An investigation into the suppression of the photo-Fenton reaction in the presence of α-pinene SOA

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Motivation
The photo-Fenton reaction is a known source of OH in cloud water. [1] We have previously seen a suppression in the presence of α-pinene secondary organic aerosol (SOA), however the mechanism of this suppression is unknown.

Guiding question
By what mechanism does the presence of α-pinene SOA suppress the photo-Fenton reaction?

The photo-Fenton reaction
Photocatalytic cycle involving iron and hydrogen peroxide

Hypothesis
α-pinene SOA is largely composed of organic acids. It is possible that these acids are complexing with iron, making it unavailable for reaction.

Approach
• Using pinonic acid, a major component of α-pinene SOA [2], perform the photo-Fenton reaction in varying conditions.
• Use UV-vis spectroscopy of iron/pinonic acid solutions to infer complexation.

Experimental results
Two main conclusions arise from this study:
1. There is a clear overall suppression of OH formation in the presence of pinonic acid
2. There is significant direct photolysis of the iron-oxalate complex, leading to the formation of OH, but not of the iron-pinonate complex

Experimental methods
Benzoic acid is used as a radical trap, forming para-hydroxybenzoic acid (pHBA), allowing for the quantification of total OH production.

Reactions were irradiated by a solar simulator for a total of 60 minutes in 10mL quartz vials. Reaction flask contents: 5µM FeSO₄, 15µM H₂O₂, 1mM Benzoic acid, (150µM Oxalic acid, 1500µM Pinonic acid). Analysis by HPLC detecting pHBA (λ=256nm).

Visual abstract
[Diagram showing the photo-Fenton reaction and downstream reactions leading to OH production]

What does this mean?
• From UV-vis experiments, we suspect there is complexation of oxalic acid and pinonic acid to iron (read: Complexation)
• Based on the lack of OH production resulting from complex photolysis, it is possible that iron is being sequestered by pinonic acid, reducing its effective concentration in solution

Experimental methods

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References