Chemical Physics Letters 706 (2018) 175–181

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Clustering of highly oxidized organic acid with atmospheric NO_3^- and HSO_4^- ions and neutral species: Thermochemistry and implications to new particle formation

Alexey B. Nadykto [a,b,c,*], Jason Herb [a], Fangqun Yu [a], Kirill M. Nazarenko [b]

[a] Atmospheric Science Research Center, State University of New York at Albany, 251 Fuller Road, Albany, NY 12203, USA
[b] Department of Applied Mathematics, Moscow State University of Technology “Stankin”, 1a Vadkovsky ln., Moscow, Russia
[c] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Department of General Physics, Kashirskoe shosse 31, Moscow 115409, Russian Federation

ARTICLE INFO

Article history:
Received 24 January 2018
In final form 30 May 2018
Available online 31 May 2018

Keywords:
New particle formation
Highly oxidized molecules (HOM)
Nucleation thermochemistry
Organonitrates
H_2SO_4
Aliphatic amines
Atmospheric nucleation
Hydrogen bonding clusters
Density Functional Theory

ABSTRACT

Molecular clusters containing the selected highly oxidized molecule (HOM) $C_{10}H_{14}O_7$, 2-Methyl-5-[(1S, 2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid, and common trace neutral and ionic atmospheric species, such as H_2SO_4, NH_3, H_2O, methylamine and dimethylamine molecules and airborne HSO_4^- and NO_3^- ions, have been investigated using the Density Functional Theory. Optimization of geometries have been conducted at PW91PW91 level using 6-311++G(3df,3pd) basis set. The results have been discussed in terms of structural, energetic, and atmospheric perspectives. It is shown that the $C_{10}H_{14}O_7$ may impact new particle formation by forming stable hydrogen-bonded clusters with ionic and neutral species such as strongly bonded HOM-NO_3^- organonitrates (ONs) and HOM-HSO_4^- complexes and, possibly, HOMH_2SO_4-amine clusters.

1. Introduction

Both neutrals and ions may impact the New Particle Formation (NPF), which in turn controls concentrations of cloud condensation nuclei (CCN) and strongly affects the Earth’s climate and the air quality [1–7]. The origin, charge state and chemical composition of newly born aerosol nanoparticles and rates, at which they are nucleating in the Earth’s atmosphere are a subject of long-going debates and one of the main sources of uncertainties in assessing the global climate change [8–11].

A number of neutral species, including ammonia [9,12–14], amines [15–23], organic acids [24–29] and HOMs [10,11,30–35] may play a role in enhancing the binary nucleation of H_2SO_4 and H_2O (BHN) [36,37]. The impact of common organic acids on BHN was pointed out first by Zhang et al. [24] and later confirmed in [25–29]. Aliphatic amines, organic derivatives of ammonia produced by a number of biogenic and anthropogenic sources, were considered to be the strongest enhancers of the BHN up until now [17–23].

Rates, at which multicomponent pre-nucleation clusters and nucleating particles are produced in the Earth’s atmosphere, are controlled by two key factors, Gibbs free energies of cluster formation and concentrations of nucleating vapors. Sulfuric acid, whose concentrations in the atmosphere vary from $\sim 10^6$ to 10^8 cm^{-3} (0.04–3.7 pptv) is the key atmospheric nucleation precursor, while ammonia, methylamine and dimethylamine are the strongest bases/stabilizers of binary clusters that are present in the atmosphere in significant concentrations. In particular, atmospheric concentrations of ammonia and amines are in the range from <0.1 to several tens ppbv and from <0.1 to several tens pptv, respectively [11,18]. The impacts of the difference in atmospheric concentrations of principle stabilizers of binary sulfuric acid-water clusters on multicomponent atmospheric nucleation rates have been discussed in some detail in the past [16–19]. In particular, it has been shown that the advantage in the thermodynamic stability of ternary clusters containing methylamine or dimethylamine over those containing ammonia may be offset by much higher atmospheric concentration of ammonia [16,18,19]. For example, the recent work [19] demonstrates that a ratio of

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[*] Corresponding author at: Atmospheric Science Research Center, State University of New York at Albany, 251 Fuller Road, Albany, NY 12203, USA.
E-mail address: anadykto@gmail.com (A.B. Nadykto).

https://doi.org/10.1016/j.cplett.2018.05.080
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atmospheric concentrations of ammonia and amines $\frac{[\text{Amines}]}{[\text{Ammonia}]} > 0.001$ is needed in order for amines to dominate ternary homogeneous nucleation in the Earth's troposphere.

More recently, it was proposed that highly oxidized molecules (HOMs) play, alongside with H_2SO_4, an important role in NPFs [10,11,30–35]. For example, a large source of low-volatility secondary organic aerosol (SOA) produced during the ozonolysis of α-pinene and other endocyclic monoterpenes was reported by Ehn et al. [30] based on data recorded on SMEAR II -station in Hyytiälä, Finland. The most abundant ozonolysis products of typical concentrations of 10^6–10^7 cm^{-3} in there were found to be $C_{10}H_{14}O_7$, $C_{10}H_{14}O_9$, $C_{10}H_{16}O_9$ and $C_{10}H_{14}O_{11}$. Laboratory chamber study of Schobesberger et al. [10] indicates that HOMs such as monoterpenes' oxidation products can cluster with the sulfuric acid and growth further to large sizes. The recent laboratory experiment of Riccobono et al. [31] reveals "a nucleation mechanism involving the formation of clusters containing sulfuric acid and oxidized organic molecules from the very first step." However, the high frequency of NPFs observed in the spring and much less frequent or even absent nucleation events in the summer over forest areas indicate that a dominant role in the NPFs is more than likely played by H_2SO_4 due to HOM concentrations being much higher in the summer than in spring [5]. It is quite clear that HOMs can stabilize binary of H_2SO_4 - H_2O clusters under laboratory conditions [31]; however, their influence on BHN under typical atmospheric conditions, where HOMs, H_2SO_4 and H_2O coexist with other neutral and ionic species, is yet to be fully understood.

Ions, which are produced mainly by radon decay, gamma radiation, and cosmic radiation [38,39], are present in the atmosphere in concentrations ranging from $\sim 10^2$ to $\sim 5 \times 10^3$ cm^{-3} [40–42]. Primary ions (singly charged positive ions, including H_3O^+, N_2^+ and O_2^+, and free electrons), which are produced via ionization of air molecules, transform into small ions within less than a second [42]. The relevance of negative airborne ions to new particle formation is well-established, and HSO_4^- and NO_3^- are common airborne ions actively participating in NPF in the Earth's troposphere [31–33,42–44]. Typically, ionic species have great growth advantage over neutrals [45–48]. Airborne ions enhance the NPFs via the Ion Mediated Nucleation (IMN) involving H_2SO_4 and H_2O, other neutral species and ions [45,46]. Ions were shown to strongly enhance BHN and ternary nucleation of sulfuric acid, ammonia and H_2O (THN) [9,11,49,50] while playing a smaller role in nucleation of amines. The impact of ions on nucleation of HOMs remains controversial. Kirkby et al. [11] claim that ions strongly enhance unary nucleation of pure organic species in the absence of H_2SO_4, while Bianchi et al. [32] observed only a weak enhancement in NPFs involving HOMs in the free troposphere. Naturally charged HOMs ($C_{10}H_{14}O_7$, $C_{10}H_{16}O_7$, $C_{10}H_{14}O_8$ $C_{10}H_{16}O_8$, $C_{10}H_{16}O_9$, $C_{14}H_{14}O_7$, $C_{10}H_{16}O_{10}$, $C_{10}H_{14}O_{11}$ and $C_{10}H_{15}O_9$ of unknown chemical identity) observed [33] during the day were bonded to nitrate (NO_3-) or bisulfate (HSO_4-) ions, forming organonitrates (ONs) or HSO_4- HOM, respectively, with ONs being predominant. At night, the HOM ions were mainly composed of HOMs clustered with NO_3^-.

In the present work, clustering of the selected $C_{10}H_{14}O_7$ HOM, 2-Methyl-5-[(1S,2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid, with the common atmospheric neutral and ionic nucleation agents has been investigated. The formation of mono-and heteromolecular dimers and trimers consisting of $C_{10}H_{14}O_7$, H_2SO_4, H_2O and common neutral (ammonia (NH_3), methylamine (MA) and dimethylamine (DMA)) and ionic (HSO_4^- and NO_3^-) trace species has been studied using the Density Functional Theory. A comprehensive analysis of structural and thermodynamic properties of clusters being investigated has been performed and atmospheric implications of the obtained results have been discussed.

2. Methods

In the present work, the PW91PW91/6-311++G(3df,3pd) method that predicts geometries, vibrational spectrums, dipolar properties and thermodynamics of clusters consisting of atmospherically-relevant species in a very good agreement with experiments and higher level *ab intio* data [17,51–56], has been applied. This method is particularly known for accurately predicting cluster formation free energies, which control the thermodynamic stability of nucleating clusters and, alongside with gas-phase concentrations of reactants, cluster number concentrations under atmospheric conditions. We have carried out a comprehensive conformational search using the basin hopping algorithm, as implemented in Biovia Materials Studio 8.0 [57] and our own "search machine" , which is based on the mesh created around clusters, with molecules to be attached to the cluster placed in the mesh nodes, and blind search algorithm. The geometry optimization was a three –stage process: preliminary optimization of the guess/generated geometries by semi-empirical PM3 method and selection of isomers located within 15 kcal mol^{-1} of the Gibbs free energy for the current global minimum to proceed to the second stage, where they were optimized with PW91PW91/CBSB7 method. Finally, the most stable isomers differing from the current global minimum by less than 5 kcal mol^{-1} were optimized using PW91PW91/6-311++G(3df,3pd) method. Computations were carried out using the Gaussian 09 suite of programs [58]. The 2-Methyl-5-[(1S,2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid has been chosen out of a number of $C_{10}H_{14}O_7$ species of known geometries based on the preliminary assessment of the stability of heteromolecular different $C_{10}H_{14}O_7$ -H_2SO_4 dimers using a sequence of the PM3 and PW91PW91/6-31+G* methods. A complete set of Cartesian geometries of global minima and local minima located within 3 kcal mol^{-1} of the global minima are shown in the Supplementary Materials.

3. Results and discussion

Fig. 1 presents the equilibrium geometries of the most stable isomers of heteromolecular dimers and trimers composed of 2-Methyl-5-[(1S,2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid and trace atmospheric species represented by the sulfuric acid H_2SO_4, ammonia NH_3, methylamine (CH_3NH_2), dimethylamine ($(CH_3)_2NH$) and H_2O. Eight equilibrium isomers of 2-Methyl-5-[(1S,2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid have been identified within 10 kcal mol^{-1} from the global minimum. The global minimum is shown in Fig. 1, while other equilibrium isomers are given in Fig. S1. Variations in C—C, C—O, C—H and O—H bonding lengths from one isomer to the other are small and range from a fraction of percent to less than 2% in all the cases studied here. Nonetheless, the Gibbs free energy of the isomers differ by up to 7.98 kcal mol^{-1} due to the different orientation of CH_3, OCOH, CH_2OH, COH and CH groups with the respect to C_4O ring.

As seen from Fig. 1, all the most stable heteromolecular dimers of ($C_{10}H_{14}O_7$) with neutral atmospheric species such as H_2SO_4, NH_3, CH_3NH_2, $(CH_3)_2NH$ and H_2O dimers are linear chains. In contrast, the pure ($C_{10}H_{14}O_7$) dimer has closed cyclic form. The trimers $(C_{10}H_{14}O_7)(H_2SO_4)(CH_3NH_2)$, $(C_{10}H_{14}O_7)(H_2SO_4)((CH_3)_2NH)$ and $(C_{10}H_{14}O_7)_2(H_2SO_4)$ are deformed linear chains, while both $(C_{10}H_{14}O_7)(H_2SO_4)(NH_3)$ and $(C_{10}H_{14}O_7)(H_2SO_4)(H_2O)$ clusters contain cyclic structures. The formation of neutral heteromolecular dimers and trimers is not accompanied by proton transfer, with the exception of $(C_{10}H_{14}O_7)(H_2SO_4)(CH_3NH_2)$, $(C_{10}H_{14}O_7)(H_2SO_4)((CH_3)_2NH)$ and $(C_{10}H_{14}O_7)(H_2SO_4)(NH_3)$ clusters, where a single hydrogen atom was transferred from H_2SO_4 to base molecules