Chemical Physics 472 (2016) 198–207

Contents lists available at ScienceDirect

Chemical Physics

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

Clustering of amines and hydrazines in atmospheric nucleation

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ARTICLE INFO

Article history:
Received 30 December 2015
In final form 7 April 2016
Available online 13 April 2016

Keywords:
Hydrazine clusters
Molecular complexes
Aerosol nucleation
Hydrogen bond

ABSTRACT

It has been proved that the presence of amines in the atmosphere can enhance aerosol formation. Hydrazine (HD) and its substituted derivatives, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), which are organic derivatives of amine and ammonia, are common trace atmospheric species that may contribute to the growth of nucleation clusters. The structures of the hydrazine and amine clusters containing one or two common nucleation molecules (ammonia, water, methanol and sulfuric acid) have been optimized using density functional theory (DFT) methods. The clusters growth mechanism has been explored from the thermochemistry by calculating the Gibbs free energies of adding an ammonia, water, methanol or sulfuric acid molecule step by step at room temperature, respectively. The results show that hydrazine and its derivatives could enhance heteromolecular homogeneous nucleation in the earth's atmosphere.

1. Introduction

Aerosol particles are known to have a significant influence on global climate change and atmospheric visibility and even human health [1–4]. New particle formation from gas-to-particle conversion represents a major source of atmospheric particles [5]. Better understanding at the molecular level of the mechanism of how new particles nucleate and grow in the atmosphere helps improving atmospheric models and climate prediction [6]. Several mechanisms have been proposed to explain nucleation events, including binary H_2SO_4–H_2O, ternary H_2SO_4–H_2O–NH_3, ion-induced and nucleation enhanced by organic compounds [7]. In aerosol formation, the clusters must cross an energy threshold—the nucleation barrier [8]. When the critical nucleus forms, aerosol growth becomes spontaneous [7,9]. In general, molecular interactions including hydrogen bonding represent the first step in the nucleation process [10].

Sulfuric acid has been identified as the key species in atmospheric particle formation [8,11]. Water is an active nucleation agent involved in the formation of initial clusters. Formation of hygroscopic products can lead to further growth of nanoparticles through the uptake of H_2O. It is commonly accepted that trace atmospheric species besides H_2SO_4 and H_2O are involved in new particle formation in the earth's atmosphere. Quantum chemical investigations predict that clusters containing only sulfuric acid and water cannot grow in the boundary layer [12]. The neutral H_2SO_4–H_2O cluster must be stabilized with ammonia, amines, or organic compounds in order to nucleate [13–16]. Modeling work suggested that almost half of the global cloud condensation nuclei (CCN) in the atmospheric boundary layer may originate from the nucleation of aerosols from trace condensable vapors [17]. Ternary homogeneous nucleation (THN) involving sulfuric acid, water and ammonia have been intensively studied recently [18–23]. The concentrations of NH_3 in the many tens of parts per trillion by volume (pptv) range were observed to dramatically promote the rate of particle nucleation [22]. Methanol is the primary simplest alcohol which has been identified to contribute to heterogeneous reactions in air, with concentration in the 1–20 ppb range in rural areas [7]. Besides interacting with existing aerosol particles, methanol is a good hydrogen bond donor to form hydrogen-bonded complexes in the atmosphere. Methanol–amine complexes as model atmospheric complexes have been frequently studied by vibrational spectroscopy [24,25].

It is commonly recognized that molecular complexes and pre-nucleation clusters are at the initial stage of new particle formation [26]. Common atmospheric sources of ammonia and amines include vegetation, biomass burning, animal farms, cooking, vehicular emissions and various industrial processes [27]. Many theoretical and experimental investigations have focused on the participation of amines in atmospheric nucleation [28,29]. In order to advance the understanding of atmospheric nucleation phenomena, hydrogen-bonded complexes of binary H_2SO_4–H_2O clusters with methyl-, dimethyl- and trimethylamines representing common atmospheric organic species were established by quantum chemical study [29]. Based on experimental and modeling results,

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http://dx.doi.org/10.1016/j.chemphys.2016.04.007

ternary bases such as ammonia and amines, as well as organics enhance the nucleation rates by a factor of 100–1000 in the lower troposphere [30]. Amines have recently been proposed as possible stabilizers of binary pre-nucleation clusters. It has now been demonstrated from modeling of field observations, and from controlled experiments in the CLOUD chamber at CERN, that amines are important in new particle formation through their gas phase acid–base reaction with atmospheric acids (HNO_3, HCl, H_2SO_4) to form the respective ammonium salts [7]. Among amines, dimethylamine (DMA) is the strongest stabilizer [29]. The amine ternary nucleation rates with 5 pptv DMA are enhanced over 1000 times, compared with 250 pptv ammonia according to CLOUD chamber experiments [30], though in general the concentration of amines is 1–2 orders of magnitude lower than that of ammonia in the atmosphere [7]. Erupe et al. reported laboratory observations of the effect of trimethylamine (TMA) on H_2SO_4–H_2O nucleation under aerosol precursor concentrations typically found in the lower troposphere ([H_2SO_4] of 10^6–10^7 cm^{-3}; [TMA] of 180–1350 pptv) [28]. Both amines and NH_3 are important nucleation species, but under dry atmospheric conditions, amines may have stronger effects on nucleation than NH_3 [28].

Hydrazines are derivatives of ammonia or amines with one or more hydrogen atoms replaced by an amino group. In common with amines, the dominate emission source for hydrazines in the atmosphere is anthropogenic activity [31]. Hydrazine (N_2H_4, HD), monomethylhydrazine (CH_3NHNH_2, MMH) and unsymmetrical dimethylhydrazine ($(CH_3)_2NNH_2$, UDMH) form an important group of diamine based rocket propellants. Unburned liquid rocket propellants are often ejected into the tropospheric air and subsequently interact with atmospheric molecules and radicals. They can react with the atmospheric constituents (water, sulfur dioxide, oxygen, ozone, etc.) in the atmosphere environment [32–35]. Computational studies of reactions of hydrazine and its derivatives with atmospheric oxidants such as NO_2, O atom and OH radical have been reported [36–40]. The abstraction of an H atom from CH_3NHNH_2 by NO_2 forms CH_3NNH_2 and nitrous acid (HONO), which undergoes further decomposition and chain reactions to regenerate the OH radical [40,41]. At ambient temperature and pressure, the dominant products of the reactions of NO_2 with cis-/trans-CH_3NHNH and CH_2NHNH_2 radicals would be expected to be HONO with trans-CH_3NNH and CH_2NNH_2 radicals, respectively [36]. The O atom rate coefficients for the reactions with N_2H_4, CH_3NHNH_2 and $(CH_3)_2NNH_2$ at 296 K were measured to be $(0.99 \pm 0.12) \times 10^{-11}$, $(1.60 \pm 0.34) \times 10^{-11}$ and $(2.30 \pm 0.34) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively [33]. The gas phase reaction kinetics of OH radical with N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$ were reported to be $(6.10 \pm 1.00) \times 10^{-11}$, $(6.50 \pm 1.30) \times 10^{-11}$ and $(5.00 \pm 2.00) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively [42]. Besides, the hydrazino group ($-NHNH_2$) is a fairly strong proton acceptor, therefore strong hydrogen bond interactions and proton transfer processes are expected to occur between hydrazines and proper atmospheric molecules [43]. Due to the various possibilities of hydrogen bonding interaction, we predict that hydrazine and its derivatives are likely to play a role in the initial steps of nucleation.

In the present work, density functional theory (DFT) calculations have been performed to elucidate the role of hydrazines in the formation of clusters with common atmospheric nucleation precursors. It has been reported that a cluster containing as few as two sulfuric acid and one or two DMA molecules is already stable against evaporation [44]. We focused on the interactions in the clusters between hydrazines and up to two ammonia, water, methanol and sulfuric acid molecules. The amine–water and amine–sulfuric acid clusters have been reported before, either experimentally or theoretically [29,45]. The structures and thermochemical properties of amine heterodimers and heterotrimers were also calculated for comparison with hydrazines. The implications of the hydrazine clusters in the atmospheric aerosol nucleation have been discussed, which sheds light on the mechanism of the new particle formation (NPF) containing hydrazines in the atmosphere.

2. Computational details

All the calculations were performed using Gaussian 09. Search for the initial geometries of complexes and their monomers was executed by using Becke's three-parameter hybrid functional (B3LYP) in conjunction with the split valence polarized basis set 6-31G(d,p). We further optimized the most stable structures by the B3LYP, M06-2X, ωB97X-D and B3LYP-D3 functionals with the aug-cc-pVTZ basis set on all atoms except for the sulfur atom. To improve the energy convergence, the recommended tight d functions were included for the sulfur atom, namely, aug-cc-pV(T+d)Z [46,47]. The commonly used B3LYP functional demonstrated a very good prediction of geometric parameters [14]. The M06-2X and ωB97X-D functionals have been illustrated to perform well for applications of non-covalent interactions and thermochemistry [25,48]. Combined the dispersion correction with the B3LYP functional, B3LYP-D3 functional was found to be an excellent choice for the geometry and energy prediction [49]. The final geometries and energies at the B3LYP-D3/aug-cc-pVTZ level were obtained and used to investigate the heterodimer and heterotrimer clusters of amines and hydrazines with ammonia, water, methanol and sulfuric acid.

To understand the interaction in the clusters, the binding energies (*BE*) corrected with zero point vibrational energies (ZPVE), enthalpies ($\Delta H^0_{298\ K}$) and Gibbs free energies ($\Delta G^0_{298\ K}$) of stepwise accretion of ammonia, water, methanol and sulfuric acid molecules were calculated. The complexation energy has been calculated as $BE = E(A\cdots B) - E(A) - E(B)$, without correction for basis set superposition error (BSSE). The typical counterpoise (CP) correction may exaggerate basis-set related errors for large basis set like aug-cc-pVTZ [50,51].

3. Results and discussion

3.1. Geometrical analysis

The geometries of heterodimer and heterotrimer clusters of the amines and hydrazines with ammonia, water, methanol and sulfuric acid were optimized with the B3LYP, ωB97X-D, M06-2X and B3LYP-D3 methods. The optimized structures of the most stable clusters at the B3LYP/aug-cc-pVTZ level are shown in Figs. 1–8. Other stable structures of the clusters are given in the Supplementary data. Methylhydrazine (MMH) has been determined to have both inner and outer *skew* rotamers by microwave spectrum, infrared and Raman investigations [52,53]. As shown in Fig. S1, the terms "inner" and "outer" indicate the position of the methyl group. In the outer form, the methyl group is located farthest from the hydrogen atoms of the amino group. The other *skew* configuration is known as the inner form.

3.1.1. Heterodimers

The structures and binding patterns of the ammonia and amine-containing clusters are quite similar. Due to the existence of the $-NHNH_2$ group, hydrazine heterodimer with one ammonia molecule formed a five-membered ring via two N–H···N bonds. Fig. 1 illustrates the difference between the structures of amine and hydrazine heterodimer with ammonia. For the MMH–NH_3 complexes, the inner and outer *skew* rotamers of MMH form different conformers. In the inner conformation, the N–H bond adjacent to