Oxidized Amines Enhance Particle Formation More Than Amines

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Sulfuric acid (SA) plays a key role in atmospheric particle formation.

Bases such as methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA) are known to enhance SA-driven clustering.

The role of oxidized amines in particle formation and growth is unknown.
Trimethylamine oxide (TMAO) is an oxidation product of trimethylamine

- Weak base in aqueous phase
- Strong base in gas phase
- Zwitterionic bond between $\text{N}^+$ and $\text{O}^-$
- Steric hindrance by 3 methyl groups

How do TMAO and SA form clusters at atmospheric conditions?
1SA1TMAO heterodimer is very stable, $\Delta G = -21.8$ kcal/mol.

Alkylamines form less stable heterodimers with $\Delta G$ values of
Due to 3 methyl groups, TMAO can form only one H-bond with SA.

Due to zwitterionic structure, TMAO is capable of forming stable ion-dipole clusters with SA.
Cluster growth

Main growth pathways at 298 K, [SA]=[TMAO]=1 ppt

- Particle growth occurs close to the acid:base ratio of 1:1
TMAO enhances particle formation more than studied alkylamines under same conditions (at 298 K, [base]=1 pptv)
Factors influencing formation rates

Possible base properties affecting the ability to enhance clustering

<table>
<thead>
<tr>
<th></th>
<th>gas basicity</th>
<th>$pK_a$</th>
<th>dipole</th>
<th>H-bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>206.8</td>
<td>10.6</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>DMA</td>
<td>214.6</td>
<td>10.7</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>TMA</td>
<td>219.8</td>
<td>9.8</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>TMAO</td>
<td>229.6</td>
<td>4.7</td>
<td>5.2</td>
<td>1</td>
</tr>
</tbody>
</table>

- None of the factors alone can be used as a proxy for particle formation efficiency
Conclusions

- TMAO is stronger stabilizer in particle formation than alkylamines
- High gas basicity together with high dipole moment overcome low aqueous basicity and steric hindrance of 3 methyl groups
- More than one base property is related to its capability to enhance clustering
Thanks for your attention!

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