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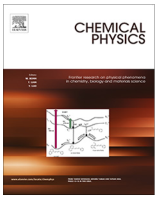

An investigation about the structures, thermodynamics and kinetics of the formic acid involved molecular clusters

Rui Zhang [a], Shuai Jiang [b], Yi-Rong Liu [b], Hui Wen [c], Ya-Juan Feng [b], Teng Huang [c], Wei Huang [b,c,*]

[a] School of Electronics and Information Engineering, Anhui Jianzhu University, Hefei, Anhui 230601, China
[b] School of Information Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China
[c] Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

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ABSTRACT

Despite the very important role of atmospheric aerosol nucleation in climate change and air quality, the detailed aerosol nucleation mechanism is still unclear. Here we investigated the formic acid (FA) involved multicomponent nucleation molecular clusters including sulfuric acid (SA), dimethylamine (DMA) and water (W) through a quantum chemical method. The thermodynamics and kinetics analysis was based on the global minima given by Basin-Hopping (BH) algorithm coupled with Density Functional Theory (DFT) and subsequent benchmarked calculations. Then the interaction analysis based on ElectroStatic Potential (ESP), Topological and Atomic Charges analysis was made to characterize the binding features of the clusters. The results show that FA binds weakly with the other molecules in the cluster while W binds more weakly. Further kinetic analysis about the time evolution of the clusters show that even though the formic acid's weak interaction with other nucleation precursors, its effect on sulfuric acid dimer steady state concentration cannot be neglected due to its high concentration in the atmosphere.

1. Introduction

Atmosphere new particle formation has attracted lots of research for decades as they can influence the radiative forcing, climate change and human health significantly. New particle formation could be regarded as two distinct stages: nucleation and subsequent growth [1]. Mostly, the free energy barrier needs to be overcome for nucleation while the Kelvin barrier needs to be surmounted for growth [2–4]. According to Intergovernmental Panel on Climate Change (IPCC) 2013, the aerosol effects (direct & indirect) on climate change have been the largest uncertainty. Recent simulation studies [5–7] indicate that aerosol nucleation appears to dominate the total particle number concentration in many parts of the troposphere. However, the detailed aerosol nucleation mechanism is still mysterious even though many advances have been achieved in the recent years [8–13].

In 2007, Kurtén et al. [14] and Nadykto et al. [15] independently reviewed the advances obtained at that time for aerosol nucleation molecular clusters studies and pointed out the significance of applying quantum chemistry into atmospheric aerosol nucleation area. From then on, till today, a large amount of quantum chemical calculations papers have been published focusing on various systems including sulfuric acid, ammonia [16], amines [17], organic acid [18–21] and organics oxidation products [22], especially focusing on their thermodynamics. Very recently, the kinetic studies about them have got lots of attention due to their excellent agreement between theoretical values and the experimental ones [23]. The kinetics studies could be tracked back to the 90's, however, the recent advances derived from the coupling between quantum chemistry based thermodynamic data and the kinetic birth-death equations [24].

In this study, one of the most popular organic acid in the atmosphere, formic acid (FA) interacting with the other common aerosol nucleation precursors including sulfuric acid (SA), dimethylamine (DMA) and water (W) was investigated. First, the quantum chemical method was benchmarked. Then after obtaining the global minima, their binding features were given with the aid of ElectroStatic Potential (ESP) analysis. Then the interaction analysis was made based on the analysis of topology and atomic charges. Finally, the thermodynamics and kinetics were analyzed to investigate the relation between Gibbs free energy change and evaporation rates as well as the effect of formic acid on the steady state concentration of sulfuric acid dimer.

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* Corresponding author at: School of Information Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China.
E-mail address: huangwei6@ustc.edu.cn (W. Huang).

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2. Methodology

2.1. Global minima search: Basin-Hopping (BH) algorithm coupled with Density Functional Theory (DFT)

The global minima of $(FA)_m(SA)_n(DMA)_p$ (m = 0–2, n = 0–2, p = 0–2), $(FA)_1(W)_1$ and $(FA)_1(SA)_1(DMA)_1(W)_n$ (n = 1–3) were searched by BH algorithm coupled with DFT implemented in Dmol^3 [25] except that the structures of $(SA)_1(W)_1$ and $(SA)_2$ were from the literature [34] calculated under the same combination of method and basis set with the same accuracy. In previous studies, this BH algorithm coupled with DFT method has been successfully applied to atmospheric relevant molecular clusters [26–29]. The number of BH searches ranged from 2 to 5 according to the cluster size. Every search was performed with 1000 Monte Carlo (MC) steps at 2000 K with randomly generated initial structures. The temperature was a crucial parameter in BH, which should be chosen carefully because it affected the tradeoff between the acceptance ratio and the sampling efficiency. At each MC step, all of the molecules were translated and rotated, and the maximum translational and rotational displacements were 2 Å and π/2, respectively. To prevent the divergence of the clusters, we compiled a function to check whether the intermolecular distances exceeded the range defined after the structure perturbation caused by the MC sampling. After each MC step, this function automatically determined whether the molecule moved more than 5 Å, which could cause the optimization to fail. If a large divergence occurred, then this function automatically moved the molecules closer together. The atoms in different molecules were not permitted to be closer than 2 Å to prevent the self-consistent field (SCF) calculation from failing to converge.

In Dmol^3 [25], there were two steps in the optimization procedure: the first optimization step was at the PW91/DND level, and the second optimization step was at the PW91/DNP level. Next, these twice-optimized structures were optimized again using the Gaussian09 suite of programs [30] at the level of PW91PW91/6-311++G(3df,3pd). The default convergence criteria were defined in the Gaussian09 suite of programs [30]. Harmonic vibrational frequency analysis was performed to verify that no imaginary frequencies were present and consequently, the structure of interest represented a local or a global minimum on the potential energy surface.

2.2. Thermodynamics calculations: benchmark work for quantum chemistry method

One of the most important thermodynamic parameter for the aerosol nucleation molecular clusters is the Gibbs free energy change, ΔG. To obtain this, the method and basis set combination must be chosen wisely.

The Pople basis set 6-311++G(3df,3pd) is sufficient to produce converged structures, and the aug-cc-pV(T + d)Z basis set is generally not an improvement in nucleation clusters [31]. Based on several recent benchmark studies about nucleation clusters, we chose the most accurate density functionals (M06-2X, PW91PW91, ωB97X-D) in geometry optimization and subsequent frequency calculations procedure to obtain the Gibbs free energy change for the comparison between each other to confirm their accuracy and consistency. For comparison, B3LYP was added, too. This strategy was very similar to that in the recently published article about pinic acid binding with sulfuric acid [32] except with B3LYP added in this work. From Table 1, we could conclude that M06-2X, PW91PW91, ωB97X-D have showed very good consistency within 0.82 kcal/mol difference while B3LYP significantly overestimate the Gibbs free energy change of all the three reactions. So based on these benchmark results and the largest popularity of PW91PW91 functional in estimating the structures, vibrational frequencies and thermodynamics of nucleation clusters, we finally utilized PW91PW91/6-311++G(3df,3pd) to make the final geometry optimization and frequency calculations.

2.3. Kinetic calculations: collision rate constant and evaporation rate

The Gibbs free energy change mentioned above is an important parameter to indicate whether the clustering process is spontaneous or not. To further check the stability of molecular clusters, the properties including the mass and radius of clusters are fed into the collision rate constant calculations. In addition, the evaporation rate would be derived from the detailed balance with the collision rate constant and the Gibbs free energy change involved. The collision rate constant is normally calculated from the gas kinetic theory [33]:

$$\beta_{ij} = \left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6k_bT}{m_i}+\frac{6k_bT}{m_j}\right)^{1/2}\left(V_i^{1/3}+V_j^{1/3}\right)^2 \tag{1}$$

$$\gamma_{(i+j)\to i} = \beta_{ij}\frac{P_0}{k_bT}\exp\left(\frac{\Delta G_{i+j}-\Delta G_i-\Delta G_j}{k_bT}\right) \tag{2}$$

where β and γ is collision rate constant (unit: $m^3\ s^{-1}$) and evaporate rate (unit: s^{-1}) respectively, i and j is the collision cluster, k_b is Boltzmann constant (unit: J/K), T is temperature (unit: Kelvin), m is mass (unit: kg), V is volume (unit: m^3), P_0 is pressure in STP (standard temperature and pressure, T = 298.15 K and P = 1 atm) conditions, ΔG is the Gibbs free energy change derived from quantum chemistry calculations.

The birth-death equations represent the time evolution of cluster with each size including the collision and evaporation processes [24]:

$$\frac{dc_i}{dt}=\frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}c_jc_{i-j}+\sum_{j}\gamma_{(i+j)\to i}c_{i+j}-\sum_{j}\beta_{i,j}c_ic_j-\frac{1}{2}\sum_{j<i}\gamma_{i\to j}c_i-CoagS \tag{3}$$

where c represents concentration (m^{-3}), t is the simulation time (s), β, γ, i and j are the same symbols as those in Eqs. (1) and (2), CoagS is the coagulation sink (s^{-1}). The steady state is reached when the Ordinary Differential Equations (ODEs) are solved in convergence and the simulation time is long enough that the cluster concentration in each size changes no more.

3. Results and discussion

3.1. The global minima of the investigated clusters

Interesting binding features could be seen from the global minima of FA-involved clusters given in Fig. 1. For $(FA)_1(W)_1$ cluster, structures of FA and W both are planar, however, the cluster is not planar with a dihedral angle of 114 degree. Moreover, FA forms a cycle structure with SA with hydrogen atom in the hydroxyl in each molecule being the proton donor. Since there is only one amino group in DMA, the FA naturally becomes the proton donor molecule, but the stronger acidity of SA comparing with that of FA, in $(FA)_1(SA)_1(DMA)_1$ cluster, SA turns to be the proton donor with binding with DMA directly and FA binds with SA and DMA. However, in the hydrate cluster, FA only binds with SA while W and SA bind with DMA directly. And since all the strong binding groups including hydroxyl group in acid and amino group in DMA are occupied in $(FA)_1(SA)_1(DMA)_1(W)_1$, few room left for the binding of more water molecules, resulting in the very weak Gibbs free energy change of $(FA)_1(SA)_1(DMA)_1(W)_2$ and