

Computational approach for studying the participation of ketodiperoxy acids in atmospheric new particle formation

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The formation and early growth of atmospheric aerosols are currently believed to involve sulfuric acid (SA) together with bases, ions and oxygenated organic compounds. It has recently been shown that monoterpene autoxidation products may take part in atmospheric new particle formation, but the specific molecular structures are still unknown (Rissanen, 2014). As a proxy for monoterpene oxidation products we have used a ketodiperoxy acid ($C_6H_8O_7$) identified from cyclohexene autoxidation.

We present calculated Gibbs free energies of formation for clusters consisting of $C_6H_8O_7$, sulfuric acid, water, ammonia and/or dimethylamine (DMA). For sampling the cluster structures, we have used semi-empirical PM6 method. For optimizing the geometries, we used density functional theory (DFT) with three different density functional (M06-2X, PW91, ω B97X-D). For calculating the binding energies of the clusters, we used a high level coupled cluster method (DLPNO-CCSD(T)).

We identified that $C_6H_8O_7$ interacts very weakly with itself and sulfuric acid (Fig. 1) (Elm, 2015). The origin of the weak clustering of the $C_6H_8O_7$ is due to the formation of strong internal hydrogen bonds and the lack of a strong hydrogen bond acceptor.

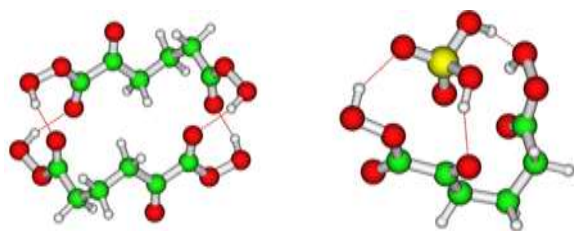


Figure 1. $C_6H_8O_7$ forms intermolecular hydrogen bonds with itself (left) and sulfuric acid (right).

The water, ammonia and DMA molecules form hydrogen bonds to vacant carbonyl group in the $C_6H_8O_7$ compound (Org). The (Org)(SA)(NH₃) and (Org)(SA)(DMA) clusters exhibit a proton transfer from sulfuric acid to the bases. In the case of ammonia this indicates that the presence of the $C_6H_8O_7$ promotes the proton transfer, which is not observed in the (SA)(NH₃) cluster. The presence of H₂O, NH₃ or DMA is found to enhance the interaction between Org and SA (Table 1).

Table 1. Average Gibbs free energy (ΔG) in kcal/mol for $C_6H_8O_7$ (Org) cluster formation reactions.

Calculated using DFT/6-31++G(d,p) optimized geometries and a DLPNO-CCSD(T)/def2-QZVPP electronic energies.

Reaction	ΔG
Org + SA \leftrightarrow (Org)(SA)	-0.2
Org + (SA) ₂ \leftrightarrow (Org)(SA) ₂	0.1
Org + (SA)(H ₂ O) \leftrightarrow (Org)(SA)(H ₂ O)	-1.3
Org + (SA)(NH ₃) \leftrightarrow (Org)(SA)(NH ₃)	-4.0
Org + (SA)(DMA) \leftrightarrow (Org)(SA)(DMA)	-8.0

As the formation free energy of the (Org)(SA) cluster is 0.2 kcal/mol, this indicates that water, ammonia and DMA are capable of stabilizing the clustering of $C_6H_8O_7$ by 1.1, 3.8 and 7.8 kcal/mol, respectively. However, the reaction free energies are relatively low and the $C_6H_8O_7$ could readily re-evaporate.

The addition of second $C_6H_8O_7$ to the (Org)(SA)(X) cluster is thermodynamically unfavourable in all cases. Adding a second sulfuric acid to the (Org)(SA)(X) cluster is favourable with Gibbs free energies -1.7, -9.5 and -11.8 kcal/mol for X=H₂O, NH₃ or DMA, respectively. However, the addition of a second $C_6H_8O_7$ to the (Org)(SA)₂(X) cluster is not favourable. Several other formation paths were considered, but none of them predict the formation of two Org containing clusters (Elm, 2016).

Results of this study leads to the conclusion that autoxidation products containing only peroxy acids, hydroperoxide and carbonyl groups cannot be key species in the initial steps of new particle formation and thereby only contributes to the growth of atmospheric particles. Multi-carboxylic acids will most likely produce stable clusters at atmospheric conditions and thereby should be the focus for further investigations on the effect of highly oxidized organic compounds in new particle formation.

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