Quantum chemical studies on peroxodisulfuric acid–sulfuric acid–water clusters

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A B S T R A C T

We have applied a multistep quantum chemistry method to study the formation energetics and binding patterns of sulfuric acid–peroxodisulfuric acid–water clusters, with special focus on the O–O bridge. The length of the O–O bridge correlates linearly with the average length of S–O bonds next to it. The clustering of peroxodisulfuric acid with sulfuric acid and water is thermodynamically favorable, as is the replacement by peroxodisulfuric acid of one (but only one) of the sulfuric acid molecules in a sulfuric acid–water cluster. However, the presence of $H_2S_2O_8$ does not enhance the addition of sulfuric acid to the clusters.

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1. Introduction

The sulfur cycle is one of the most important geochemical processes in the Earth's atmosphere. In addition to affecting human and ecosystem health, sulfur compounds have a central role in the formation of both primary and secondary aerosol particles, some of which act as cloud condensation nuclei, modifying the Earth's radiative balance. The effect of the increase in atmospheric aerosol particles is estimated to be the single greatest source of uncertainty in the global estimates of anthropogenic radiative forcing [1].

The most important sulfur-containing aerosol precursor gas is sulfur dioxide, SO_2, which is produced from combustion processes, volcanoes and the oxidation of organic (mostly biogenic) sulfur compounds. In the gas phase, SO_2 is oxidized to sulfuric acid, H_2SO_4, via a series of reactions initiated by the OH radical [2]:

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad (a)$$

$$HSO_3 + O_2 \rightarrow HSO_5 \qquad (b)$$

$$HSO_5 \rightarrow SO_3 + HO_2 \qquad (c)$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \qquad (d)$$

where M is a catalyst. In the liquid phase (e.g. inside cloud droplets), several other oxidation pathways exist [2]. Alternative oxidation pathways have been proposed also for the gas phase, but so far their atmospheric relevance is unknown. Sulfuric acid formed in reaction (d) is thought to be the single most important molecule for new-particle formation in the Earth's atmosphere (e.g. Kulmala et al. [3] or Faloona [4]), though other compounds such as water and base molecules are also believed to play a role [5–7]

A few years ago, experimental measurements [8,9] on new-particle formation from H_2SO_4 vapor produced in different ways gave reason to expect that other sulfur-containing compounds are also involved in the nucleation process. Specifically, the threshold concentration of H_2SO_4 required for nucleation was measured to be 1–3 orders of magnitude lower if H_2SO_4 was produced in situ via SO_2 oxidation, compared to the case where H_2SO_4 was taken from liquid sample. This observation motivated a number of studies [10–13] on alternative nucleation pathways in the sulfur–oxygen–hydrogen system. These included both alternative oxidation mechanisms for SO_2, as well as the co-nucleation of sulfuric acid with other sulfur–oxygen–hydrogen compounds. In our previous study [11], we were able to rule out any direct enhancement of sulfuric acid nucleation by several sulfur–oxygen–hydrogen compounds such as H_2SO_5 or HSO_3. The only sulfur–oxygen–hydrogen compound able to bind more strongly to H_2SO_4 than another H_2SO_4 molecule was peroxodisulfuric acid, $H_2S_2O_8$. As the lifetime of HSO_3 is very short due to the high rate of reaction (b), and the high concentration of molecular oxygen,

the formation of this peroxo acid would most likely involve reactions of HSO_5. For example, self-reaction of HSO_5 would produce $H_2S_2O_8$ plus an oxygen molecule:

$$HSO_5 + HSO_5 \rightarrow H_2S_2O_8 + O_2 \qquad \text{(e)}$$

Though these types of reactions have been proposed already in the 1980s by Friend et al. [14], experimental, or even computational data, on their rates or yields are nonexistent. Partial support for the possible existence of alternative HSO_5 reaction products was given by Kurtén et al. [15], who found, based on computational results, that the lifetime of HSO_5 with respect to dissociation into SO_3 and HO_2 (Reaction (c)) is significantly increased by hydration.

Unfortunately for this line of study, recent reanalysis of the experimental data [16] has resolved the previous experimental discrepancy between experiments with different H_2SO_4 production mechanism without need to invoke the participation of either alternative H_2SO_4 formation pathways, or alternative sulfur-containing compounds. The earlier laboratory experiments have been affected the by size–sensitivity of the counting efficiency of particle detectors and the dependence of H_2SO_4 production and loss mechanisms on the SO_2 and H_2SO_4 concentration profiles. Although sulfur–oxygen–hydrogen compounds other than H_2SO_4 are thus no longer needed to explain the experimental data, kinetic modeling [15] still indicates that they may be formed in at least moderate amounts. Also, very recent ambient ion concentration measurements by Ehn et al. [17] demonstrate the presence in the atmosphere of a large variety of sulfur–oxygen–hydrogen species in addition to H_2SO_4 and its clusters. For example, the SO_5^- ion, possibly formed by proton loss from HSO_5, was detected at concentrations around one-fifth of the dominant ion HSO_4^-. This implies that bimolecular reactions involving HSO_5 may have non-negligible yields in the atmosphere. $HS_2O_8^-$ ions, with an integer mass of 193 a.m.u., were not identified in the study by Ehn et al. [17]. This may be due to a lower proton affinity (relative to HSO_4^-.), low concentrations, or a combination of both. On the other hand, the region of the mass spectrum just below 200 a.m.u contained several as yet unidentified low-intensity peaks, so the presence of low to moderate concentrations of $H_2S_2O_8$ cannot be ruled out by their data.

In addition to their possible – albeit likely minor - role in sulfuric acid – dominated nucleation, $H_2S_2O_8$ and its clusters are also an interesting study object in their own right. The nature and behavior or S–O–O bonds are of central interest in understanding the atmospheric sulfur cycle. S–O–O bonds are found in reaction intermediates of the SO_2 + OH oxidation chain shown above, as well as in other, more hypothetical, SO_2 oxidation pathways. These include the reactions of SO_2 with peroxo radicals [2,18] or Criegee intermediates [2,19]. Recently, experimental evidence of the existence of a peroxo isomer of the sulfate radical anion (SO_4^-) has been presented by Zama et al. [20]. In addition to understand the characteristics of S–O–O bonds in isolated molecules, the effect of clustering on the bond properties is also likely to be important for atmospheric chemistry, as indicated e.g. by the recent evidence for the catalytic effect of water clustering on atmospheric reactions of sulfur-containing compounds (see e.g. Jørgensen and Kjaergaard [21]).

Peroxodisulfuric acid, a peroxo acid containing a S–O–O–S bridge structure, presents a unique opportunity to study S–O–O bonds as it is, compared to the abovementioned reaction intermediates, fairly stable and long-lived. In this study, we have investigated H_2SO_4–$H_2S_2O_8$–H_2O clusters computationally, with specific focus on the properties of the S–O–O bonds, and the effect of clustering on the S–O–O–S bridge. We hope that our computational data will eventually be complemented by experimental data to increase our understanding of sulfur–oxygen bonding in the atmosphere.

2. Methods

Calculations on clusters have been performed using a systematic multi-step approach recently developed by our group. This method is described elsewhere [22,23] so only the relevant details are given here.

The initial molecule and cluster geometries were taken from earlier computational studies [22,11] when possible, or generated with the DL_POLY_2 [24] molecular dynamics (MD) program. We used both intact sulfuric acid molecules and the bisulfate - hydronium ion pair in our simple MD annealing. The details of the force-field construction and annealing procedure used to generate input structures are identical to those used by Loukonen et al. [5] and force field parameters for $H_2S_2O_8$ are given in the supplementary material.

The set of reasonable cluster structures obtained from the MD annealing were optimized using the SIESTA program [25]. The gradient-corrected BLYP functional [26] and the double-ζ polarized (DZP) functions were used.

Finally, we calculated single point energies using the Turbomole program suite [27]. Energies were computed at the RI-MP2/aug-cc-pV(T + d)Z level. Single-point calculations on the $(H_2SO_4)\cdot(H_2O)$ cluster in an earlier study [28] shows that second order Møller–Plesset perturbation theory [29] MP2 calculations reproduce well the higher level (CCSD(T)) energies, which are computationally too demanding to calculate for our fairly large clusters. The resolution of identity (RI) approximation Møller–Plesset perturbation theory (RI-MP2) produces binding energies that are essentially identical to normal MP2 [30,31]. The aug-cc-pV(T + d)Z basis set is identical to aug-cc-pVTZ for hydrogen, oxygen and nitrogen atoms, and contains one extra set of d-orbitals for the sulfur atoms [32]. The choice of basis set was based on previous results [33] which indicate that basis-set effects beyond the aug-cc-pV(T + d)Z level are, at least with the MP2 method, too small (under 0.5 kcal/mol in terms of binding energy per molecule) to justify the computational effort of using e.g. a quadruple-zeta-basis.

To obtain a more realistic picture of the stability of clusters in the atmosphere, we also need to consider the free energies. Thermal contributions to enthalpies and entropies and the free energies were computed using ideal gas, rigid rotor and harmonic oscillator approximations. Vibrational harmonic frequencies were calculated using SIESTA (BLYP/DZP). Gibbs formation free energy ΔG is calculated at standard conditions: reference pressure $p = 1$ atm and $T = 298$ K.

We used Quantum Theory – Atoms-in-Molecules (QTAIM) based methods to study the O–O-bridge in the peroxodisulfuric acid molecules. The analyzed electron density distribution provides information about the bonds between atoms. The variables used to describe the bond strength are the bond length, and the electron density at the bond critical point (BCP). The bond path is the line of maximum electron density between nuclei and the BCP corresponds to the minimum value of the density along this line [34]. We carried out the QTAIM-analysis using the AIM2000 program [35].

The level of the wave function calculations used for the QTAIM analysis was B3LYP/6-31+g(d) [36–38], and the wave functions were generated using the Gausian 03 program suite [39]. The same computational level was used to calculate atomic charges from electrostatic potentials using a grid-based method by Breneman and Wiberg [40]. This method is commonly used to create input charges for molecular mechanics calculations. The cluster structures studied are shown in Figs. 1–3. The clusters have been drawn using the MOLEKEL 4.3.linux visualization package [41]. Bonds are depicted as single or double in Figs. 1–3 based on the default values of the bond lengths in the MOLEKEL program. The sulfur atoms are depicted in yellow, oxygen atoms in red and hydrogen atoms in white. The hydrogen bonds are indicated with dotted lines.