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A molecular-scale study on the hydration of sulfuric acid-amide complexes and the atmospheric implication

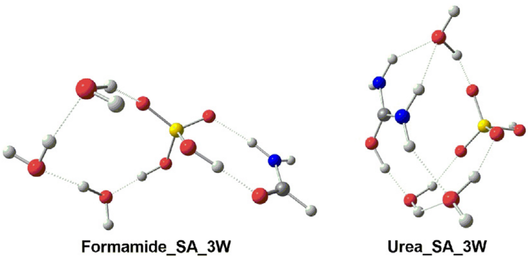
Pu Ge [a], Gen Luo [a], Yi Luo [a, *], Wei Huang [b], Hongbin Xie [c], Jingwen Chen [c]

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*
[b] *School of Environmental Science & Optoelectronic Technology, University of Science and Technology of China, Hefei, Anhui 230026, China*
[c] *Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China*

HIGHLIGHTS

- No proton-transfer to C=O group occurs in formamide clusters.
- High concentration of formamide compensates its unfavorable interaction with SA.
- Proton transfer to water is significant when highly hydrated at low temperature.
- Interaction between SA and C=O group play important role in amide clusters.
- The amine substituent in amides affects the cluster structures and properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Amides are ubiquitous in atmosphere. However, the role of amides in new particle formation (NPF) is poorly understood. Herein, the interaction of urea and formamide with sulfuric acid (SA) and up to four water (W) molecules has been studied at the M06-2X/6-311++G(3df,3pd) level of theory. The structures and properties of (Formamide)(SA)(W)$_n$ ($n = 0$–4) and (Urea)(SA)(W)$_n$ ($n = 0$–4) clusters were investigated. Results show that the interaction of SA with the C=O group of amides plays a more important role in amide clusters compared with the NH_2 group. Proton transfer to water molecule become dominant in highly hydrated amide clusters at lower temperatures. There is no proton transfer to C=O group in formamide clusters. The Rayleigh light scattering intensities of amide clusters are comparable to that of amine and oxalic acid clusters reported previously. Moreover, unhydrated (Amide)(SA) clusters have similar or even higher ability than hydrated SA clusters to participate in ion-induced nucleation. In comparison with formamide, urea has more interacting sites and its clusters have higher Rayleigh light scattering intensities, larger dipole moment, stronger interaction with SA and lower water affinity. The intermolecular interaction in (Formamide)(SA) is slightly weaker than that of SA dimer, which may be compensated by the high concentration of formamide, thus enabling formamide to participate in initial steps of NPF. This study may bring new insight into the role of amides in initial steps of NPF from molecular scale and could help better understand the properties of amide-containing organic aerosol.

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* Corresponding author.
E-mail address: luoyi@dlut.edu.cn (Y. Luo).

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1. Introduction

Aerosols impact climate forcing (Haywood and Boucher, 2000), air quality (Von Schneidemesser et al., 2015) and public health (Dimitriou and Kassomenos, 2017; Saikia et al., 2016). Improving knowledge about the formation process of aerosol particles is necessary to evaluate their effects. A main origin of atmospheric aerosols is new particle formation (NPF) which comprises nucleation process and subsequent growth (Zhang et al., 2011). Sulfuric acid (SA) is a key component in nucleation (Kuang et al., 2008). Besides, the prominent enhancing effect of organics has been proposed (Almeida et al., 2013). Studies show that one SA molecule and one organic molecule could be involved in the rate-limiting step of the nucleation process (Xie et al., 2017a; Metzger et al., 2010). Olenius pointed out that the strong interaction of dimethylamine (DMA) and SA could lead to a barrierless nucleation process by addition of (DMA)(SA) cluster (Olenius et al., 2013). The enhancing ability of organics in NPF could be evaluated by their interaction with SA.

Among the 160 different organic NH_x-containing compounds identified in the atmosphere (Ge et al., 2011), there are about 80 species for which the molecules contain substructures of NH_x ($x = 1, 2$) connecting to π bonds, featuring a p-π conjugate structure (Xie et al., 2017b). Amides could be the most abundant in these p-π conjugate compounds which could reach the few ppbv level in urban Shanghai, China (Yao et al., 2016). The detection of high concentrations of amides in the ambient air urges a complete understanding on their atmospheric sinks. Formamide, as the simplest amide, is a high production volume chemical with an annual global production of several hundred thousand tons (Bunkan et al., 2016). Extensive studies focus on the atmospheric origin of formamide as the major oxidation product of monoethanolamine (MEA) (Xie et al., 2014; Zhu et al., 2013) and methylamine (MA) (Borduas et al., 2016). Besides, the oxidation of formamide has been widely studied to form isocyanic acid (Bunkan et al., 2016; Borduas et al., 2015). Formamide has also been detected in atmospheric particles (Ge et al., 2011). Therefore there is a possible removal of formamide by interaction with SA due to participation in NPF as a sink for formamide. The enhancing ability of amides to NPF has been studied by many researchers. Glasoe pointed out that urea and acetamide have enhancing effect toward nucleation but are much weaker than amines (Glasoe et al., 2015). Recently, Kumar demonstrated that urea could stabilizing SA by forming the strongest clusters compared with nitric acid, methanesulfuric acid and formic acid, thus may play an important role in NPF (Kumar et al., 2018). Besides, Chen suggested that gaseous alkylamides could be uptaken by suspended SA particles and measured their multiphase uptake coefficients (Chen et al., 2017a). However, the role of formamide as potential nucleation stabilizer remains almost unexplored.

In spite of the pioneering work by Kumar, knowledge on the detailed information of proton transfer and the properties of urea clusters is limited. Amine group in urea clusters is not the proton acceptor as in the case of alkylamine (Kumar et al., 2018). The effects of amine group, acting as substituent, on the cluster structures and properties together with the effect on the stabilizing ability of urea towards SA are unexplored, which may enrich the chemistry of amine functional group in NPF. Formamide and urea, differing by an amine substitution, may have different performance on the initial steps of NPF. Besides, by investigating urea and formamide clusters, some distinct characteristics of amide clusters could be elucidated, therefore providing a more comprehensive knowledge on the role of amides in NPF.

In this study, the interaction of formamide and urea with SA has been computationally studied to evaluate the enhancing ability of amides in initial steps of NPF, the characteristics of amide clusters and the effects of amine substitution. In view of that hydration could affect nucleation rates by affecting the mobility, stability and lifetime of clusters (Nadykto et al., 2009) and could promote proton transfer in clusters (Temelso et al., 2012a; Miao et al., 2015), hydration effect was therefore also considered with up to four water (W) molecules (Kumar et al., 2018) to investigate the proton transfer in amide clusters. The structures and properties of $(Urea)(SA)(W)_n$ and $(Formamide)(SA)(W)_n$ $(n = 0–4)$ clusters were presented. Besides, the effects of amine substitution were also discussed.

2. Computational details

In this study, the Global Reaction Route Mapping (GRRM) program (version 14) was used in combination with the Gaussian 09 program package (Frisch et al., 2009) to search for the global minima of $(Urea)(SA)(W)_n$ and $(Formamide)(SA)(W)_n$ $(n = 0–4)$ clusters. The scaled hypersphere search (SHS) method, which is an uphill-walking technique, was utilized to automatically explore the reaction pathway from a given equilibrium structure (EQ) (Maeda and Ohno, 2005; Ohno and Maeda, 2004, 2006). Such an exploration of reaction pathways is executed by detecting and following anharmonic downward distortions (ADDs) (Maeda and Ohno, 2008). This ADD following is a new concept based on a kind of principle that has arisen from deep considerations on the feature of potential energy surface (PES). To effectively detect the ADD, a given EQ-centered hypersphere surface is introduced in the SHS technique. During the reaction pathway following on the scaled hypersphere surface, the conventional optimization scheme and downhill-walking technique may be utilized. By detecting and following all of the ADDs for a given EQ, the SHS method can find transition states, dissociation channels, and other EQs. Such detection and following are automatically done for each newly found EQ via a one-after-another manner. Since the occurrence of a chemical reaction shows an ADD as a symptom and the lowest-energy minimum should not be out of connection with other EQs on the global PES, most of the important EQs at the low-energy region should be found by the SHS method. After the reaction pathways are traced for all the obtained EQs, the global potential energy surface may be figured. As shown in the applications to $(H_2O)_8$ and $H^+(H_2O)_8$, the search for known important structures as well as global potential energy minimum of H-bond clusters has been achieved (Maeda and Ohno, 2007; Luo et al., 2007). Specifically, molecular energy and its gradient (Hessian matrix) were calculated at the HF/6-31G level for efficiency of exploration (Lin et al., 2014). The following conditions were imposed on GRRM calculations: (1) start with 24 randomly created conformations; (2) to accelerate pathway exploration via ADD, the largest ADD (LADD) technique was applied by setting the parameter LADD to be 5; (3) optimize the structure only for EQs and skip the optimization of the transition structures (Omori et al., 2014).

Since over 1000 isomers were obtained for larger clusters, isomers within a certain energy range were selected for optimization. As the cluster systems become larger and the configurations get more complex, the energy difference between the isomers gets smaller due to the flexible hydrogen bond networks, thus an energy range of 4–7 kcal/mol of the global minimum is identified for different sizes of $(Urea)(SA)(W)_n$ and $(Formamide)(SA)(W)_n$ $(n = 0–4)$ clusters. The obtained geometries were re-optimized at the level of M06-2X/6-311++G(3df,3pd) (Zhao and Truhlar, 2007). Frequency calculations were operated for each stationary point to identify the structure is a stable one. Such a method was reported to give reasonable results for similar clusters (Elm et al., 2012; Ge et al., 2018). In order to evaluate the reliability of the M06-2X