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Strong Hydrogen Bonded Molecular Interactions between Atmospheric Diamines and Sulfuric Acid

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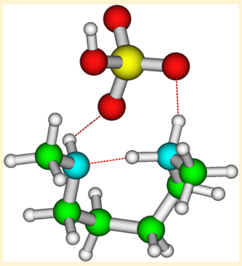
Supporting Information



ABSTRACT: We investigate the molecular interaction between methyl-substituted *N,N,N′,N′*-ethylenediamines, propane-1,3-diamine, butane-1,4-diamine, and sulfuric acid using computational methods. Molecular structure of the diamines and their dimer clusters with sulfuric acid is studied using three density functional theory methods (PW91, M06-2X, and ωB97X-D) with the 6-31++G(d,p) basis set. A high level explicitly correlated CCSD(T)-F12a/VDZ-F12 method is used to obtain accurate binding energies. The reaction Gibbs free energies are evaluated and compared with values for reactions involving ammonia and atmospherically relevant monoamines (methylamine, dimethylamine, and trimethylamine). We find that the complex formation between sulfuric acid and the studied diamines provides similar or more favorable reaction free energies than dimethylamine. Diamines that contain one or more secondary amino groups are found to stabilize sulfuric acid complexes more efficiently. Elongating the carbon backbone from ethylenediamine to propane-1,3-diamine or butane-1,4-diamine further stabilizes the complex formation with sulfuric acid by up to 4.3 kcal/mol. Dimethyl-substituted butane-1,4-diamine yields a staggering formation free energy of −19.1 kcal/mol for the clustering with sulfuric acid, indicating that such diamines could potentially be a key species in the initial step in the formation of new particles. For studying larger clusters consisting of a diamine molecule with up to four sulfuric acid molecules, we benchmark and utilize a domain local pair natural orbital coupled cluster (DLPNO-CCSD(T)) method. We find that a single diamine is capable of efficiently stabilizing sulfuric acid clusters with up to four acid molecules, whereas monoamines such as dimethylamine are capable of stabilizing at most 2−3 sulfuric acid molecules.

1. INTRODUCTION

The formation of new particles in the ambient atmosphere is a complex phenomena, and the mechanisms still remain largely unknown. Sulfuric acid is believed to be a common precursor to drive gas to particle conversion in many environments,[1] but another component is required to explain observed new particle formation rates.[2−4] Highly oxidized organic compounds have been shown to be directly involved in new particle formation, but the exact participating molecules remain elusive.[5−7] Atmospheric bases such as ammonia and amines are candidate species to stabilize sulfuric acid clusters in the lower troposphere, via acid−base reactions.[8−21] Kurtén et al.[22] found that the molecular interaction between amines and sulfuric acid was significantly stronger than the corresponding interactions with ammonia. Sulfuric acid−amine clusters were shown to enhance the further growth into larger clusters, and it was identified that the stronger interaction of amines with sulfuric acid was able to overcome the fact that the concentration of amines most likely is 2−3 orders of magnitude lower than ammonia. The recent work by Almeida et al.[23] performed at the CLOUD chamber at CERN shows that 3 ppt of dimethylamine can enhance new particle formation rates more than 1000-fold compared with the case with ammonia and was sufficient to produce particle formation rates of the same order of magnitude, as observed in the atmosphere.

Recently, it was shown that atmospheric diamines are even more potent at enhancing new particle formation compared with previously studied monoamines (i.e., an amine with a single amino group, such as dimethylamine) and ammonia.[24] Using flow tube experiments Jen et al.[24] found that diamines produced 10 times more particles than dimethylamine and 100 times more than methylamine. Measurements on atmospheric amine concentrations are, however, sparse. Recently, Sipilä et al.[25] reported a bisulfate cluster based atmospheric pressure chemical ionization mass spectrometer, developed for high sensitivity toward amines, with threshold down to 150 ppq. During a campaign in Hyytiälä in spring 2013 they were unable to observe any dimethylamine concentrations above their detection threshold. This could indicate that dimethylamine concentrations in the Hyytiälä forest are too low to drive the observed new particle formation rates. Jen et al.[24] monitored diamine concentration at three different sites. In the summer of 2009 at a site at Jefferson Street in Atlanta, diamine concentrations often exceeded monoamines by a factor of 3. During the spring of 2013, diamine concentrations were found to be comparable to concentrations of monoamines at an industrial agriculture and oil extraction/refinement site in Lamont. During the summer of 2012 at a site in Lewes near the ocean and industrial agriculture, the diamine concentrations were found to be far lower than those of trimethylamine. This

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indicates that diamines can reach and even exceed the concentration of monoamines, but not consistently at all sites. As diamines are more basic than monoamines, they could have the potential to form new particles at even lower concentrations than monoamines such as dimethylamine.

Although current instruments do measure the neutral cluster population during the initial steps of new particle formation, quantum chemical calculations provide complementary information to help deconvolute the complex cluster dynamics and provide insights into instrument uncertainties (e.g., ionization of clusters and ion decomposition). Using computational methods, we explore the thermochemistry of the initial steps in the formation of molecular clusters consisting of sulfuric acid and ammonia/monoamines/diamines. Using high level coupled cluster theory, we accurately determine the binding energies of the clusters. This allows for a detailed analysis of the stabilizing effect that ammonia, amines, and diamines exhibit on sulfuric acid clusters.

2. METHODS

2.1. Computational Details. Geometry optimizations and frequency calculations were performed using the Gaussian09 program, revision B.[26] Thermochemistry was evaluated by using the harmonic oscillator and rigid rotor approximations at 298.15 K and 1 atm. We utilize the DFT functionals M06-2X, PW91, and ωB97X-D, as they have shown good performance for studying the formation of atmospheric molecular clusters.[27−31] Explicitly correlated coupled cluster calculations were run with Molpro 2012.1,[32] and domain local pair natural orbital (DLPNO) coupled cluster calculations were performed with ORCA.[33] We will refer to the CCSD(T)-F12a/VDZ-F12 and DLPNO-CCSD(T) methods simply as F12 and DLPNO, respectively.

2.2. Model Systems. To investigate the molecular interaction between sulfuric acid and diamines, we have chosen a set of compounds that allow us to analyze both the degree of substitution and effect of carbon chain length. We investigate substituted *N*,*N*,*N*′,*N*′-ethylenediamines with one to four methyl groups. This yields six different possible compounds: the unsubstituted ethylenediamine (EDA), methylethylenediamine (me-EDA), two dimethylethylenediamines (*N*,*N*-dime-EDA and *N*,*N*′-dime-EDA), trimethylethylenediamine (trime-EDA), and tetramethylethylenediamine (tetra-me-EDA). To study the effect of carbon chain length, the EDA compound is compared with propane-1,3-diamine (PDA) and butane-1,4-diamine (BDA, also know as putrescine). The molecular structure of the reactants have been identified using the systematic rotor approach implemented in the Avogadro software.[34] The lowest identified Gibbs free energy molecular structures are shown in Figure 1, calculated at the M06-2X/6-31++G(d,p) level of theory. The number of identified conformations within 3 kcal/mol of the lowest free energy structure are shown in the parentheses. To model the clustering with sulfuric acid, each of the conformations within 3 kcal/mol of the lowest conformer (up to 20) are used as input for a sampling technique guided by numerous semiempirical calculations.[35,36] Each conformation is subjected to 300 randomly oriented sulfuric acid molecules, randomly distributed around the diamines and relaxed using the semiempirical PM6 method. The different conformers are then identified by the total energy and dipole moment based on a M06-2X/6-31+G(d) single-point energy calculation. Subsequently, all different conformations are geometry optimized and frequencies are calculated at the M06-2X/6-31++G(d,p) level of theory. The lowest Gibbs free energy structures are also optimized using the PW91 and ωB97X-D functionals with the 6-31++G(d,p) basis set. It should be noted that when discussing the free energy difference between different conformers, we refer to data obtained at the M06-2X/6-31++G(d,p) level of theory. The single-point energies of all three obtained structures are then corrected using a high level F12 calculation. The Gibbs free energies are calculated as an average over all three values and the sensitivity of the computed Gibbs free energy to the quantum chemical method is represented as one standard deviation (σ).

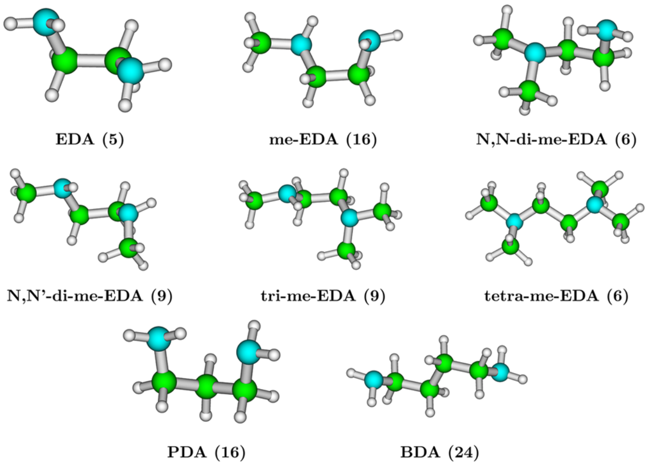


Figure 1. Lowest Gibbs free energy molecular structure of the studied diamines calculated at the M06-2X/6-31++G(d,p) level of theory. The number of identified conformations within 3 kcal/mol of the lowest is shown in the backets. Color coding: green = carbon, blue = nitrogen, and white = hydrogen.

We study the reaction free energies of the complex formation between sulfuric acid and different amines:

$$H_2SO_4 + \text{amine} \leftrightharpoons (H_2SO_4)(\text{amine})$$

where the amine is methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), or one of the eight diamines, leading to a total of 11 reactions. We have conducted a sensitivity analysis on the performance of the applied DFT methods for these 11 reactions. Full details are shown in the Supporting Information, but in brief, we find the following:

- The DFT binding energies are the largest source of errors in calculating the formation free energies, with maximum errors up to 3.3 kcal/mol for PW91/6-311++G(3df,3pd).
- Reducing the basis set from a large 6-311++G(3df,3pd) basis set to the smaller 6-31++G(d,p) basis set only introduces minor errors (less than 1 kcal/mol) in the thermal contribution to the free energy.
- Reducing the basis set only has a minor effect on the subsequent calculation of the binding energy using highly accurate Coupled Cluster methods.

These findings are consistent with our recent studies on a large test set of clusters[37] as well as various other organic compounds such as pinic acid,[38] and highly oxidized ketodiperoxy acid compounds.[39,40]

3. RESULTS AND DISCUSSION

3.1. Cluster Formation. The lowest identified Gibbs free energy structures of the studied diamine−sulfuric acid complexes are shown in Figure 2. The corresponding Gibbs free energies of formation are shown in Table 1. The formation of the sulfuric acid dimer $(SA)_2$ and the interaction between sulfuric acid (SA) and NH_3, MA, DMA, and TMA are shown for comparison.

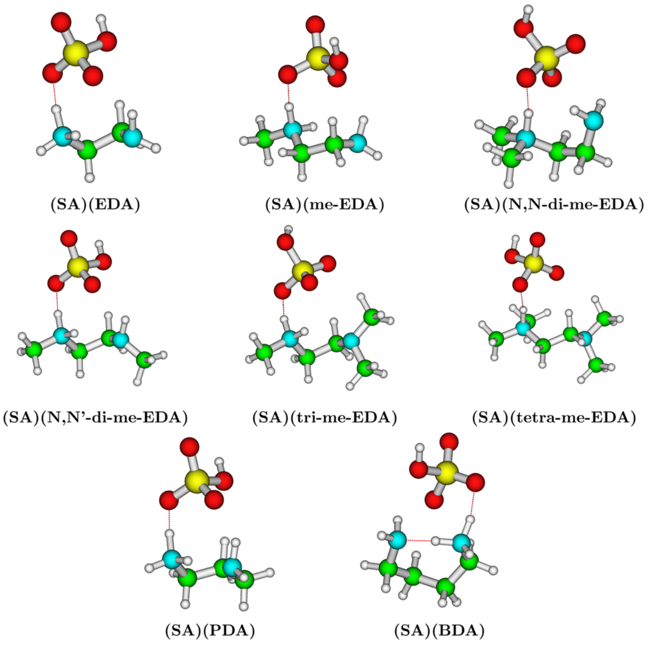

(SA)(EDA) (SA)(me-EDA) (SA)(N,N-di-me-EDA)
(SA)(N,N'-di-me-EDA) (SA)(tri-me-EDA) (SA)(tetra-me-EDA)
(SA)(PDA) (SA)(BDA)

Figure 2. Lowest Gibbs free energy molecular structure of the complex formation between diamines and sulfuric acid calculated at the M06-2X/6-31++G(d,p) level of theory. Color coding: green = carbon, red = oxygen, yellow = sulfur, blue = nitrogen, and white = hydrogen.

3.1.1. Comparison between Different Amines. As expected, all the amines and diamines show more favorable formation free energies than ammonia and the sulfuric acid dimer. The formation free energies for the clustering with sulfuric acid of the monoamines are seen to follow methylamine < dimethylamine < trimethylamine, in agreement with the basicity of the compounds. Taking the uncertainties (of which some part are illustrated by the σ-values) into account, this trend is in agreement with the work by Jen et al. where a ranking of methylamine < trimethylamine ≤ dimethylamine was seen.[41] As trimethylamine is bulkier than dimethylamine, the slight disagreement between the experiment and the calculations could also be due to the neglect of hydration. The N−H group in dimethylamine is capable of forming secondary hydrogen bonded interactions with water molecules, which is not possible for trimethylamine.

Table 1. Average Formation Free Energies (ΔG) of Diamine−Sulfuric Acid Complexes[a]

cluster		ΔG	(σ)
$(SA)_2$		−6.0	0.2
$(SA)(NH_3)$		−5.2	0.2
(SA)(MA)	p	−8.2	(0.5)
(SA)(DMA)	s	−11.9	(0.9)
(SA)(TMA)	t	−12.2	(0.3)
(SA)(EDA)	p,p	−11.1	(0.2)
(SA)(me-EDA)	p,s	−14.7	(0.4)
(SA)(*N*,*N*-dime-EDA)	p,t	−12.2	(0.2)
(SA)(*N*,*N*′-dime-EDA)	s,s	−14.2	(0.1)
(SA)(trime-EDA)	s,t	−14.3	(0.2)
(SA)(tetra-me-EDA)	t,t	−13.4	(0.3)
(SA)(PDA)	p,p	−14.9	(0.3)
(SA)(BDA)	p,p	−15.4	(0.2)

[a] p, s, and t refer to primary, secondary, and tertiary amines. The 6-31++G(d,p) basis set was used for optimizing the geometries with M06-2X, PW91, and ωB97X-D. CCSD(T)-F12a/VDZ-F12 was used to obtain the binding energies. The σ-value is the standard deviation of all three results, indicating the sensitivity to the quantum mechanical method. All values are reported in kcal/mol at 298.15 K and 1 atm.

3.1.2. Comparison between Different Diamines. A single proton transfer from sulfuric acid to the diamines is observed in all cases. Several of the diamines contain nonequivalent amino groups. For instance, Me-EDA contains both a primary and a secondary amino group and we observe that the secondary amino group acts as the proton acceptor. The conformation where the primary amine is protonated is found to be 3.0 kcal/mol higher in free energy (M06-2X/6-31++G(d,p) level of theory). The ternary amine is seen to be protonated in the (SA)(*N*,*N*-dime-EDA) complex, with the conformation where the primary amine acts as acceptor being 0.9 kcal/mol higher in free energy. For the (SA)(trime-EDA) complex the secondary amino group acts as the proton acceptor, with the conformation where the ternary amino group is protonated being 1.9 kcal/mol higher in free energy. This is curious, as further substitution should yield a higher basicity; i.e., the ternary amine moiety should show a higher interaction energy. The proton affinity of the ternary amino group in trime-EDA is 3.8 kcal/mol higher than the secondary group at the M06-2X/6-31++G(d,p) level of theory, further indicating that it has the highest basicity. This discrepancy between the formation free energy for the cluster with sulfuric acid and the basicity is found to be due to several secondary interactions being present in the complexes: Table 2 shows the hydrogen bond distance between the protonated amine and sulfuric acid ($NH^+\cdots OS$), the nonprotonated amine and sulfuric acid distance ($NH\cdots OS$), and the distance between the protonated and nonprotonated amine ($NH^+\cdots N$). It is seen that the secondary interaction from one amino group to the other yields a high stabilization in the complexes. In the (SA)(*N*,*N*-dime-EDA) and (SA)(tetra-me-EDA) complexes where a ternary amino group is protonated, it is not possible to have a secondary hydrogen bond interaction neither to the other amino group nor to the sulfuric acid. This is reflected in the formation free energies of these complexes which are around 1−2 kcal/mol higher in free energies than the

Table 2. Hydrogen Bond Lengths (Å) in the Primary ($NH^+\cdots OS$) and Secondary ($NH\cdots OS$ and $NH^+\cdots N$) Interactions

cluster	$NH^+\cdots OS$	$NH\cdots OS$	$NH^+\cdots N$
(SA)(EDA)	1.46048	2.16088	2.18736
(SA)(me-EDA)	1.50486	2.14213	2.19610
(SA)(*N*,*N*-dime-EDA)	1.52684	2.49157	
(SA)(*N*,*N*′-dime-EDA)	1.50448	2.22116	2.17574
(SA)(trime-EDA)	1.52251		2.22277
(SA)(tetra-me-EDA)	1.47489		
(SA)(PDA)	1.49689	2.03822	1.87808
(SA)(BDA)	1.63570	2.13772	1.63912

other methyl-substituted EDAs (Table 1). If the ternary amine was protonated in the (SA)(trime-EDA) complex, the $NH^+\cdots N$ hydrogen bond would not be present, leading to a lower stability. In all the other complexes, the protonated amino group hydrogen bonds with the second amino group, and the amino group that is not protonated is seen to interact with sulfuric acid, leading to more favorable complexes. This illustrates that the interaction strength with sulfuric acid follows a primary < tertiary < secondary pattern for these methyl-substituted EDAs, due to the presence of secondary hydrogen bonded interactions.

3.1.3. Comparison between Mono- and Diamines. The unsubstituted EDA is seen to have a slightly higher formation free energy for the cluster with sulfuric acid ($\Delta G = -11.1$ kcal/mol) than dimethylamine and trimethylamine, with formation free energies of −11.9 and −12.2 kcal/mol, respectively. Although EDA has an electronic binding energy to sulfuric acid similar to that for TMA, the bent structure leads to a higher entropy penalty, which then yields a less favorable formation free energy. All the methyl-substituted diamines show a more favorable formation free energy for the clustering with sulfuric acid than the monoamines. This can be attributed to the higher basicity of the diamines and, as discussed above, by the secondary interactions to the second amino group made possible by the proton transfer. The highest stability is observed for the monosubstituted me-EDA, with a formation free energy of −14.7 kcal/mol for the clustering with sulfuric acid.

3.1.4. Effect of Carbon Chain Length. As the carbon chain increases, there is seen a significant lowering in the cluster formation free energies. The formation free energy of the (SA)(PDA) complex is −14.9 kcal/mol, as opposed to −11.1 kcal/mol for the (SA)(EDA) complex. The (SA)(BDA) complex is slightly more stable with a formation free energy of −15.4 kcal/mol. As seen in Table 2, this trend can be explained by the decreased distance in the $NH^+\cdots N$ hydrogen bond length, which leads to a significant increase in the strength of the secondary interactions.

These findings indicate that increasing the carbon chain length and having secondary amino groups in the diamine both yield a more favorable formation free energy for the cluster with sulfuric acid. To investigate whether this effect is additive, we tested the addition of two methyl groups to the BDA compound (*N*,*N*′-dime-BDA). By only doing a full conformer search on the reactant, and manually constructing the cluster using similar hydrogen bond patterns as given in Figure 2, we obtain a ΔG-value of −19.1 kcal/mol with $\sigma = 0.3$ for *N*,*N*′-dime-BDA clustering with sulfuric acid (complex shown in Figure 3).

The favorable formation free energy of the (SA)(*N*,*N*′-dime-BDA) complex would yield an evaporation rate of essentially zero, indicating that when it collides with a sulfuric acid molecule it will stick indefinitely. Such compounds could potentially be important precursors for forming new particles, under the premise that they are present in the atmosphere. It should be noted that the formation of these sulfuric acid–amine complexes cannot be directly translated into new particle formation rates. The stability of larger clusters that are able to re-evaporate into the system can significantly change the dynamics of cluster formation.[42] To better understand the stability of larger clusters, we will in the following two sections look closer at clusters containing up to four sulfuric acid.

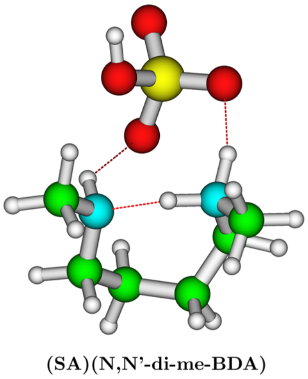


Figure 3. Lowest Gibbs free energy molecular structure of the (SA)(*N*,*N*′-dime-BDA) complex, calculated at the M06-2X/6-31++G(d,p) level of theory.

3.2. Application of the DLPNO Method. For studying clusters larger than the simple acid–base pair, accurate F12 calculations become computationally too expensive. The emergence of the new DLPNO method allows an accurate treatment of larger clusters. We recently applied the DLPNO method to $(H_2SO_4)_{1-5}(NH_3)_{1-5}$ and $(H_2SO_4)_{1-4}((CH_3)_2NH)_{1-5}$ clusters.[43] To further test the applicability of the DLPNO method for calculating the binding energy of sulfuric acid–base clusters, we compare the DLPNO binding energies with F12 for the above 11 acid–base formation reactions. The calculations are all performed on top of the DFT/6-31++G(d,p) optimized molecular structures and hence any difference in the binding energies between the functionals originate from the slight variation in the molecular structure obtained when they are optimized with the different functionals. We evaluate the DLPNO energies for each separate functional; i.e., we have a total of 33 binding energies to assess. Table 3 shows the mean absolute error (MAE), mean signed error (MSE), and maximum error (MaxE) in the DLPNO binding energies compared with the F12 results, depending on the basis set used in the DLPNO calculation.

Table 3. Mean Absolute Error (MAE), Mean Signed Error (MSE), and Maximum Error (MaxE) in the DLPNO Binding Energies Compared with CCSD(T)-F12a/VDZ-F12 Results[a]

basis set	MAE	MSE	MaxE
cc-pVDZ	2.2	2.0	3.9
cc-pVTZ	1.5	1.5	2.3
cc-pVQZ	1.1	1.0	2.1
aug-cc-pVDZ	1.3	−1.3	3.6
aug-cc-pVTZ	0.5	−0.4	1.4
CBS(2−3)	0.6	0.5	1.7
CBS(3−4)	0.5	0.4	1.6

[a] CBS(2-3) and CBS(3-4) refer to complete basis set extrapolation using the cc-pVXZ basis set. All values are in kcal/mol.

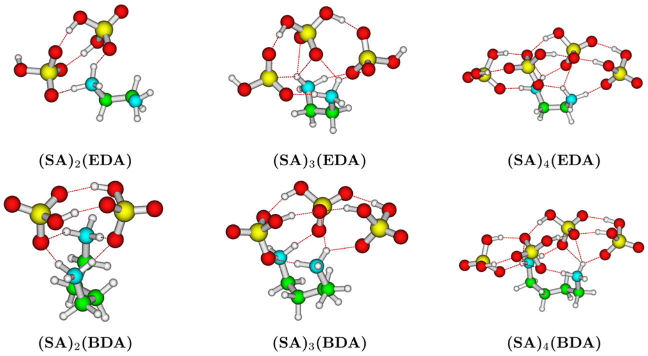
The MAE and MaxE drop gradually for DLPNO/cc-pVXZ (X = D, T, or Q) with increasing cardinal number. From the MSE it is evident that the cc-pVXZ basis sets yield a consistent underestimation of the binding energy compared with F12 results. Even when a quadruple-ζ basis set is applied, the DLPNO method exhibits a MAE of 1.1 kcal/mol. Complete basis set (CBS) extrapolation of the correlation energy is performed using the default formula in the ORCA program:

$$E_{\text{corr}}^{(\infty)} = \frac{X^{\beta}E_{\text{corr}}^{(X)} - Y^{\beta}E_{\text{corr}}^{(Y)}}{X^{\beta} - Y^{\beta}}$$

where $E_{\mathrm{corr}}^{(\infty)}$ is the extrapolated correlation energy and $E_{\mathrm{corr}}^{(X)}$ and $E_{\mathrm{corr}}^{(Y)}$ are the correlation energies calculated using a basis set with cardinal number X and Y, respectively. The theoretical value for β is 3, but it has been shown that $\beta = 2.4$ performs better for the 2−3 extrapolation.[44,45] We use the default ORCA values of $\beta = 2.46$ for CBS(2−3) and $\beta = 3.05$ for CBS(3−4), with CBS(2−3) implying extrapolation from cc-pVDZ to cc-pVTZ and CBS(3−4) implying extrapolation from cc-pVTZ to cc-pVQZ. Complete basis set extrapolation is seen to significantly improve the results, with a MAE of 0.6 kcal/mol for CBS(2−3). We only get a slight improvement by doing 3−4 extrapolation where a MAE of 0.5 kcal/mol is obtained. Both CBS(2−3) and CBS(3−4) yield a consistent underestimation of the binding energy compared with F12 results, as reflected by the MAE and MSE being similar in magnitude. Adding diffuse functions to the basis set is seen to significantly improve the basis set convergence. The binding energies calculated using the aug-cc-pVXZ (X = D or T) basis sets yield a relative consistent overestimation of the binding energy. The aug-cc-pVTZ basis set yields a performance similar to that of the CBS(2−3) extrapolation. It should be noted that the DLPNO and F12 methods are differently constructed, and identical results are not to be expected. Our comparison indicates that to study the binding energy of larger clusters where F12 is out of reach, DLPNO/CBS(2−3) can be used as a good compromise between accuracy and computational efficiency.

3.3. Larger Clusters.

In section 3.1 it was found that diamines yield a stronger interaction with sulfuric acid compared to monoamines. To identify whether diamines can further enhance the addition of sulfuric acid molecules, we look at the reaction free energies for forming $(H_2SO_4)_{1-4}$(Base) clusters, with Base = NH_3, DMA, EDA, or BDA. The cluster structures have been sampled in a fashion similar to that described in section 2.2, and the $(H_2SO_4)_{2-4}$(EDA) and $(H_2SO_4)_{2-4}$(BDA) clusters are depicted in Figure 4. Figure 5 presents the corresponding calculated reaction free energies using DFT/6-31++G(d,p) optimized geometries, with a DLPNO single-point energy correction at the complete basis set (CBS) limit, as a function of sulfuric acid molecules. The CBS limit was calculated using 2−3 extrapolation as described above. The shown error bars correspond to one standard deviation. As also mentioned in the previous section, the values calculated using DLPNO/CBS(2−3) should yield a consistent underestimation of the binding energies compared to F12 results, indicating that the values presented can be assumed to be an upper bound. The values for each reaction are also shown in the Supporting Information.


$(SA)_2$(EDA) $(SA)_3$(EDA) $(SA)_4$(EDA)

$(SA)_2$(BDA) $(SA)_3$(BDA) $(SA)_4$(BDA)

Figure 4. Lowest Gibbs free energy molecular structure of the $(H_2SO_4)_{2-4}$(EDA) and $(H_2SO_4)_{2-4}$(BDA) clusters calculated at the M06-2X/6-31++G(d,p) level of theory.

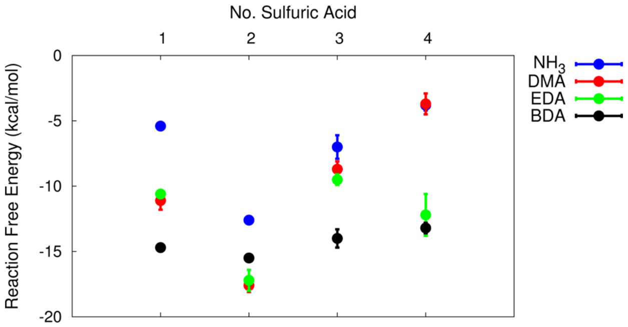


Figure 5. Reaction free energies for forming $(H_2SO_4)_{1-4}$(Base) clusters, with Base = NH_3 (blue circle), DMA (red circle), EDA (green circle), or BDA (black circle) as a function of sulfuric acid molecules. Calculated using DFT/6-31++G(d,p) optimized geometries and a DLPNO-CCSD(T)/CBS(2−3) single-point energy correction. The error bars corresponds to one standard deviation. All values are presented in kcal/mol, at 298.15 K and 1 atm.

We observed a second proton transfer for all the clusters except $(SA)_2$(EDA). The alternative molecular structure of $(SA)_2$(EDA), where a second proton transfer did take place was found to be 3.0 kcal/mol higher in free energy. In the $(SA)_2$(EDA) cluster the two sulfuric acid molecules exclusively interact with a single amino group. The conformation where both amino groups interact with sulfuric acid, was found 1.8 kcal/mol higher in free energy. The absent interaction with the second amino group is caused by a strong interaction between the formed bisulfate ion and the neutral sulfuric acid. For the $(SA)_2$(BDA) cluster the longer carbon chain of the diamine allows the protonated BDA molecule to bend around the $(HSO_4^-)_2$ pair, leading to a favorable interaction. The addition of a third sulfuric acid molecule allows a second proton transfer in the $(SA)_3$(EDA) cluster. Counterintuitively, this cluster has two S−OH groups that do not participate in hydrogen bonding. The $(SA)_3$(EDA) cluster where all hydrogen bond donor groups participate in hydrogen bonding in a fashion similar to that seen for the $(SA)_3$(BDA) cluster was found to be 1.7 kcal/mol higher in free energy. This is seen to cause an increase in the reaction free energy for forming $(SA)_3$(EDA) compared to the second addition of a sulfuric acid molecule. Due to the longer carbon backbone length the BDA molecule is able form a $(SA)_3$(BDA) cluster where all the hydrogen bonds are paired. The addition of the fourth sulfuric acid yields similar $(SA)_4$(EDA) and $(SA)_4$(BDA) clusters, with the $(HSO_4^-)_2$ pair residing in the middle of the cluster. The two remaining sulfuric acid molecules interact with the $(HSO_4^-)_2$ pair while simultaneously interacting with the two amino groups.

To consider a cluster to be stable would require that the formation rate of the cluster is equal to the evaporation rate. At typical atmospheric concentrations of sulfuric acid (a few ppt) and ppt levels of bases would imply that at least a reaction free energy of −12 kcal/mol would be required to yield a stable cluster.[38] In the following we will refer to cluster stability as to whether a cluster reaction is in the proximity of this value or not.

For ammonia the initial complex formation with sulfuric acid have a reaction free energy of −5.4 kcal/mol. The addition of a second sulfuric acid is significantly more favorable with $\Delta G = -12.6$ kcal/mol as it is accompanied by a full proton transfer. The following third and fourth addition of a sulfuric acid molecule to ammonia clusters are seen to yield higher reaction free energies of −7.0 and −3.8 kcal/mol. This suggests that ammonia is only capable of efficiently stabilizing a maximum of two sulfuric acid molecules, and to some extent a third sulfuric acid molecule. This is of course highly dependent on the atmospheric concentration of ammonia, which can be several orders of magnitude higher than the amines studied here. As DMA has a higher basicity than ammonia, the first three additions of sulfuric acid molecules are seen to be more favorable, with reaction free energies of −11.1, −17.6, and −8.7 kcal/mol, respectively. The fourth addition is seen to be similar to the ammonia case with a reaction free energy of −3.7 kcal/mol. DMA shows a trend similar to that for ammonia and is only capable of efficiently stabilizing two sulfuric acid molecules, with the third only being mildly stabilized.

The diamines show a different mechanism for stabilizing the clusters. The first three additions of sulfuric acid molecules to EDA is seen to have reaction free energies similar to those for DMA, with ΔG-values of −10.6, −17.2, and −9.5 kcal/mol, respectively. The fourth addition of sulfuric acid to EDA is seen to be significantly more favorable than for DMA, with a reaction free energy of −12.2 kcal/mol. This implies that EDA can efficiently stabilize an additional sulfuric acid molecule compared to the case with DMA. This further drop in reaction free energy can be understood on the basis of the $(H_2SO_4)_4(EDA)$ cluster structure, where all the hydrogen bonds are paired. Furthermore, the sulfuric acid molecules are both capable of being stabilized through a direct interaction with the amino groups not only via proton transfer reactions but also by secondary hydrogen-bonded interactions. The complex formation between BDA and sulfuric acid is significantly more favorable than for NH_3, DMA, or EDA. This can be attributed to the higher basicity of the compound. The second addition of a sulfuric acid molecule to BDA is seen to be slightly less favorable than for DMA and EDA, with a reaction free energy of −15.5 kcal/mol. The third and fourth additions show relatively reaction free energies similar to those of the initial two, with ΔG-values of −14.0 and −13.2 kcal/mol. This indicates that each addition of sulfuric acid molecules to BDA is favorable and relatively constant, and that BDA is capable of efficiently stabilizing up to four sulfuric acid molecules. The study by Jen et al. showed that EDA and BDA were able to enhance new particle formation events by up to 1 order of magnitude compared to DMA, and that diamine clusters could be formed with only a single diamine molecule whereas monoamine clusters would require more than one monoamine. This is further corroborated by our calculations, as diamines are seen to be able to efficiently stabilize additional sulfuric acid molecules compared to NH_3 and DMA. Though both EDA and BDA were found to yield 10 times more particles than DMA,[24] we here identify that the mechanism for the cluster growth by adding sulfuric acid molecules are inherently different for the two diamines. This shows that not only the higher basicity of the diamines compared to that for monoamines is the determining factor but also the molecular structure of the diamine influences the cluster formation with sulfuric acid. To fully understand the involvement of diamines in atmospheric new particle formation, further work is needed to obtain larger $(SA)_n(\text{diamine})_m$ clusters consisting of several diamines and sulfuric acid molecules, which allows kinetic modeling using for instance the Atmospheric Cluster Dynamics Code (ACDC).[46] Furthermore, hydration influences the stability of molecular clusters and should also be studied.

4. CONCLUSIONS

We have investigated the molecular interaction between methyl-substituted *N,N,N′,N′* -ethylenediamines, propane-1,3-diamine, butane-1,4-diamine, and sulfuric acid. The studied diamines are bound equally or more strongly to sulfuric acid than dimethylamine is. We find that diamines that contain one or more secondary amino groups stabilize the complex formation with sulfuric acid most efficiently. The formation free energy of the complexes are seen to be highly dependent on secondary hydrogen bond interactions. Changing the carbon backbone length from ethylenediamine to propane-1,3-diamine, or butane-1,4-diamine yielded a further stabilization. Methyl substitution and elongating the carbon chain length to form *N,N′*-dimethyl-1,4-butanediamine together result in a formation free energy of −19.1 kcal/mol for the clustering with sulfuric acid, indicating that such diamines could potentially be important compounds in the initial steps in new particle formation, if present in the atmosphere. For studying larger clusters consisting of diamines and up to four sulfuric acid molecules, we have benchmarked the DLPNO-CCSD(T) method against F12 results. We find that the DLPNO method using 2−3 complete basis set extrapolation is a good compromise between accuracy and efficiency. Using DLPNO to study larger clusters, we find that a single diamine is capable of efficiently stabilizing sulfuric acid clusters with up to four acid molecules. The mechanism for stabilizing the clusters is found to depend not only on the higher basicity of the diamine compounds but also on the specific carbon chain length. This indicates that to fully understand the involvement of diamines in atmospheric new particle formation further work is needed to obtain larger $(SA)_n(\text{diamine})_m$ clusters to allow kinetic modeling using, for example, the ACDC code.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b03192.

DFT sensitivity analysis and calculated formation free energies (PDF)
Cartesian coordinates in XYZ format (ZIP)

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Notes

The authors declare no competing financial interest.

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