010), the ability to detect and characterize even charged sub 3 nm clusters remains limited. Furthermore, neutral clusters can only be detected by charging them, but the complex chemistry of the charging process complicates the interpretation of such measurements (Kurtén et al., 2011). On the other hand, neutral pathways account for 90 % of atmospherical new particle formation (Kulmala et al., 2007), and understanding neutral cluster formation is, therefore, a key issue.

At present, the most accurate way to study small neutral clusters is by quantum chemistry. It can, in principle, be applied to any system, and requires no experimental input data. The methods can first be tested against ionic cluster measurements, and then used for neutral clusters to gain information that could not be obtained experimentally.

In a recent experimental study, Bzdek et al. (2010a) studied base substitution in small sulfuric acid – ammonia – dimethylamine (DMA) clusters. In this contribution, we present a quantum chemistry-based study of the same system, and show that our method is able to reproduce the experimental results. Further, we extend our discussion to base substitution in electrically neutral clusters and point out some important differences.

2 Theory and computational methods

2.1 Quantum chemistry details

Calculations were performed using a multi-step method presented by Ortega et al. (2011). The methods are briefly described here, and a more detailed account of the effect of the basis set and level of theory can be found in Ortega et al. (2011).

For each cluster, a sample of around 5 to 20 initial guess geometries was taken from earlier studies when possible, or constructed using chemical intuition and pre-optimized with molecular dynamics using the SPARTAN program (Wave function, Inc., 2006). It has to be noted that as the size of the cluster grows, the number for conformers grows, so for large clusters the existence of a cluster more stable that those that we have found cannot be ruled out.

The initial guess geometries were optimized with the Gaussian09 program (Frisch et al., 2009) using the B3LYP hybrid functional (Becke, 1993) and a CBSB7 basis set (Montgomery et al., 1999), which were found to be the best compromise between accuracy and computational effort in a previous study on molecular clusters (Ortega et al., 2011). This basis set is used in the optimization and frequency part of the CBS-QB3 method (Montgomery et al., 1999), which is very accurate but unfortunately computationally too heavy for our large clusters. We did not, however, use the scaling factors associated to the CBSB7 basis, since they are optimized for intramolecular covalent bonds and overestimate the strength of weaker intermolecular bonds. Vibrational and rotational contributions to the Gibbs free energy were calculated within the standard rigid-rotor harmonic-oscillator ideal gas (RRHO) approximation (see e.g. Ortega et al., 2008) using the Gaussian09 program.

For the most stable configurations, we computed a more accurate value of the electronic energy with the TURBOMOLE program (Ahlrichs et al., 1989) using the RI-CC2 method (Hättig and Weigend, 2000) and an aug-cc-pV(T+d)Z basis set (Dunning et al., 2001). According to previous basis set extrapolation results (Kurtén et al., 2007a,b), a larger basis set would improve the results relatively little and this choice should be adequate for our purposes.

2.2 Cluster dynamics

The time-dependence of cluster concentrations is governed by the birth-death equations (see e.g. Vehkamäki, 2006; Kulmala, 2010)

$$\frac{dC(\{N_1, N_2, ..., N_n\})}{dt} =$$

$$\sum_{j=1}^{n} \Big[C_j \times C(\{N_1, ..., N_j - 1, ..., N_n\}) \times \beta_j(\{N_1, ..., N_j - 1, ..., N_n\})$$

$$- C_j \times C(\{N_1, ..., N_j, ..., N_n\}) \times \beta_j(\{N_1, ..., N_j, ..., N_n\})$$

$$- C(\{N_1, ..., N_j, ..., N_n\}) \times \gamma_j(\{N_1, ..., N_j, ..., N_n\})$$

$$+ C(\{N_1, ..., N_j + 1, ..., N_n\}) \times \gamma_j(\{N_1, ..., N_j + 1, ..., N_n\}) \Big], \tag{1}$$

where $C(\{N_1, ..., N_n\})$ is the concentration of clusters with N_1 molecules of type 1 etc., $\beta_j(\{N_1, ..., N_n\})$ is the collision coefficient of these clusters with molecules of type j, $\gamma_j(\{N_1, ..., N_n\})$ is the evaporation rate of molecules j from such a cluster and C_j is the concentration of molecules j. Here we have assumed that only single molecules can stick to clusters and evaporate from them, and processes involving more than one cluster can be neglected.

For neutral processes, we have used the collision frequency derived from kinetic gas theory,

$$\beta_j(\{N_i\}) = (8\pi kT)^{1/2} \left(\frac{1}{m(\{N_i\})} + \frac{1}{m_j} \right)^{1/2} \left(r(\{N_i\}) + r_j \right)^2, \tag{2}$$

where $m(\{N_i\})$, m_j, $r(\{N_i\})$ and r_j are the masses and radii of the cluster and the molecule, respectively, k is the Boltzmann constant and T is the temperature. For ionic clusters, we have calculated the collision frequency as proposed by Su and Bowers (1973),

$$\beta_j(\{N_i\}) = 2\pi Z e \left(\frac{1}{m(\{N_i\})} + \frac{1}{m_j} \right)^{1/2} \left[\alpha_j^{1/2} + c\mu_j \left(\frac{2}{\pi kT} \right)^{1/2} \right]. \tag{3}$$

The first term in the square brackets corresponds to the Langevin collision rate, which depends on the polarizability α_j of the colliding molecule. The second term is the collision frequency of a polar molecule (dipole moment μ_j) with an ion, calculated assuming that the dipole moment is constantly pointing in the lowest energy direction, and scaled by a numerical factor $c \in [0,1]$. (The value $c = 1$ would correspond to the dipole being perfectly locked towards the ion, whereas $c = 0$ would mean that the rotation of the molecule is unaffected by the electric field and it behaves effectively as a non-polar molecule.) We have used the value $c = 0.15$ suggested by Su and Bowers (1973). $Z \times e$ is the charge of the cluster.

The evaporation rate of molecules j from a cluster is

$$\gamma_j(\{N_1,...,N_n\}) = \frac{P_0}{kT} \beta_j(\{N_1,...,N_j-1,...,N_n\}) \tag{4}$$
$$\times \exp\left[\frac{\Delta G(\{N_1,...,N_n\}) - \Delta G(\{N_1,...,N_j-1,...,N_n\})}{kT} \right],$$

where ΔG are the Gibbs free energies of formation of clusters from monomers at some reference pressure P_0 (Ortega et al., 2011).

The radii used in the neutral collision coefficients were calculated from bulk liquid densities assuming spherical droplets and ideal mixing. In the case of charged clusters, we used experimental gas-phase values for the dipole moments and polarizabilities, except for the sulfuric acid polarizability for which an experimental value was (to our knowledge) not available, we used a computational estimate. The values are listed in Table 1. For calculating the evaporation rates, we used the Gibbs free energies from quantum chemistry.

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In our kinetic model we have assumed for all collisions a sticking factor of unity, i.e. that the colliding molecule sticks to the cluster irrespective of the collision geometry and kinetic energy. The effect of energy non-accommodation to sticking factors is likely to be small for the clusters studied here, as they are both strongly bound and have several tens of vibrational degrees of freedom (Kurtén et al., 2010). The experimental results by Bzdek et al. (2010a,b) also suggest that sticking coefficients are close to unity.

3   Results

The formation free energies of the clusters are given in Table 2 for charged clusters and in Table 3 for neutral mixed base clusters. Results for pure sulfuric acid, sulfuric acid – ammonia and sulfuric acid – DMA clusters have been presented previously by Ortega et al. (Ortega et al., 2011). For simplicity, the cluster names are written in terms of sulfuric acid (SA), ammonia (Am) and DMA molecules, and the extra proton attached to one base molecule and giving the overall positive charge is not included explicitly. In many cases, one or even two protons have also been transfered from each acid molecule to the bases. The coordinates of the most stable conformer of each cluster are given in the Supplement.

In addition to the ground state electronic energy E_{elec}, we present the Gibbs free energy G and the enthalpy H at $T = 298$ K and $P = 1$ atm. The formation free energies are calculated relative to neutral molecules, except for one positively charged $(CH_3)_2NH_2^+$ ion in case of positive clusters, or one positively charged NH_4^+ ion for charged sulfuric acid – ammonia clusters with no DMA. In order to calculate energy differences between charged clusters with and without DMA, the reaction energy of the proton transfer $NH_4^+ + (CH_3)_2NH \rightarrow NH_3 + (CH_3)_2NH_2^+$ ($\Delta^{pt}E_{elec} = -18.67$ kcal mol^{-1}, $\Delta^{pt}G = -18.54$ kcal mol^{-1}, $\Delta^{pt}H = -18.25$ kcal mol^{-1}, $\Delta^{pt}S = 0.98$ cal/(mol K)) must be taken into account. Evaporation rates calculated according to Eqs. (2–4) are listed in Tables 2 and 3.

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3.1 Base substitutions

According to our simulations, the basic mechanism of the base substitution (see Fig. 1 for the one acid case) is as follows: when a DMA molecule collides with an ammonia containing cluster and sticks to it, the number of base molecules compared to acids grows and the cluster becomes unstable. The evaporation rate of ammonia from the cluster is typically several orders of magnitude larger than that of DMA, and an ammonia molecule will be evaporated in a fraction of a second. Consequently, the cluster stabilizes, and remains as it is until an other molecule sticks to it. The overall mechanism can, however, be more complex, as the clusters may also evaporate or grow depending on the monomer concentrations.

3.1.1 Positive clusters

To test our quantum chemistry results, we have applied our kinetic model to the system studied experimentally by Bzdek et al. (2010a) using Fourier transform ion cyclotron resonance mass spectroscopy. A small concentration ($1\,\mathrm{cm}^{-3}$ in our study) of $[(SA)_2 \cdot (Am)_3]^+$ clusters was let to react with neutral DMA gas at a pressure of 1.2×10^{-8} Torr (same pressure as in the experiment), and the concentrations of different clusters were monitored as a function of time. A comparison of our results and the results by Bzdek et al. is presented in Fig. 2.

The results agree very well, and the small differences are mainly due to the simple treatment of collision rates and sticking factors used in our study. We also get the same result as Bzdek et al. that $[(SA)_2 \cdot (DMA)_3]^+$ and $[SA \cdot (DMA)_2]^+$ clusters do not undergo any base substitutions when subjected to pure ammonia gas at any pressure.

In the case of positive ions, the clusters where the number of base molecules is larger by one than the number of acids seem to be by far more stable than any other clusters. The reaction mechanism of a $[(SA)_2 \cdot (Am)_3]^+$ cluster in DMA gas is similar for DMA concentrations ranging from 5×10^{-9} Torr to 2×10^{-6} Torr,

$$[(SA)_2 \cdot (Am)_3]^+ + DMA \rightarrow [(SA)_2 \cdot DMA \cdot (Am)_3]^+ \rightarrow [(SA)_2 \cdot DMA \cdot (Am)_2]^+ + Am$$

$$[(SA)_2 \cdot DMA \cdot (Am)_2]^+ + DMA \rightarrow [(SA)_2 \cdot (DMA)_2 \cdot (Am)_2]^+ \rightarrow [(SA)_2 \cdot (DMA)_2 \cdot Am]^+ + Am$$

$$[(SA)_2 \cdot (DMA)_2 \cdot Am]^+ + DMA \rightarrow [(SA)_2 \cdot (DMA)_3 \cdot Am]^+ \rightarrow [(SA)_2 \cdot (DMA)_3]^+ + Am \ ,$$
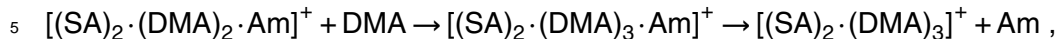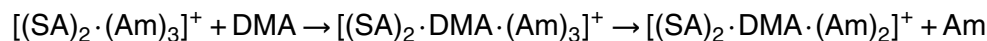
where the second reaction on each line happens several orders of magnitude faster than the first. In lower pressures, the clusters start to evaporate slowly, first becoming $[SA \cdot (DMA)_2]^+$ clusters and in even lower pressures single $(CH_3)_2NH_2^+$ ions.

In the atmosphere, the sulfuric acid concentration is of the order of 10^6 cm^{-3} or higher (Eisele and Tanner, 1993), the DMA concentration ranges approximately from 10^7 to 10^{10} cm^{-3} (Ge et al., 2011) and the ammonia concentration is typically between 10^9 and 10^{12} cm^{-3} (Ge et al., 2011). In these conditions, the collision rates of acid and base molecules with positively charged clusters would be higher than the evaporation rates of many clusters. In addition to the base substitution process discussed in this study, the clusters would then be able to grow.

3.1.2 Neutral clusters

The first difference to be noted between charged and neutral clusters is that the collision coefficients of the smallest clusters are nearly one order of magnitude smaller for neutrals, meaning that the monomer concentrations must be ten times higher to produce comparable collision rates for clusters of the same size. Further, the numbers of acid and base molecules in especially stable clusters do not behave as systematically as for positive clusters.

In Figs. 3 and 4, we present two hypothetical experiments analogous to that in Fig. 2 but with neutral clusters. These do not correspond to a real atmosphere-like situation, but simply provide an example showing the dangers of drawing conclusions about neutral systems directly based on charged cluster measurements.

In Fig. 3, neutral $(SA)_2 \cdot Am$ clusters (concentration $1\,cm^{-3}$) are let to react with DMA gas at a pressure of 10^{-6} Torr, which is the lowest pressure where the clusters do not evaporate before the base exchange can happen. Similarly to the positive case, the ammonia molecule is replaced by a DMA at collision rate. Then, as opposed to the

5 charged case, a second DMA molecule colliding with the cluster will also be attached to it, leading to the formation of a $(SA)_2 \cdot (DMA)_2$ cluster. The $(SA)_2 \cdot (Am)_2$ cluster, on the other hand, is not stable and would lose the second ammonia molecule with an evaporation rate of $1.8 \times 10^3\ s^{-1}$. A similar asymmetry between the different bases was also observed experimentally by Bzdek et al. (2010b) for positive clusters – but

10 only for clusters with at least 3 acids and 4 bases, and even then the uptake coefficient of the additional DMA molecule was very small. This difference can at least partly be explained by noting that the positive clusters have an excess proton which effectively turns one base molecule into its conjugate acid.

Figure 4 presents a similar simulation but with DMA pressure 1.2×10^{-8} Torr as in

15 the experimental study with charged clusters. Here evaporation competes with substitution, and the sensitivity of the model to the accuracy of energies becomes apparent. Since the free energies only appear in energy differences between colliding species and collision products, absolute errors related to the quantum chemistry methods mostly cancel out. There remains, however, the possibility that we have not found

20 the global minimum energy structure for all clusters, which can lead to an error of even several $kcal\,mol^{-1}$. We have roughly estimated the effect of such errors on the modeled concentrations by lowering the Gibbs free energy of one species at a time by $1\,kcal\,mol^{-1}$ and rerunning the simulation. This provides some useful information about the sensitivity of the model to the energies of different clusters. The largest un-

25 certainty in this particular system results from the relative stabilities of the $(SA)_2 \cdot Am$ and $(SA)_2$ clusters and hence the evaporation rate of the initial cluster. Once an ammonia molecule has evaporated, the remaining sulfuric acid dimer will break up and a fraction of the free sulfuric acid will form $SA \cdot DMA$ clusters. The final partitioning between these one-acid species depends on the formation energy of the $SA \cdot DMA$

clusters, but this is a minor error source compared to the evaporation rate of the initial cluster. The concentrations of the short-lived species $(SA)_2 \cdot Am$ and $(SA)_2 \cdot DMA$ depend slightly on the evaporation rate of ammonia from the initial cluster, but they tend to zero in any case.

In general, if a cluster is extremely stable or if it is extremely unstable with respect to one evaporation pathway, small errors in its evaporation rates are unlikely to affect the overall process. However, if a cluster can participate in different collision and evaporation processes with similar rates, the accuracy of the rate coefficients can be crucial.

In the atmosphere, the concentrations of sulfuric acid and DMA are large enough to enable the formation and growth of clusters, though other molecules (e.g. organic acids) are also likely to be involved in growth processes, and may dominate above some particle size. Water vapor is present at a much higher concentration, and will probably be somehow involved. On one hand it stabilizes the clusters, but on the other hand it also competes with the bases, so the overall effect is uncertain and will have to be studied in detail in the future. Further, the concentrations of small clusters soon become comparable to the monomer concentrations, and cluster-cluster collisions can no longer be neglected. For some large clusters, splitting into two clusters can also be more favourable than evaporation of single molecules (Ortega et al., 2011).

4 Conclusions

We have used a multi-step quantum chemistry method to calculate free energies of positively charged and neutral sulfuric acid – ammonia – dimethylamine clusters. These have been used to study the kinetics of the substitution of ammonia by DMA. In the charged case, we have compared our results with experimental observations and found a very good agreement.

Our results show that there are some major differences between the charged and neutral systems. For neutrals, collisions occur less frequently, and on the other hand the clusters are not as strongly bound and evaporate faster. The composition of the

most stable clusters is different in the two cases, because the positive clusters have an excess proton, and the protonated base molecule acts effectively as an acid. Some key features, however, are similar in neutral and charged clusters. Both ammonia and DMA stabilize sulfuric acid clusters significantly, but the effect is even stronger for DMA. All ammonia molecules in small sulfuric acid clusters will be replaced by DMA at collision frequency.

In the atmosphere, the concentration of ammonia is typically a few orders of magnitude larger than that of DMA, and sulfuric acid therefore collides more frequently with ammonia. Due to the extremely effective substitution of DMA for ammonia, the vast majority of sub-nanometer sulfuric acid clusters in the atmosphere are, however, likely to contain DMA.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/30853/2011/ acpd-11-30853-2011-supplement.pdf.

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Table 1. Properties of the modeled species.

	Bulk density ($\mathrm{kg\,m^{-3}}$)	Polarizability ($\mathrm{\AA^3}$)	Dipole moment (D)
Sulfuric acid	1830[a]	6.2[b]	2.73[c]
Ammonia	696[a]	2.81[a]	1.47[a]
Dimethylamine	680[a]	6.37[a]	1.01[a]

[a] Lide (2010–2011), [b] Nadykto and Yu (2003), [c] Kuczkowski et al. (1981).

Table 2. Formation free energies (kcal mol^{-1}) and monomer evaporation rates of charged sulfuric acid (SA) – ammonia (Am) – dimethylamine (DMA) clusters.

	ΔE_{elec}	ΔG	ΔH	γ_{SA}	γ_{DMA}	γ_{Am}
[SA·Am]$^+$	−20.90	−15.60	−20.13	1.80×10^{-1}		
[SA·DMA]$^+$	−19.29	−10.83	−18.19	9.73×10^{2}		
[(SA)$_2$·Am]$^+$	−47.43	−26.87	−45.38	1.70×10^{2}		
[(SA)$_2$·DMA]$^+$	−43.75	−22.89	−41.46	4.55×10^{1}		
[(Am)$_2$]+	−26.75	−20.59	−26.44			3.45×10^{-5}
[DMA·Am]$^+$	−22.13	−13.79	−20.87		8.48×10^{-14}	6.24×10^{0}
[(DMA)$_2$]+	−26.23	−16.32	−25.53		8.21×10^{-2}	
[SA·(Am)$_2$]$^+$	−57.24	−37.54	−54.16	1.44×10^{-2}		2.76×10^{-6}
[SA·DMA·Am]$^+$	−52.72	−31.78	−49.26	2.34×10^{-3}	1.10×10^{-15}	1.50×10^{-5}
[SA·(DMA)$_2$]$^+$	−65.60	−44.58	−61.47	6.64×10^{-11}	5.60×10^{-15}	
[(SA)$_2$·(Am)$_2$]$^+$	−84.60	−52.01	−80.48	7.49×10^{-1}		1.21×10^{-8}
[(SA)$_2$·DMA·Am]$^+$	−80.24	−46.59	−75.93	4.16×10^{-1}	2.69×10^{-18}	1.37×10^{-7}
[(SA)$_2$·(DMA)$_2$]$^+$	−94.36	−58.85	−89.29	1.04×10^{0}	1.28×10^{-16}	
[SA·DMA·(Am)$_2$]$^+$	−72.16	−41.21	−67.75		1.62×10^{-6}	4.04×10^{3}
[SA·(DMA)2·Am]$^+$	−84.26	−50.73	−78.89		3.87×10^{-4}	1.04×10^{6}
[(SA)$_2$·(Am)$_3$]$^+$	−119.34	−72.94	−111.92			1.47×10^{-5}
[(SA)$_2$·DMA·(Am)$_2$]$^+$	−115.64	−67.33	−108.11	2.04×10^{-9}	4.40×10^{-15}	1.98×10^{-5}
[(SA)$_2$·(DMA)$_2$·Am]$^+$	−129.23	−78.68	−120.88	9.19×10^{-11}	8.55×10^{-14}	9.18×10^{-5}
[(SA)$_2$·(DMA)$_3$]$^+$	−137.73	−88.18	−128.94		8.99×10^{-12}	
[(SA)$_2$·DMA·(Am)$_3$]$^+$	−132.06	−73.04	−123.15		6.36×10^{-4}	2.12×10^{6}
[(SA)$_2$·(DMA)$_2$·(Am)$_2$]$^+$	−145.57	−84.27	−136.00		1.10×10^{-2}	2.55×10^{6}
[(SA)$_2$·(DMA)$_3$·Am]$^+$	−160.38	−97.67	−149.94		3.50×10^{-4}	3.58×10^{3}

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Table 3. Formation free energies (kcal mol^{-1}) and monomer evaporation rates of neutral sulfuric acid (SA) – ammonia (Am) – dimethylamine (DMA) clusters.

	ΔE_{elec}	ΔG	ΔH	γ_{SA}	γ_{DMA}	γ_{Am}
SA·DMA·Am	−42.01	−18.49	−37.65		1.45×10^2	8.24×10^7
(SA)$_2$·DMA·Am	−82.14	−43.88	−75.6	2.79×10^{-9}	2.99×10^{-5}	4.27×10^3
(SA)$_3$·DMA·Am	−112.68	−60.65	−104.26	6.06×10^{-3}	4.37×10^{-10}	7.07×10^0
SA·DMA·(Am)$_2$	−49.96	−14.98	−44.34		2.08×10^8	6.36×10^{12}
(SA)$_2$·DMA·(Am)$_2$	−100.05	−46.44	−92.17	1.07×10^{-13}	4.02×10^0	2.46×10^8
(SA)$_3$·DMA·(Am)$_2$	−140.28	−73.97	−129.25	8.41×10^{-11}	1.75×10^{-8}	3.45×10^0
SA·(DMA)$_2$·Am	−59.06	−22.57	−53.14		1.63×10^7	3.77×10^8
(SA)$_2$·(DMA)$_2$·Am	−109.67	−58.24	−100.73	8.96×10^{-17}	5.11×10^{-1}	5.82×10^8
(SA)$_3$·(DMA)$_2$·Am	−147.53	−80.56	−136.06	5.67×10^{-7}	4.68×10^{-5}	3.67×10^0
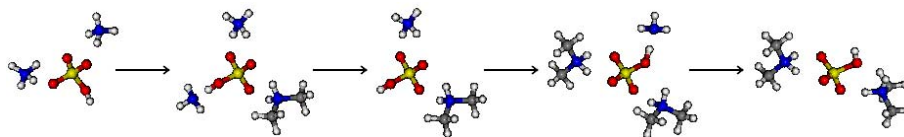
Fig. 1. Substitution of ammonia by DMA in a positively charged one acid - two base cluster.
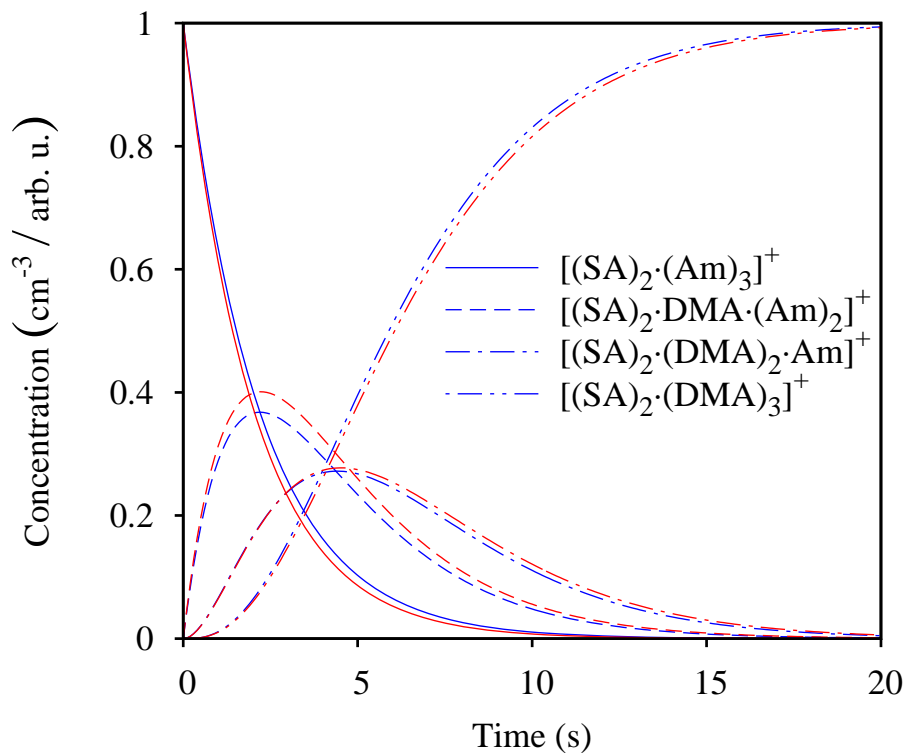
Fig. 2. Reaction of $[(SA)_2 \cdot (Am)_3]^+$ clusters with DMA gas at a pressure of 1.2×10^{-8} Torr. Blue: modeled concentrations in cm^{-3}, red: experimentally observed relative concentrations (Bzdek et al., 2010a).

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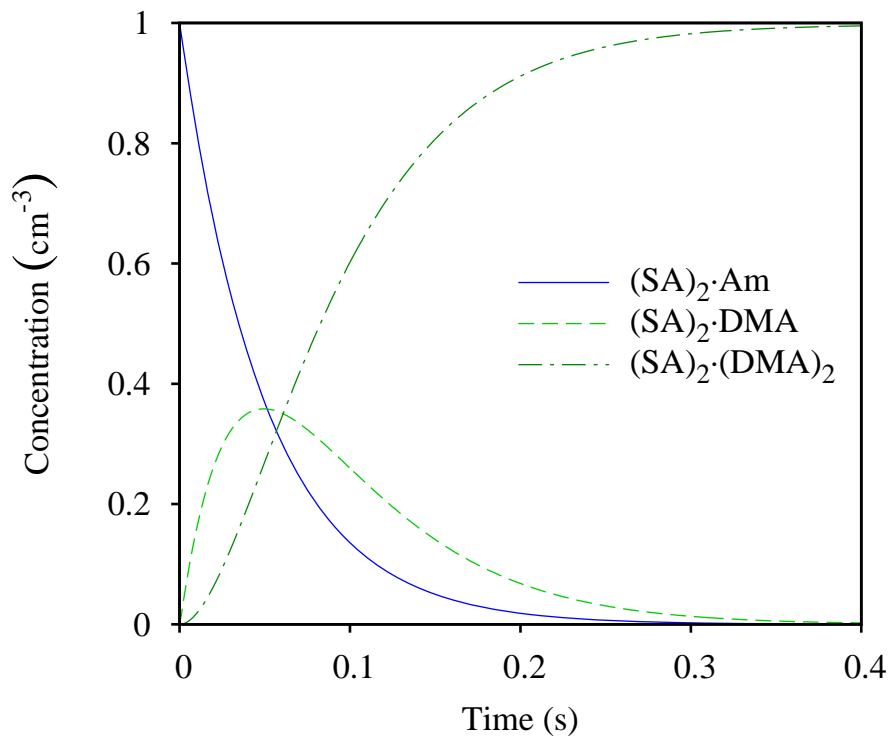Full Screen / Esc

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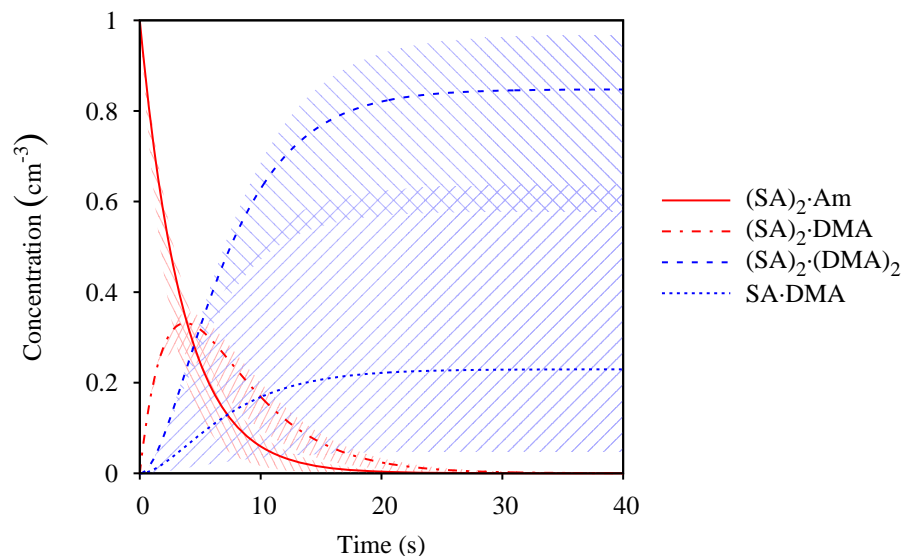**Fig. 3.** Reaction of $(SA)_2 \cdot Am$ clusters with DMA gas at a pressure of 10^{-6} Torr.

Fig. 4. Reaction of $(SA)_2 \cdot Am$ clusters with DMA gas at a pressure of 1.2×10^{-8} Torr. The sensitivity of the dynamics to cluster formation energies is seen by lowering the Gibbs free energy of one species at a time by $1\,\mathrm{kcal\,mol^{-1}}$ and rerunning the simulation (shaded area).