New model developments of SOA formation in the aqueous phase

Chemical processes in cloud droplets vs aqueous particles

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SOA formation in the aqueous phase (aqSOA)

...of cloud droplets

Parameterization of SOA formation from glyoxal

...of aqueous (deliquesced) particles

- Derivation of individual rate constants based on lab studies
- Quantifying differences to cloud chemistry

First model studies

Comparison of cloud- and particle-SOA
Evidence in current models of ‘missing SOA’

Correlation of highly oxidized aerosol (O/C) and RH!

- ‘Traditional SOA’
  $0.02 < O/C < 0.8$

- aqSOA from glyoxal
  $1 < O/C < 2$

- aqSOA from methylglyoxal
  $0.4 < O/C < 1$
I. Cloud chemistry

Liquid water content ~ 0.1-1 g m⁻³
Lifetime of cloud droplet ~ minutes
Solute concentration µM - mM

CO₂

CH(OH)₂CH(OH)₂

K_{effH(T)}

K_H(T)

CHOCOOH

CHOCHO

OH

O/C

1

1-2

1.5-2

2

• Oxidation by OH
• Acid formation
• Formation and loss are pH dependent
• T and pH dependencies for all rate constants are known

Δ

Liquid water content
Lifetime of cloud droplet
Solute concentration

CO₂

CH(OH)₂CH(OH)₂

k₁(T) OH

(CHOCHO)

k₂(pH, T) OH

(COOH)₂

k₃(pH, T) OH

CO₂

Aqueous phase

Gas phase

µM - mM

CO₂

CH(OH)₂CH(OH)₂

K_{effH(T)}

K_H(T)

CHOCOOH

CHOCHO

OH

O/C

1

1-2

1.5-2

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• Oxidation by OH
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Simplification of cloud chemistry: aqSOA formation from glyoxal

\[
\frac{d[SOA]}{dt} = k_{\text{overall}} \cdot [\text{Gly}]_{\text{gas}} \cdot [\text{OH}]_{\text{gas}} \cdot \text{LWC} \cdot \text{Factor}
\]

**Factor:**
- Deviation from thermodynamic equilibrium \([\text{Gly}]_{\text{aq}} = K_{H}^{\text{Gly}} \cdot [\text{Gly}]_{\text{gas}}\)
- Loss processes Oxalic acid/Oxalate + OH → CO₂
How to derive the empirical ‘factor’?

~100,000 box model simulations using ‘detailed cloud chemistry’

0.01 ppb ≤ [Gly]_{gas} ≤ 1 ppb
10^4 \text{ cm}^{-3} ≤ [\text{OH}]_{gas} ≤ 7 \cdot 10^6 \text{ cm}^{-3}
0.01 \text{ g m}^{-3} ≤ \text{LWC} ≤ 1.5 \text{ g m}^{-3}
275 \text{ K} ≤ T ≤ 300 \text{ K}
2 ≤ \text{pH} ≤ 6.5

\[ \frac{d[\text{SOA}]}{dt} \text{ ng m}^{-3} \text{ s}^{-1} \]

\[ k_{\text{overall}}(T) \cdot [\text{Gly}]_{\text{gas}} \cdot [\text{OH}]_{\text{gas}} \cdot \text{LWC} \]

\[ k_{\text{aq}, \text{Gly}} \cdot K_H \cdot K_{\text{OH}} \]

\[ k_{\text{OH}, \text{H}} \cdot K_H \]

\[ \text{Net Production} = \text{Prod} - \text{Loss} \]
Resulting parameterization

Deviation from ‘ideal behavior’ (1:1) scales with

- glyoxal concentration
- temperature ($K_H$)
- pH (oxalate loss)

OH consumption $\Rightarrow [OH]_{aq \text{ (equil)}}$

$\pm \sim 30\%$

**Factor** = $a_1 + a_2 [y(pH) + A(pH) \cdot \exp(C(pH) \cdot [Gly]_{gas})] + a_3 \cdot T + a_4 [Gly]_{gas}$

Coefficients: $a_1, a_2, a_3, a_4, y(pH), A(pH), C(pH)$
II. SOA formation in aqueous particles

Complex mechanism:
- Surface and bulk processes
- Reversible and irreversible
- Photochemistry/dark chemistry
- Solute (activity) dependent
- Oligomerization (Products?)

LWC ~ $10^{-6} - 10^{-4}$ g m$^{-3}$
Particle lifetime ~ days
Solute concentration ~ M

Ervens and Volkamer, ACP, 2010
Quantifying chemical differences between cloud and particle chemistry

**Laboratory studies**
Glyoxal uptake on aqueous aerosol (different seed composition), in the presence of OH/hv

*Volkamer et al., ACP, 2009*

**Model studies**
Simulations of chamber conditions
Assumed ‘cloud chemistry’

\[ \text{OH(aq)} + \text{Glyoxal(aq)} \rightarrow \text{SOA} \]

Cloud chemistry reaction scheme underestimates photochemical SOA formation by more than two orders of magnitude!

Additional photochemical process(es)

\[ \text{Glyoxal} \rightarrow \text{SOA} \text{ with } 0.8 \text{ s}^{-1} < k_{\text{photochem}} < 7 \text{ s}^{-1} \]

can account for the discrepancy

\[ k_{\text{photochem}} = f(\text{particle composition, hygroscopicity}) \]
Model simulations: Cloud vs particle SOA

**Parcel model**
Prescribed RH, liquid water content, temperature, pressure…

**Model results:** 2.5 h < time < 3.5 h

**Cloud SOA**
(oxalic, glyoxylic, glycolic, pyruvic acid):
- \( \sim 1 \mu g m^{-3} \) after 3 hours \( f(LWC, \text{time}) \)
- Sink: Oxidation and evaporation

**Particle SOA**
Oligomers, org. N-compounds
Steady increase (no sink – correct?)
- Several \( \mu g m^{-3} \) after a few hours

SOA formation in clouds and aqueous particles about equally efficient
Conclusions

- Aqueous phase chemistry is important for the SOA budget (mass, O/C)
- Cloud droplets/ aqueous particles = different aqueous phases

Parameterization of in-cloud aqSOA formation as $f([\text{Gly}]_{\text{gas}}, \text{pH}, T)$

Kinetic data for particle-aqSOA based on laboratory studies
- Application of process model (e.g., MCMA-2003; CARES; CalNex…)
- Lab studies to extent parameter space (pH, seed, species…)

SOA formation from glyoxal in cloud droplets and particles might yield similar amounts of highly oxidized aqSOA mass (O/C > 1)