Kinetics of the gas-phase reactions of nitrate radicals with dimethylphenols

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Chemistry in the Troposphere
The troposphere acts as a giant reactor where gaseous (organic, inorganic), aerosol, etc. interact with reactive species (O\(_3\), OH, NO\(_x\)) that affect their degradation.

**Two types of chemistry**
- **Day-time** 
  - Reaction: NO\(_x\) + radicals
  - Reaction: O\(_3\) + radicals
- **Night-time** 
  - Reaction: NO\(_x\) + radicals
  - Reaction: O\(_3\) + radicals

Photochemical Smog - Definition
The photochemical smog is a mixture of gases (NO\(_x\), O\(_3\), CO, BC and VOC) that react with the products of fuel combustion in the presence of solar energy. The process involves the formation of secondary pollutants such as ozone, nitrogen oxides, peroxyacylnitrates, and many other organic compounds.

Aims of this project
- Determine rate coefficients for the reaction NO\(_x\) + DMPs = products
- Identity and quantify the products
- Develop chemical mechanism
- Determine the secondary reactions involved

All this is done in order to evaluate the environmental impact of DMPs.

Experimental Data

<table>
<thead>
<tr>
<th>DMP</th>
<th>Rate Coefficients &amp; Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4 DMP</td>
<td>3.3 x 10^-11</td>
</tr>
<tr>
<td>2,6 DMP</td>
<td>2.9 x 10^-11</td>
</tr>
<tr>
<td>3,4 DMP</td>
<td>3.5 x 10^-11</td>
</tr>
<tr>
<td>3,5 DMP</td>
<td>4.0 x 10^-11</td>
</tr>
</tbody>
</table>

Reaction rates of DMPs and other organic aerosols are first order with respect of NO\(_x\) and second order with respect of DMPs.

Dimethylphenols - Why?
- They are the main products of the atmospheric oxidation (e.g., ozone, oxygen) of dimethylphenols (DMPs). As a result, they are a major contributor to the formation of atmospheric turbulence and air pollution.
- Analyze gaseous precursors of organic aerosils.

The Atmospheric Smog Chamber
To reproduce the atmospheric conditions in an atmospheric smog chamber it is used. Here are reported its characteristics:
- 3.5 m x 3.5 m x 3.5 m chamber
- 4 sample (0.25 m diameter)

The Relative Rate Method
The relative rate method of the DMP and of a reference molecule are measured in presence of NO\(_x\). Knowing that the DMP and the reference react with NO\(_x\).

The Data Analysis

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<th>DMP</th>
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</thead>
<tbody>
<tr>
<td>2,4 DMP</td>
<td>5.6 x 10^-12</td>
</tr>
<tr>
<td>2,6 DMP</td>
<td>5.2 x 10^-12</td>
</tr>
<tr>
<td>3,4 DMP</td>
<td>5.8 x 10^-12</td>
</tr>
<tr>
<td>3,5 DMP</td>
<td>6.0 x 10^-12</td>
</tr>
</tbody>
</table>

We wish to thank EPA and NDFP for supporting this research and the CRC lab crew.

References

- Atmospheric Data

Summary
- Determined rate coefficients & lifetimes
- Identified and quantified the products
- Developed chemical mechanism
- Determined the secondary reactions involved

Further Work
- Catalytic smog chamber and more reactions
- Aerosol formation studies
- DMP chemical formation