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Authors

Xu, Jing
Finlayson-Pitts, Barbara J
Gerber, R Benny

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Proton Transfer in Mixed Clusters of Methanesulfonic Acid, Methylamine, and Oxalic Acid: Implications for Atmospheric Particle Formation

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Jing Xu,[†] Barbara J. Finlayson-Pitts,[†] and R. Benny Gerber*,[†,‡]

[†]Department of Chemistry, University of California, Irvine, California 92697-2025, United States
[‡]Institute of Chemistry, Fritz Haber Research Center, Hebrew University of Jerusalem, Jerusalem 91904, Israel

S Supporting Information

ABSTRACT: Understanding the properties of atmospheric particles made of several components is a very challenging problem. In this paper, we perform quantum chemical calculations for small multicomponent clusters of atmospheric relevance that incorporate methanesulfonic acid (MSA), methylamine (MA), oxalic acid (OxA), and water (H_2O). Potential correlations between theoretical predictions of proton transfer in the small clusters and findings of recent experiments on formation of particles of detectable sizes (>2 nm) from the same components are studied. It is proposed that proton transfer from the acid to the amine in the 1:1 clusters correlates with experiments on particle formation in systems, such as MSA-MA and MSA-MA-OxA. In the case of OxA + MA, which has been observed to give few particles, proton transfer does not occur for the 1:1 cluster but does for the 2:2 cluster. Adding H_2O to OxA-MA promotes the occurrence of proton transfer, and corresponding particles are slightly enhanced. The partial charge on the MA component increases by adding OxA or H_2O to MSA-MA, which is correlated with enhanced particle formation compared to MSA-MA alone. Ab initio molecular dynamics simulations show that proton transfer at room temperature ($T = 298$ K) and high temperature ($T = 500$ K) is little affected compared with the equilibrium structure ($T = 0$ K). These results suggest that small cluster calculations may be useful in predicting the formation of multicomponent particles in the atmosphere.
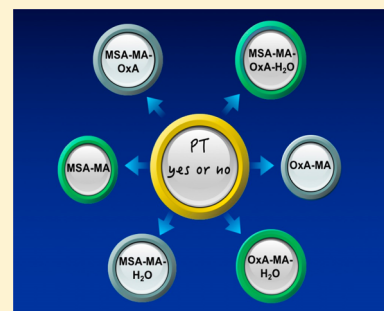
INTRODUCTION

The formation and growth of new particles in the atmosphere is a major research topic in atmospheric chemistry,[1−5] with many experimental,[6−8] theoretical,[9−11] and modeling[12−15] studies focused on this topic. However, understanding the processes involved in particle formation and growth at a molecular level is still rather incomplete, particularly where multiple components and organic compounds are involved. One of the most common components of atmospheric particles is sulfuric acid (H_2SO_4),[4,5,16−22] which can form particles in binary systems with water (H_2O),[23−25] ammonia (NH_3),[18,26−30] or amines.[18,31−38] Ternary systems involving sulfuric acid with water and ammonia or amines have also been studied both experimentally and theoretically.[17,25,28,33,39−49]

There is less known about other acids such as methanesulfonic acid (MSA) formed from the oxidation of organosulfur compounds in air.[50,51] Studies of binary systems of MSA with water,[52−55] ammonia or amines,[56−59] and ternary systems involving MSA-NH_3/amines-H_2O,[57−61] MSA-H_2SO_4-dimethylamine (DMA),[62] and MSA-H_2SO_4-H_2O[63,64] have been reported. Quantum chemical calculations of geometries and energies for small clusters have been used to shed light on acid−base interactions and particle formation in the case of sulfuric acid.[26,28−31,42−44,65]

It has been suggested that organic species may also play a role in particle formation involving acids.[4,5,16,66−75] Some quantum chemical calculations for small clusters composed of an organic acid, a base, and water have been reported, such as binary oxalic acid (OxA) with NH_3,[76] ternary OxA-NH_3-H_2O,[77,78] OxA-H_2SO_4-H_2O,[73] OxA-H_2SO_4-NH_3,[79] succinic acid-DMA,[9] and OxA-DMA-H_2O.[80] Proton transfer reactions and intermolecular interactions of small organic acids in clusters have also been investigated both experimentally and theoretically.[81−89] To our knowledge, there have been no theoretical studies of the impact of organic acids on particle formation from MSA so far. Recently, Arquero et al.[90] experimentally studied the role of the dicarboxylic acid OxA in new particle formation from vapor phase MSA, methylamine (MA), and H_2O. The key experimental results summarized in Figure 1 show: (1) the MSA-MA reaction generates detectable particles efficiently; (2) the addition of water vapor at concentrations representing tens of % relative humidity (RH) leads to enhanced particle formation in the MSA-MA reaction; (3) the addition of oxalic acid vapor to the MSA-MA system
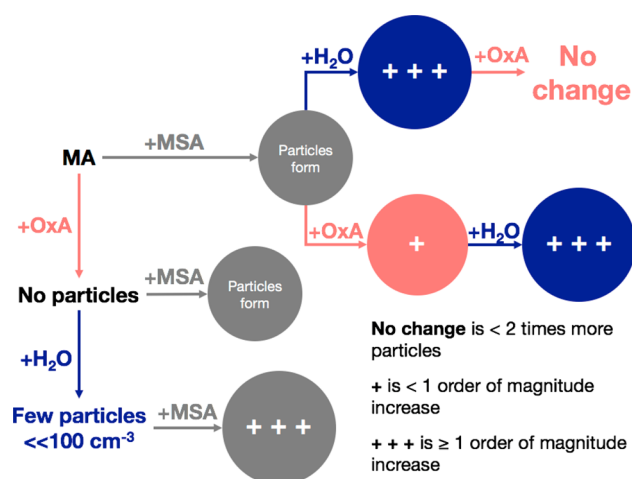
Figure 1. Summary of results from experimental studies[90] with MSA, OxA, MA, and H_2O.

leads to a small increase in particle formation at the concentrations at which OxA can be added (~17 ppb); (4) essentially no particles are formed from OxA + MA; (5) the addition of water to OxA + MA increases particle formation by ~1 order of magnitude from the low level in the absence of water. In addition, the limit of detection for particles is typically ~2 nm mobility diameter in the experimental studies, so that the observation of particle formation reflects both nucleation and growth to detectable sizes.

Although small clusters may be very different in structure from the corresponding larger configurations found in particles, it is of great interest to determine whether particle formation could be predicted based on small cluster calculations. This could be a major advantage, since calculations for small species are not computationally demanding, and they can provide molecular-level insight into the initial adhesion steps in clusters. To pursue possible connections between the experimentally measured particles and theoretically calculated small clusters made of the same components, we report the results of quantum chemical calculations of the mixed acid−base clusters of MSA, MA, and OxA in the presence or absence of water, and the structures of each monomer are shown in Figure 2. The equilibrium structures, binding energies, charge distributions, roles of the different components, and the interactions between them are explored. The occurrence (or not) of proton transfer
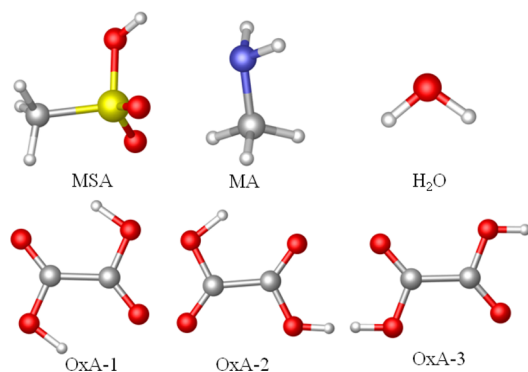

Figure 2. Structures of MSA, MA, H_2O, and three low-lying isomers of OxA. (●) Yellow is sulfur, red is oxygen, blue is nitrogen, gray is carbon, white is hydrogen.

from acid to base greatly affects other properties of the cluster, including structure and binding energy. The potential role of proton transfer as related to particle formation is considered by comparison to experimental formation of the corresponding particles.[90]

■ THEORETICAL METHODS

All of the electronic structure calculations were done using B3LYP[91−93] with Grimme's dispersion correction[94] and using the Dunning's augmented double-ζ correlation-consistent basis set aug-cc-pVDZ.[95] In our previous studies of acid−base clusters, B3LYP-D3 has been shown to be able to give reasonable predictions for geometry and structures, vibrational frequencies, energies, enthalpies, and Gibbs free energies.[57−59] Bork et al.[96] reported a computational benchmarking study of Gibbs free binding energies in the acetonitrile-HCl hydrogen-bonded complex. The comparison of experimental and theoretical ΔG values showed that MP2 and B3LYP-D3 predictions were within the experimental range, while CCSD-(T) provided high-quality binding energies. For more reliable relative energies, the MP2[97−99]/aug-cc-pVDZ and CCSD-(T)[100,101]/aug-cc-pVDZ//B3LYP-D3/aug-cc-pVDZ values were used as a reference for our test calculations on binary complexes (OxA-MA and MSA-MA). On the whole, the B3LYP results for the relative energies of different conformers are in accord with the MP2 and CCSD(T) results. Most important, the lowest-energy conformers according to B3LYP are also the lowest according to MP2 and CCSD(T) (see Table S1 in Supporting Information). Partial charges (δ) at B3LYP-D3/aug-cc-pVDZ level were calculated using natural bond orbital (NBO) analysis.[102,103] To explore temperature effects on cluster properties, specifically on proton transfer and charge separation within the clusters, Born−Oppenheimer molecular dynamics (BOMD) simulations were performed using the BLYP-D/6-31+G(d) potential on-the-fly. To enhance possible temperature effects and accelerate the calculation, room temperature (298 K) and the very high temperature of 500 K were used to obtain the dynamics during 50 ps. The time step used was 0.98 fs. As discussed later, despite the high temperature, the effects on proton transfer were relatively modest. All calculations were performed using the Q-CHEM 4.3 program package.[104]

■ RESULTS AND DISCUSSION

This study focused on the lowest-energy structures for two-component clusters (binary complexes), for example, MSA-MA and OxA-MA; three-component clusters (ternary complexes) including MSA-MA-H_2O, OxA-MA-H_2O, and MSA-MA-OxA; and the four-component cluster (quaternary complex) MSA-MA-OxA-H_2O. These combinations have been studied experimentally,[57,90] providing a data set to which the theoretical results can be compared. The most stable structures of the various complexes, computed at the B3LYP-D3/aug-cc-pVDZ level, are shown in Figure 3. The partial charges (δ) of each component of the clusters are also shown in Figure 3. In addition to the lowest-energy structures, some higher-energy isomers were computed (see Table S2), and in several cases the energy gap from the most stable structure of the complex was found to be quite small. In most cases we studied, the partial charge distribution in lower-energy structures does not differ significantly from that of the most stable structure. We probe here the hypothesis that the properties of the particles that
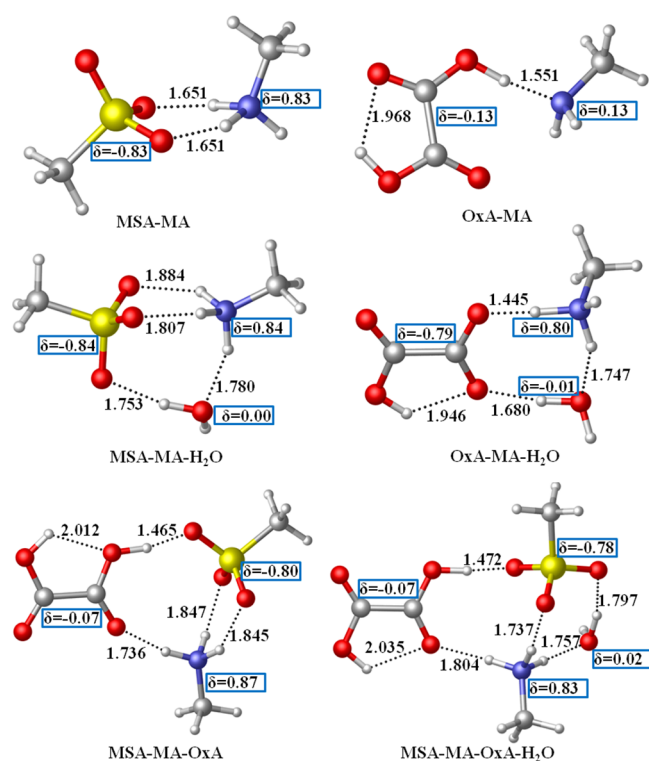
Figure 3. Key geometrical parameters (in angstroms) of most stable structures of each complex and partial charges δ (in atomic units) at the level of B3LYP-D3/aug-cc-pVDZ.

Table 1. Dissociation Energies^a (D_e) at the Level of B3LYP-D3/aug-cc-pVDZ

	D_e (kcal/mol)
MSA-MA → MSA + MA	18.15
OxA-MA → OxA + MA	15.97
MSA-MA-H$_2$O → MSA-MA + H$_2$O	16.90
OxA -MA-H$_2$O → OxA-MA + H$_2$O	11.33
MSA-MA-OxA → MSA-MA + OxA	21.32
MSA-MA-OxA → OxA-MA + MSA	23.49
MSA-MA-OxA-H$_2$O → MSA-MA-OxA + H$_2$O	16.28
MSA-MA-OxA-H$_2$O → MSA-MA-H$_2$O + OxA	20.70
MSA-MA-OxA-H$_2$O → OxA-MA-H$_2$O + MSA	28.43

^{a}A positive value for D_e corresponds to an endothermic process.

= 0.87, and δ = 0.83, respectively. Similar to MSA-MA, these multicomponent ionic clusters have high dissociation energies, ranging from 16.28 to 28.43 kcal/mol (see Table 1). This stability against dissociation is favorable for presence of clusters, and for contribution to particle growth.

An interesting case of a ternary complex is OxA-MA-H$_2$O. As discussed above, there is no proton transfer for the OxA-MA two-component clusters. However, one proton is transferred from OxA to MA when water is added to OxA-MA (see Figure 3). The charge separation increases from δ = 0.13 to δ = 0.80. The effect of H$_2$O to OxA-MA is discussed in more detail below.

Proton Transfer in Clusters As Related to Formation of Detectable Particles. Finding the relationship between quantum chemical calculations of small clusters and the corresponding experiments can help to make predictions for experimental studies of multicomponent clusters. Here, we summarize whether proton transfer in a small cluster has a qualitative correlation with the formation of particles made of the same components. On the basis of the most stable structures in Figure 3, we summarize the assumed criterion of proton transfer in each complex in Table 2. First, for 1:1 binary

Table 2. Proton Transfer in Each Complex

ratio		proton transfer^a	partial charge δ on MA
1:1	MSA-MA	√	0.83
1:1	OxA-MA	X	0.13
2:2	(OxA-MA)$_2$	√	0.82
1:1:1	MSA-MA-H$_2$O	√	0.84
1:1:1	OxA-MA-H$_2$O	√	0.80
1:1:1	MSA-MA-OxA	√	0.87
1:1:1:1	MSA-MA-OxA-H$_2$O	√	0.83
1:1	MSA-NH$_3$[61]	X	
2:2	(MSA-NH$_3$)$_2$[56]	√	
1:1	MSA-TMA[58]	√	

^{a}A check mark means proton transfer exists in the most stable structure, and X means it does not.

contain many molecules are related to the charge distribution in the corresponding clusters made of the same components.

Proton Transfer. In acid−base particles, proton transfer from the acid moiety to the base moiety may take place, depending on the strengths of the acid and the base. The proton transfer considered here is for the equilibrium structure of the cluster. Temperature effects will be discussed later. We define proton transfer to occur in the present context if the partial charges on the acid and base moieties are at least of magnitude 0.5. (In fact, for the systems studied the typical values of δ in the case of proton transfer are of the order of 0.75−0.85; there are no borderline cases).

First, for 1:1 binary complexes when the acid is MSA and the base is MA, the most stable structure of MSA-MA in Figure 3 involves a pronounced proton transfer (δ = 0.83). An ion pair [CH$_3$SO$_3$]$^-$ [H$_3$NCH$_3$]$^+$ is formed, as is visible from both the proton location and the partial charges. However, when the acid is OxA, there is just a hydrogen bond connecting OxA to MA, in which OxA acts as the hydrogen-bond donor, and MA is the acceptor. The small δ value in this case (δ = 0.13) does not correspond to proton transfer. These results are, of course, not surprising given the much stronger acidity of MSA (pK_a = −1.9)[105] compared with that of OxA (pK_{a1} 1.2, pK_{a2} 3.6).[106,107] The occurrence of proton transfer affects the binding energy, since the charge-transfer complexes are bonded ionically, rather than by (neutral) hydrogen bonding. Hence, the dissociation energy D_e of MSA-MA listed in Table 1 is 18.15 kcal/mol, compared to 15.97 kcal/mol for OxA-MA.

For 1:1:1 ternary complexes and the 1:1:1:1 quaternary complex, proton transfer occurs in all cases involving MSA, that is, MSA-MA-H$_2$O, MSA-MA-OxA, and MSA-MA-OxA-H$_2$O. In these complexes (see Figure 3), all the protons are transferred from MSA to MA, and the partial charge on MA δ is δ = 0.84, δ

complexes, our calculations show that there is no proton transfer in OxA-MA, but there is in MSA-MA. Experimental studies by Arquero et al.[90] showed that OxA and MA formed essentially no particles (less than 5 cm^{-3}), while significant particle concentrations (order of 1 × 10^5 cm^{-3}) were measured from MSA-MA. For the ternary complexes (the 1:1:1 clusters of MSA-MA-H$_2$O and MSA-MA-OxA) and the quaternary complex (the 1:1:1:1 complex MSA-MA-OxA-H$_2$O) significant particle concentrations are formed^d (in the range of 1 × 10^5

cm^{-3} measured experimentally),[90] and significant proton transfer from the MSA is predicted. For the interesting case of OxA-MA, there is no proton transfer for the OxA-MA, and very few OxA-MA particles (<5 cm^{-3}) were observed in the experiments under dry conditions; however, there is proton transfer in OxA-MA-H$_2$O, and slightly increased concentrations of particles (<100 cm^{-3}) were found in the experiments when water was added to OxA-MA. The expectation based on proton transfer considerations is that particles should be formed in the presence of water, but this does not predict the efficiency of particle formation compared to MSA-MA-H$_2$O. In short, on a qualitative basis, particles are detected experimentally in this acid−base system in cases in which theory predicts that the corresponding small clusters exhibit proton transfer.

The connection between proton transfer in small clusters and particles we proposed can also be applied in other known systems. For example, trimethylamine (TMA) was found to form particles with MSA, while at similar (ppb) concentrations, NH$_3$ does not.[57] There is proton transfer in the MSA-TMA complex[58] but not in MSA-NH$_3$.[61] There is an intuitive basis for this correlation in that interactions within an ion pair A$^+$B$^-$ are expected to be stronger than between neutral, hydrogen-bonded clusters. Ionic-type bonding is likely to prevail also in the large particles, contributing to energetic stability.

Cases of Proton Transfer for the 2:2 Cluster, but Not for the 1:1 Cluster. The 1:1 OxA-MA complex shown in Figure 3 does not exhibit proton transfer. The situation is different for the dimer (OxA-MA)$_2$, which is a 2:2 cluster (Figure 4). There is transfer of one proton from each OxA
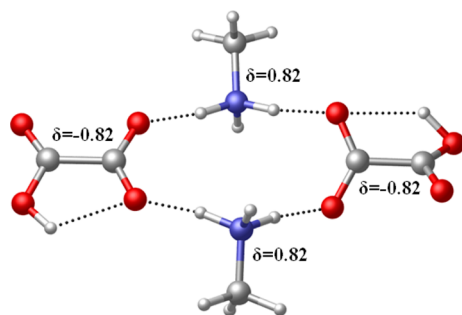

Figure 4. Most stable structure of (OxA-MA)$_2$ and partial charges at the level of B3LYP-D3/aug-cc-pVDZ.

molecule to MA, and the partial charges have a high value of δ = 0.82. There are several other clusters for which such a behavior is known. Tao and co-workers[61] have shown that proton transfer does not take place in MSA-NH$_3$. However, calculations by Dawson et al.[56] showed it does occur in (MSA-NH$_3$)$_2$. Similarly, there is no proton transfer in the 1:1 cluster H$_2$O-HCl, but one of the structures of the dimer (H$_2$O-HCl)$_2$ corresponds to (H$_3$O$^+$-Cl$^-$)$_2$.[108]

There is little particle formation for OxA-MA or for MSA-NH$_3$ at smaller (<10 ppb) base concentrations,[57,90] despite the proton transfer in the 2:2 clusters. The likely reason is that building an initial concentration of 2:2 clusters that will continue to grow efficiently requires first a population of 1:1 clusters, and these are not bound strongly enough (D_e of OxA-MA is 15.97 kcal/mol) to be present in sufficient numbers. We define this as a case of "weak growth". It may be possible that under some conditions a sufficient population of the 1:1 clusters will be created, leading to formation of the 2:2 clusters

that do manifest proton transfer and thus will lead to efficient growth from that stage on.

MSA in Multicomponent Clusters. In all the clusters where MSA is a component, the proton is transferred from MSA to MA. The interaction between MSA and other components is very strong, so the dissociation energies for removing MSA from MSA-MA-OxA and MSA-MA-OxA-H$_2$O are 23.49 and 28.43 kcal/mol, respectively. OxA and water have very little effect on the charge distribution to MSA-MA, though the effect of water is not completely negligible. See, for instance, the slightly larger charge transfer in MSA-MA-OxA (δ = 0.87) compared to that of MSA-MA (δ = 0.83). This increase in the partial charge may contribute to an enhanced propensity for particle growth beyond the main effect of proton transfer. A similar, but weaker, effect of the partial charge increase compared with MSA-MA is found for MSA-MA-H$_2$O. However, in this case the relevant charge difference is only 0.01, so one cannot be confident in attributing the consequences to this difference only.

Role of OxA in Multicomponent Clusters. For both MSA-MA and MSA-MA-OxA, the proton is transferred from MSA to MA, but the presence of OxA increases the partial charge δ on the amine from 0.83 to 0.87. OxA is found to carry a negative partial charge of δ = −0.07, which can be viewed as a small contribution to the charge transfer to the amine, the dominant role in this process being that due to the stronger acid MSA (δ = −0.80). The main effect of OxA is in providing hydrogen bonds to the MSA and MA moieties, giving rise to a very stable ring structure. The dissociation energies of MSA-MA-OxA to eject either OxA or MSA are 21.32 and 23.49 kcal/mol, respectively. The effects of OxA in MSA-MA-OxA-H$_2$O are similar in the charge transfer (δ = −0.07). OxA does contribute significantly to the strong ring structure of MSA-MA-OxA-H$_2$O by making two hydrogen bonds to the MSA moiety as a donor and to the MA as an acceptor. The dissociation energies for removing H$_2$O, OxA, and MSA from MSA-MA-OxA-H$_2$O are high, that is, 16.28, 20.70, and 28.43 kcal/mol, respectively. As noted previously, this stability against dissociation contributes to participation of the cluster in particle growth.

Most interesting is the role of OxA in OxA-MA-H$_2$O. Because of the presence of both a base and water, OxA appears in this case as a relatively strong acid, which transfers a proton to MA and has a high partial charge of δ = −0.79. Also in this case OxA is involved in two hydrogen bonds, one to water (as an acceptor) and another to MA (as a donor), forming a ring structure with an ion pair.

In summary, OxA exhibits significant acidity only in the cluster that does not contain the much stronger acid MSA, and in which both the amine and the water molecule are present. As a dicarboxylic acid, OxA contributes to the stability of the clusters through making two hydrogen bonds and forming ring structures.

Effect of Water in Multicomponent Clusters. Water is always present in the lower atmosphere, and thus understanding its role in multicomponent clusters is important. Comparison of MSA-MA-H$_2$O to MSA-MA-OxA reveals a similarity between the effects of OxA and water. Note that, experimentally, the rate of formation of detectable particles is very sensitive to the concentrations of the gas-phase precursors. Experimental limitations (e.g., vapor pressures, wall losses, etc.) are such that identical reaction conditions and concentrations of all precursors could not be used throughout. For example,

only 17 ppb of OxA could be used, while the water concentrations were many orders of magnitude larger. Both OxA and H_2O make hydrogen bonds with MSA and with MA, one bond as a donor and one bond as an acceptor. For both H_2O and OxA, this leads to fairly stable cyclic structures; the values of D_e for MSA-MA-OxA dissociating to give OxA is 21.32 kcal/mol, and 16.90 kcal/mol for MSA-MA-H_2O to give H_2O. Both OxA and H_2O increase the partial charge on the amine component when compared with MSA-MA, though the effect is stronger for OxA. In the case of OxA-MA-H_2O, water can be said to significantly enhance the role of MA as a base compared with OxA-MA, since proton transfer takes place in OxA-MA-H_2O. The same effect of H_2O also can be applied to OxA-DMA. There is no proton transfer for OxA-DMA. However, one proton is transferred from OxA to DMA with adding water to OxA-MA.[80] In none of the clusters studied was the Lewis base property of H_2O sufficient for the water to accept the proton and form H_3O^+. In summary, on the one hand, water can promote proton transfer in the weak OxA-MA cluster; on the other hand, water can also form hydrogen bonds, both as donor and acceptor. It may be reasonable to assume that this is also the role of water in the larger detectable particles.

Effect of Temperature on Proton Transfer. It is quite obvious that, in general, temperature may potentially have an effect on the occurrence of proton transfer in a system, or at least on the extent of proton transfer as measured by the partial charges (δ). Consider an acid−base system exhibiting proton transfer for the lowest-energy structure ($T = 0$ K). Structures that do not involve proton transfer and are populated at temperature T will contribute to a decrease in the mean extent of proton transfer compared with the lowest equilibrium state. High-energy structures with more pronounced proton transfer (larger δ values) than at equilibrium will contribute in the opposite direction.

To explore the effect of temperature on proton transfer, we performed Born−Oppenheimer molecular dynamics (BOMD) simulations. These were performed primarily for MSA-MA-OxA, as an example. In these dynamics simulations we explored the effect of kinetic energy available to the system at a finite temperature, on the location of the proton, including aspects such as back transfer of the proton from the base to the acid, shifts of the proton to other sites, the time scales involved in proton transfer, and the dependence on kinetic energy available, etc. The key question is, of course, whether the situation at finite temperature can affect our predictions on proton transfer made for the lowest-energy structure. To get an upper-bound estimate of the temperature effect, we used room temperature (298 K) and a very high temperature (500 K). The simulations were pursued for a duration of 50 ps. These dynamics simulations provide additional insights, since one can follow the geometry of the cluster and the location of the protons in time. At 298 K, the structure of MSA-MA-OxA does not change appreciably throughout the simulation. The proton remains bound to MA all the time, and the complex always retains the ionic structure $[\text{MSA}^-][\text{MAH}^+][\text{OxA}]$ at room temperature. Except for vibrations and rotations involving the methyl group and hydrogen bonds, MSA-MA-OxA at room temperature possesses a similar skeletal structure to that of the equilibrium geometry, while at 500 K, two types of events are seen, where the proton is transferred back temporarily from MA to MSA. In one type of event the return of the proton from MA to MSA is essentially direct between the two moieties.

Nineteen such events were seen during the simulation time, and the total time the system spends with the proton back at the MSA is 1.53 ps. Another type of event for back-donation of the proton is where the proton goes first from MSA to OxA, and from this configuration another proton from the OxA goes to MSA. We saw six events of this type, and the total time the proton spent at the MSA was 0.42 ps. Typical snapshots showing events where the MSA is temporarily back-protonated are shown in Figure 5. The bottom line, however, is that the
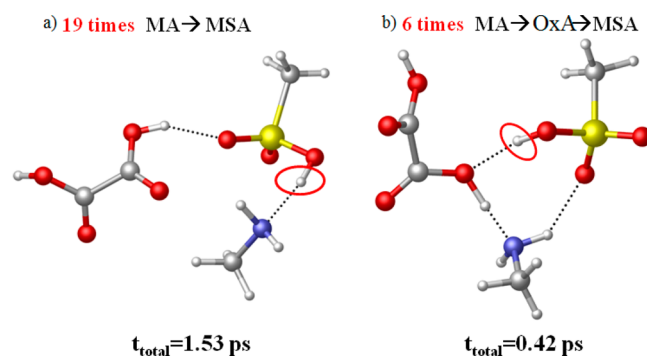

Figure 5. Typical snapshots from the dynamics ($T = 500$ K) for geometries when the proton is back at MSA. (a) Direct transfer, i.e., from MA to MSA; (b) indirect transfer, i.e., MA→ OxA → MSA. t_{total} is the total time of each type.

role of proton back-transfer to MSA is very small, as reflected in the small fraction of the time spent by the proton at MSA of the total 50 ps simulation time. The rest of the time, the system is in the ion-pair state $[\text{MSA}^-][\text{MAH}^+][\text{OxA}]$. Hence, the conclusions regarding proton transfer obtained for the equilibrium structures ($T = 0$ K) remain essentially valid also at room temperatures, and proton excursions at a high temperature (500 K) have only a small effect on their average location. The justifies our use of proton transfer calculations for the equilibrium structure as being applicable also to predictions for room-temperature systems. Future studies will be performed on larger clusters, including those containing water.

■ **CONCLUDING REMARKS**

In this paper, we studied properties of several small clusters made of all or some of the components MSA, MA, OxA, and H_2O. We explored, in particular, the occurrence of proton transfer from an acid molecule to the amine, on the partial charges of the different moieties in the cluster, and on the influence of the other components on these properties.

A question of major interest is whether connections can be found between properties of small clusters that are easy to compute, and the formation of detectable particles that have a large number of molecules of the same components. In examining the results, a qualitative but potentially important correlation is seen with recent experimental findings on the formation of detectable particles made of the same components as the clusters. Essentially the observed correlation predicts formation of particles when there is proton transfer in the corresponding small clusters. The qualitative nature of the correlation is an important limitation, but it does provide for one approach to the complex issue of particle formation in air.

The findings on the roles of different components in the clusters are also of significance. An example is the finding that the presence of MA, an amine that is a weak base, and of a

water molecule can lead to deprotonation of the weak organic acid OxA. Another example is the capability of OxA to stabilize acid−base complexes by forming cyclic structures in which OxA is both a hydrogen bond donor and a hydrogen bond acceptor. In addition, ab initio molecular dynamics simulations show that the effect of temperature on proton transfer is very small. An important merit of the results presented is that these results provide an esay-to-apply predictive tool for the particle growth, for a certain class of systems. One must keep in mind the limitations of the results. Particles are far more complex than small clusters. The physical basis for the role of proton transfer in the clusters is the importance of charge separation and ionic interactions that arise upon pronton transfer. Particles, even when made of the same components, may give rise to other mechanisms. As an example, the water content of particles may differ greatly from the 1:1:1 ratio in the small clusters studied here. Nevertheless, given the correlations observed here between clusters and particles, there is strong motivation to further explore, refine, and extend such observations, to provide additional predictive tools for cluster growth.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b01223.

Methods test for OxA-MA and MSA-MA system; optimized structures and energies of low-lying isomers (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: benny@fh.huji.ac.il.

ORCID ⓘ

Jing Xu: 0000-0001-5558-6908
Barbara J. Finlayson-Pitts: 0000-0003-4650-168X
R. Benny Gerber: 0000-0001-8468-0258

Notes

The authors declare no competing financial interest.

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