Motivation and background

Iron-complex photochemistry in the atmospheric aqueous phase

Iron is always present in concentration from ~10^{-10} M to ~10^{-10} M (fog particles). Iron sources are mainly mineral dust emissions. Iron complexes are very good absorbers in the UV-VIS actinic region. Fe-complex photolysis leads to radical production (see Fig.1). The photochemistry initiates radical chain reactions, which is related to the oxidizing capacity of the atmosphere. The Fe^{2+} budget is important for the Fenton-reaction, which can be a considerable in-situ OH source. Iron-complex photolysis modelling is currently only included in CAPRAM: oxalate is consumed through Fe-oxalato photolysis, which results in a net destruction of oxalate. This is a contradiction to field measurements, where substantial amounts of oxalate are found. Other models don't include Fe-oxalato photolysis and over-predict oxalate. Laboratory studies of iron complex photolysis processes are therefore needed.

Experimental

Measurement of overall Fe^{2+} quantum yield

• Direct photolysis in quartz-cuvee
• Measurement of Excimer laser energy with calibrated pyro-electric sensor
• Mixing of photolyzed aliquot with strong Fe^{3+} complexing agent Phenanthroline

Formation of stable Fe^{2+}-complexes between pH 2-9 (Fe(Phen))_{2}^{2+}: E^0 = 1.1 900 V/mol, 1 cm
• Measurement of Fe^{2+}-complex absorbance with UV-VIS spectrometer
• Calculation of iron speciation with speciation program (Species, Visual Minteq)

Results and discussion

Photolysis of Fe(III)-carboxylato complexes in aqueous atmospheric particles

• The quantum yields can differ up to one order of magnitude among different ligands.
• Higher quantum yields with ligands that have keto-groups (glyoxalate, pyruvate) compared to the other carboxylic acids.
• In all cases Φ_{Fe} > Φ_{lig} indicates the dependence of most Φ on secondary reactions involving reducing radicals.
• In case of malonic, glutaric, tartaric, tartric, pyruvic, glycolic and glyoxylic acid the quantum yields could be attributed to individual complexes with known stoichiometry whereas the value for succinic acid was lower in a mixture of complexes.

• For comparison (see Table 1) the quantum yields of the 1:1 Fe-tartrato complex are similar to those of the 1:2 complexes at 308 nm and invariable with respect to dissolved oxygen and wavelength.

Conclusions and Outlook

• Quantum yields of atmospherically relevant carboxylic acid complexes with iron other than oxalic are sufficiently high to play a role in atmospheric aqueous systems always mixture of suitable ligands.
• The quantum yields can differ up to one order of magnitude among different ligands.
• In dilute solutions of Fe-oxalato (cloud water) not all off the produced carboxyl radicals might ultimately lead to reduction of Fe(III)-species, this is important for the reduced iron budget
• In atmospheric aqueous systems always mixture of suitable ligands.
• Effects possibly counteract each other, influence of other unspecified side reactions possible.
• Usually a straight line with a clear left and right intercept is expected, from which the individual Φ could be calculated.
• Reasons for the non-linear behavior of the product Φ and Φ_{lig} are suspected to be the complex secondary reactions that take place after photolysis.

Table 1: Effective overall quantum yields of carboxylic acid iron-complexes obtained from excimer laser flash photolysis.

<table>
<thead>
<tr>
<th>System with Fe^{2+}</th>
<th>Fe(II) concentration [M]</th>
<th>308 nm</th>
<th>351 nm</th>
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<tr>
<td>Fe(II)-oxalato</td>
<td>10^{-5}</td>
<td>0.024</td>
<td>0.040</td>
</tr>
<tr>
<td>Fe(II)-glutarato</td>
<td>10^{-5}</td>
<td>0.099</td>
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<td>Fe(II)-malonato</td>
<td>10^{-5}</td>
<td>0.041</td>
<td>0.008</td>
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<tr>
<td>Fe(II)-succinato</td>
<td>10^{-5}</td>
<td>0.047</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe(II)-gluconic</td>
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<td>0.102</td>
<td>0.000</td>
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<tr>
<td>Fe(II)-gluconic</td>
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<td>0.04</td>
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<tr>
<td>Fe(II)-gluconic</td>
<td>10^{-5}</td>
<td>0.33</td>
<td>0.02</td>
</tr>
</tbody>
</table>

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References

Surdhar et al. (1989) Proc. R. Soc. Lond., 231, 199