Chemosphere 205 (2018) 275–285

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Towards understanding the role of amines in the SO_2 hydration and the contribution of the hydrated product to new particle formation in the Earth's atmosphere

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HIGHLIGHTS

- A new important role of amines in the Earth's atmosphere has been revealed.
- Aliphatic amines substantially reduce the barrier of the SO_2 hydration.
- SO_2 hydration products may contribute to new particle formation.

ARTICLE INFO

Article history:
Received 1 February 2018
Received in revised form
17 April 2018
Accepted 19 April 2018
Available online 21 April 2018

Handling Editor: R. Ebinghaus

Keywords:
Hydration of SO_2
Theoretical calculations
Amines
Hydrated products
New particle formation

ABSTRACT

By theoretical calculations, the gas-phase SO_2 hydration reaction assisted by methylamine (MA) and dimethylamine (DMA) was investigated, and the potential contribution of the hydrated product to new particle formation (NPF) also was evaluated. The results show that the energy barrier for aliphatic amines (MA and DMA) assisted SO_2 hydration reaction is lower than the corresponding that of water and ammonia assisted SO_2 hydration. In these hydration reactions, nearly barrierless reaction (only a barrier of 0.1 kcal mol^{-1}) can be found in the case of $SO_2 + 2H_2O +$ DMA. These lead us to conclude that the SO_2 hydration reaction assisted by MA and DMA is energetically facile. The temporal evolution for hydrated products ($CH_3NH_3^+$-HSO_3^--H_2O or $(CH_3)_2NH_2^+$-HSO_3^--H_2O) in molecular dynamics simulations indicates that these complexes can self-aggregate into bigger clusters and can absorb water and amine molecules, which means that these hydrated products formed by the hydration reaction may serve as a condensation nucleus to initiate the NPF.

1. Introduction

The studies about sulfur dioxide have attracted more attention of atmospheric scientist owing to its important role in atmospheric science. The importance mainly is due to homogeneous and heterogeneous oxidation of sulfur dioxide to sulfuric acid. Homogeneous (gas phase) oxidation of SO_2 primarily starts through the reaction with a hydroxyl radical (Davis et al., 1979; Stockwell and Calvert, 1983; González-García et al., 2009). Heterogeneous oxidation of SO_2 mainly occurs in cloud droplets (Worsnop et al., 1989; Harris et al., 2013). On the other hand, the deposition of SO_2 and other reactions involving SO_2 also is significant because only half of global atmospheric SO_2 is oxidized (Chin et al., 1996). As a non-oxidation reaction, the hydration of SO_2 in the atmosphere can occurs in many cases such as at air-water interfaces (Yang et al., 2002), in cloud droplets (Kahan et al., 2010) and in aerosols (Townsend et al., 2012).

While complexes of SO_2 with H_2O in the gas phase and at air-water interfaces has been studied in some detail in the past (Bishenden and Donaldson, 1998; Loerting and Liedl, 2001; Tarbuck and Richmond, 2005; Hirabayashi et al., 2006; Cukras and Sadlej, 2007; Steudel and Steudel, 2009; Shamay et al., 2013), a straightforward reaction of SO_2 with H_2O to form H_2SO_3 has a barrier of

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https://doi.org/10.1016/j.chemosphere.2018.04.117

greater than 30 kcal mol^{-1} (Loerting and Liedl, 2001; Liu et al., 2015a) and is therefore thermodynamically unfavorable. Although the addition of H_2O molecules helps to lower the reaction barrier, there still exists a barrier of >5 kcal mol^{-1} even if as many as four water molecules are added (Liu et al., 2015a). On the other hand, there also exist some indications that the reaction barrier may be significantly reduced by introducing a catalyst or proton acceptor (e.g. NH_3, H_2SO_4) into $SO_2\cdot(H_2O)_n$ complexes (Liu et al., 2015a, 2015b).

The important role of amines in the atmosphere is closely related to the physical chemistry of H_2SO_4–driven NPF, which is still insufficiently understood. For H_2SO_4, new particles formation cannot be initiated before $[H_2SO_4]$ of ~10^5 cm^{-3} is reached (Nieminen et al., 2009; Zhang et al., 2012). However, the peak atmospheric concentrations of H_2SO_4 of 10^6-10^7 cm^{-3} appear to be too low to explain all the NPF events frequently occurring in the lower troposphere by the binary nucleation of H_2SO_4-H_2O(Sipilä et al., 2010; Kirkby et al., 2011; Zhang et al., 2012). This has led to a conclusion that atmospheric nucleation is multi-components and involves additional stabilizers of embryonic sulfuric acid clusters against evaporation such as ammonia (Kim et al., 1998; Ball et al., 1999; Napari et al., 2002; Merikanto et al., 2007; Kirkby et al., 2011; DePalma et al., 2014), amines (Murphy et al., 2007; Kurtén et al., 2008; Loukonen et al., 2010; Smith et al., 2010; Almeida et al., 2013; Qiu and Zhang, 2013; Nadykto et al., 2015; Elm, 2017; Elm et al., 2017; Kürten et al., 2018), various organic species including highly oxidized organic compounds (Zhang et al., 2004; Nadykto and Yu, 2007; Xu et al., 2010a, 2010b; Bzdek et al., 2014; Riccobono et al., 2014; Bianchi et al., 2016; Tröstl et al., 2016), and ions (Arnold, 1980; Lovejoy et al., 2004; Sorokin and Arnold, 2007; Hirsikko et al., 2011; Kirkby et al., 2016).

Aliphatic amines, alongside with ammonia, are common atmospheric bases, which stabilize binary clusters and enhance NPF under favorable conditions. The important role of amines in NPF has first been pointed out in quantum-chemical studies (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2015; Elm, 2017; Elm et al., 2017), followed by laboratory experiments (Almeida et al., 2013; Qiu and Zhang, 2013; Kürten et al., 2014, 2018; Glasoe et al., 2015), in which their importance for atmospheric nucleation has been reaffirmed. Being organic derivatives of ammonia, DMA and MA have an obvious advantage over NH_3 in enhancing new particle formation (Murphy et al., 2007; Kurtén et al., 2008; Loukonen et al., 2010; Almeida et al., 2013; Qiu and Zhang, 2013; Glasoe et al., 2015; Nadykto et al., 2015), which is partly offset by the $[NH_3]/[amine]$ ratio of 10–100 under typical atmospheric conditions (Ge et al., 2011).

Despite being well-studied, amines have never been considered as a factor of the gas-phase hydration reaction of the sulfur dioxide. In contrast, NH_3 is known to have a fairly large impact on the gas-phase hydration of sulfur dioxide (Liu et al., 2015a), sulfur trioxide (Bandyopadhyay et al., 2017), and nitrogen dioxide (Wang et al., 2016). Since amines are derivatives of ammonia, in which one or more hydrogen atoms are replaced with alkyl or organic functional groups, they may possess stronger proton affinity than ammonia, and, thus, may be actively involved in hydrogen atom transfer (HAT) reactions, as evidenced by the recently study (He et al., 2017) showing that amines have a greater impact on the gas-phase hydration of NO_2 than NH_3.

In this paper, the role of methylamine and dimethylamine in the SO_2 hydration reaction in the Earth's atmosphere has been studied using the quantum chemical theory at CCSD(T)/aug-cc-pVDZ//M06-2X/6-311 + G (d, p) level. The impacts of MA, DMA and NH_3 on the gas-phase hydration of the SO_2 have been investigated, elucidated and discussed. Through temporal evolution, the ability of the SO_2 hydration products to self-aggregate and to capture amine and H_2O molecules has been examined via using molecular dynamics simulations. We show that the presence of DMA and MA is an important factor of the sulfur dioxide hydration, and that the hydration products may contribute to the NPF in the Earth's atmosphere.

2. Computational methods

2.1. *Quantum chemical study*

The DFT methods have been widely used in atmospheric and environmental sciences (Vereecken and Francisco, 2012; Bai et al., 2013; Qu et al., 2017). In this paper, we use M06-2X/6-311 + G (d, p) method to optimize the geometric structures. The ultrafine integration grid is used in the DFT calculation to enhance the accuracy of calculations. To verify the transition states connected with the corresponding reactants and products, the intrinsic reaction coordinate (IRC) in both directions from a saddle point was computed (Fukui, 1981). The single-point energies were refined using the high level ab initio method (III and Bartlett, 1982; Pople et al., 1987; Jr., 1989) at CCSD(T)/aug-cc-pVDZ level. The zero point energies (ZPE) were obtained from M06-2X/6-311 + G (d, p) level. Calculations were carried out using Gaussian 09 suite of programs (Frisch et al., 2010). The geometries were visualized using the CYLview software package (Legault, 2009 (http://www.cylview.org)).

2.2. *Molecular dynamics (MD) simulations*

MD simulations were performed using GROMACS 4.6.7 (Berendsen et al., 1995; Van Der Spoel et al., 2005; Hess et al., 2008) with the general AMBER force field (GAFF)(Wang et al., 2004). Geometry optimization and electrostatic potential (ESP) calculations were performed with the M06-2X/6-311 + G (d, p) level. The restrained electrostatic potential (RESP) charges based on ESP charges were assigned to each atom, which is obtained using the Antechamber module of AmberTools 17 (Case et al., 2017). After the charges were determined, files with the molecular coordinates, topology and forces field parameters from the general AMBER force field (GAFF) were generated by tleap tool of AmberTolols 17. ACPYPE (Sousa da Silva and Vranken, 2012) was used to convert these files to the GROMACS format.

The compositions of the simulated systems consisting of the SO_2 hydration products, amines, H_2O, N_2 and O_2, are shown in Table 1. For comparison, two systems involving unhydrated SO_2, amines (MA or DMA), H_2O, N_2 and O_2 also are simulated in order to illustrate whether SO_2 without hydration can aggregate and absorb amines and water molecules to form bigger clusters. The compositions of the two systems are summarized in Table S1. The initial size of all systems studied here is 20 × 20 × 20 nm^3. After the energy minimization, each system was executed in NVT (298 K) ensemble for 100 ps in order to relax, followed by 20 ns NPT ensemble simulations at 298 K and 1 bar. The velocity rescaling thermostat (Bussi et al., 2007) and Berendsen pressure coupling (Berendsen et al., 1984) were used for the temperature and pressure

Table 1
The component of the simulation system.

System	Type of cluster	$N_{cluster}$	N_{amine}	N_{water}	N_{N2}	N_{O2}
1	$CH_3NH_3^+$-HSO_3^--H_2O	10	0	10	154	41
2	$CH_3NH_3^+$-HSO_3^--H_2O	1	9 CH_3NH_2	19	154	41
3	$(CH_3)_2NH_2^+$-HSO_3^--H_2O	10	0	10	154	41
4	$(CH_3)_2NH_2^+$-HSO_3^--H_2O	1	9 $(CH_3)_2NH$	19	154	41