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Hydroxyl radicals from secondary organic aerosol decomposition in water

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Abstract

We found that ambient and laboratory-generated secondary organic aerosols (SOA) form substantial amounts of OH radicals upon interaction with liquid water, which can be explained by the decomposition of organic hydroperoxides. The molar OH yield from SOA formed by ozonolysis of terpenes (α -pinene, β -pinene, limonene) is $\sim 0.1\%$ upon extraction with pure water and increases to $\sim 1.5\%$ in the presence of Fe^{2+} ions due to Fenton-like reactions. Our findings imply that the chemical reactivity and aging of SOA particles is strongly enhanced upon interaction with water and iron. In cloud droplets under dark conditions, SOA decomposition can compete with the classical H_2O_2 Fenton reaction as the source of OH radicals. Also in the human respiratory tract, the inhalation and deposition of SOA particles may lead to a substantial release of OH radicals, which may contribute to oxidative stress and play an important role in the adverse health effects of atmospheric aerosols.

1 Introduction

Secondary organic aerosols (SOA) account for a major fraction of fine air particulate matter and have a strong influence on climate and public health (Jimenez et al., 2009; Pöschl et al., 2010; Huang et al., 2014). Formation of SOA is triggered by oxidation of volatile organic compounds followed by condensation of semi-volatile oxidation products (Hallquist et al., 2009; Donahue et al., 2012). Recently, it has been shown that extremely low volatility organic compounds (ELVOC) contribute significantly to SOA growth (Ehn et al., 2014; Jokinen et al., 2015; Mentel et al., 2015).

Particle phase chemistry and cloud processing are also efficient pathways for SOA formation and aging (Kalberer et al., 2004; Herrmann et al., 2005; Ervens et al., 2011; Shiraiwa et al., 2013). Evolution of SOA is one of the largest uncertainties in the current understanding of air quality, climate and public health (Kanakidou et al., 2005; Solomon, 2007). With regard to SOA health effects, substantial amounts of reactive

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(G1376A) with degasser (G1379B), and an auto-sampler with thermostat (G1377A). All modules were controlled by Mass Hunter software (Rev. B.05.01, Agilent). Eluents used were: 3% (v/v) acetone nitrile (Chromasolve, Sigma, Seelze, Germany) in water/formic acid (0.1% v/v , Chromasolv, Sigma, Seelze, Germany) (Eluent A), and 3% water/formic acid (0.1% v/v) in acetone nitrile (Eluent B). The flow rate was 400 nL min⁻¹ with a gradient program that starting with 3% B for 3 min followed by a 36 min step that raised eluent B to 60%. Further, the eluent B was increased to 80% at 40 min, and returning to initial conditions within 0.1 min, followed by column re-equilibration for 9.9 min before the next run. The ESI-Q-TOF instrument was operated in the positive ionization mode (ESI+) with an ionization voltage of 1900 V. Fragmentation of protonated ions was conducted using the auto MS/MS mode. Spectra were recorded over the mass range of m/z 100–3000. Data analysis was performed using the Qualitative Data Analysis software (Rev. B. 06.00, Agilent).

2.4 Kinetic modelling

The chemical reactions used to describe the BMPO/H₂O₂/Fe²⁺/H₂O system, including Fenton reactions, are listed along with their rate coefficients in Table S1 in the Supplement. From this set of 25 reactions, 16 were optimized using the MCGA method and parameter ranges are given in the Table S1 to illustrate the uncertainty arising from global optimization. For all other parameters reference values were taken from literature, which remained fixed during optimization. Kinetic rate coefficients of a large set of chemical reactions were determined using a uniformly sampled Monte Carlo search seeding a genetic algorithm (MCGA method; Berkemeier et al., 2013; Arangio et al., 2015) as the global optimization method. This algorithm optimizes a kinetic model to experimental data and avoids to getting trapped in local minima during the optimization process. In the kinetic model, ROOH represents all organic hydroperoxides without resolving individual structures. This is a simplification, which is necessary for the kinetic modelling but seems to return consistent results.

3 Results and discussion

Figure 2 indicates that EPR spectra of laboratory generated SOA by α -pinene (A), β -pinene (B), and limonene (C) were composed of four major peaks, whereas naphthalene SOA (D) exhibited no significant signals. These four peaks were also found for field samples (E) and became more prominent in the presence of Fe^{2+} (F). In addition, the same splitting was also observed in a solution of tert-Butyl hydroperoxide (G). The observed four hyperfine splittings are characteristic for BMPO-trapped OH radicals in water solution, as shown in the spectrum (H) for solutions of H_2O_2 and Fe^{2+} generating OH via the Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$) (Zhao et al., 2001).

Figure 3 shows LC-MS chromatograms of the BMPO-OH adduct (m/z 216.121) for aqueous BMPO solutions (black line) and for BMPO in aqueous β -pinene SOA extract (red line). A strong peak is observed at a retention time of 11.6 min for BMPO in aqueous β -pinene SOA extract, but not for the aqueous BMPO solution, which served as a blank. Confirmation of the BMPO structure for m/z 216.121 was achieved by comparing MS^2 spectra of $[\text{BMPO}+\text{H}^+]^+$ (m/z 200.126) from the aqueous standard and m/z 216.121. In both cases the loss of a characteristic fragment with a mass of 56.062 Da is observed (panel c and f), which corresponds to the loss of C_4H_8 from the t-butoxycarbonyl function of BMPO. Above LC-MS/MS analysis confirms the presence of OH radicals in β -pinene SOA extracts observed by EPR shown in Fig. 2.

The EPR and LC-MS/MS observations provide strong evidence that OH radicals are generated in water extracts of SOA by α -pinene, β -pinene, and limonene, as well as field fine particles, which can be enhanced by Fe^{2+} . Note that additional hyperfine splitting are observed for monoterpene SOA and especially for field samples, indicating the presence of organic radicals. Figure 4a shows that the amount of OH radicals trapped by BMPO increases as the SOA concentration increases in the aqueous phase. The OH yield from β -pinene SOA is the highest generating $\sim 1.5 \mu\text{M}$ of OH radicals at 1.5 mM SOA concentration, followed by α -pinene and limonene SOA. Naphthalene SOA has a negligible yield of OH radicals.

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For assessment of potential interferences from trace amounts of impurities such as transition metals in water, the OH yield was also measured in water with three different purity grades: Milli-Q water (18.2 M, Thermo Scientific™ Barnstead™ GenPure™ xCAD Plus ultrapure water system), TraceSELECT™ Ultra ACS reagent water (Sigma Aldrich), and Savillex water (DST-1000 Acid Purification System), which results in excellent agreement (Fig. 5) confirming that OH radicals can be formed in the absence of transition metals.

Ambient particulate matter is often associated with iron ions, which play an important role in aerosol chemistry via Fenton-like reactions (Deguillaume et al., 2005). To investigate the effects of transition metals on OH formation by SOA, different concentrations of Fe^{2+} were added in SOA water extracts. Figure 4b–d show the OH formation efficiency (molar concentration ratio of OH and SOA: $[\text{BMPO-OH}]/[\text{SOA}]$, in %) of α -pinene, β -pinene and limonene SOA as a function of molar concentration ratio of FeSO_4 to SOA ($[\text{Fe}^{2+}]/[\text{SOA}]$). The OH formation efficiency reaches maximum values of 1.5 % for β -pinene SOA, 1.1 % for α -pinene SOA, and 0.5 % for limonene. This order is the same as the order of the relative contribution of organic peroxides in these types of SOA (Docherty et al., 2005).

The observed formation of OH radicals is most likely due to hydrolysis and thermal decomposition of organic hydroperoxides (ROOH), which account for the predominant fraction of terpene SOA (Docherty et al., 2005; Epstein et al., 2014) as well as in rain water (Hellpointner and Gäb, 1989), but have little contribution for naphthalene SOA (Kautzman et al., 2010). ROOH are formed via multigenerational gas-phase oxidation and autoxidation, introducing multiple hydroperoxy functional groups forming extremely low volatility organic compounds (Crouse et al., 2013; Ehn et al., 2014). Due to the low binding energy of the O–O bond, ROOH are well-known to undergo thermal homolytic cleavage ($\text{ROOH} \rightarrow \text{RO}^\bullet + \bullet\text{OH}$). In the presence of Fe^{2+} , it has been reported that decomposition of ROOH can be enhanced mainly via Fenton-like reactions leading to heterolytic cleavage of the O–O bond in the following two ways depending on the pH and reaction environments: $\text{ROOH} + \text{Fe}^{2+} \rightarrow \text{RO}^\bullet + \text{OH}^- + \text{Fe}^{3+}$ or $\text{ROOH} + \text{Fe}^{2+} \rightarrow$

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rably important to the Fenton reaction in most conditions and SOA can be the main source of OH radicals at low concentrations of H_2O_2 and Fe^{2+} . The formed OH radicals would promote chemical aging of SOA especially in the presence of iron ions (e.g., SOA coated mineral dust particles) and may also induce aqueous-phase oxidation of sulfur dioxide forming sulfuric acid (Harris et al., 2013).

Recent studies have shown that OH radicals can trigger autoxidation reactions in the gas phase, generating highly oxidized and extremely low volatility compounds (Crouse et al., 2013; Ehn et al., 2014). We hypothesize that OH radicals formed from SOA decomposition could also trigger autoxidation in the condensed phase. Such a self-amplification cycle of SOA formation and aging may be relevant for example in the Amazon, where cloud and fog processing are important pathways forming a high fraction of SOA with high O:C ratio, resulting in an enhancement of cloud condensation nuclei activity of particles (Pöschl et al., 2010; Pöhlker et al., 2012). Organic peroxides are often used as the agent of the vulcanization processes to initiate the radical polymerization by forming free radicals, which abstract hydrogen atoms from the elastomer molecules converting them into radicals that undergo oligomerization to form elastic polymer or rubber. Similar processes might also occur in SOA particles (“SOA vulcanization”), which may contribute to formation of dimers and oligomers observed in SOA particles (Kalberer et al., 2004) possibly leading to the occurrence of an amorphous solid state (Virtanen et al., 2010; Koop et al., 2011; Shiraiwa et al., 2011; Renbaum-Wolff et al., 2013; Kidd et al., 2014).

In indoor air, terpenes are commonly found at higher concentrations than in the ambient air due to their widespread use as solvents and odorants in cleaning products and air fresheners (Weschler, 2011). Depending on precursor concentrations, the SOA concentration in indoor air can reach up to $30 \mu\text{g m}^{-3}$ with the highest contribution from limonene SOA (Waring, 2014). To evaluate potential adverse health effects by SOA deposition into the lungs, we estimated the OH production rate by SOA within the lung lining fluid (LLF) as a function of ambient SOA concentration considering breathing and deposition rates (see Supplement) (Fig. 7b). Figure 7b also shows the OH production

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rate by the Fenton reaction with typical iron (Gutteridge et al., 1996) and H_2O_2 concentrations in the LLF (Corradi et al., 2008). Patients with respiratory diseases are reported to have high H_2O_2 concentrations in the bronchoalveolar lavage (Corradi et al., 2008) (as shown in shaded purple area) and the Fenton reaction may be the main source of OH radicals for such patients. However, for healthy people with low H_2O_2 and Fe^{2+} concentrations, SOA decomposition can be more important than the Fenton process under high ambient or indoor SOA concentrations. Excess concentrations of reactive oxygen species including hydrogen peroxide, OH radicals (and potentially also organic radicals) are shown to cause oxidative stress to human lung fibroblasts, alveolar cells and tissues (Pöschl and Shiraiwa, 2015). Thus, in polluted indoor or urban megacities with high SOA concentration such as in Beijing, SOA particles may play a critical role in adverse aerosol health effects.

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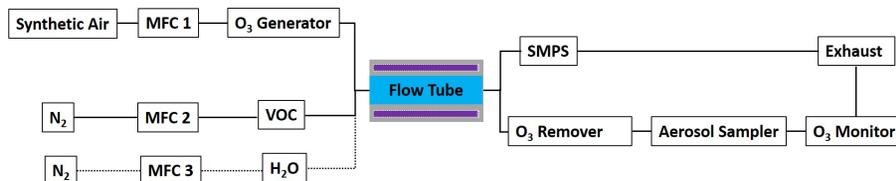


Figure 1. Schematics of the experimental setup for generation and collection of SOA particles.

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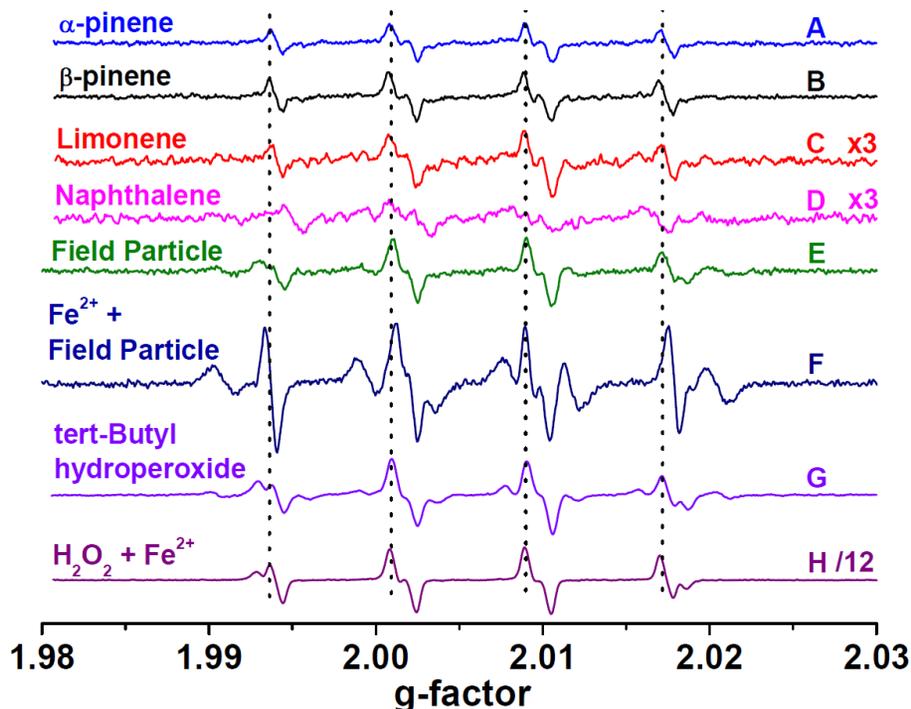


Figure 2. EPR spectra of sample solutions mixed with the spin trapping agent BMPO: (A) α -pinene SOA, (B) β -pinene SOA, (C) limonene SOA, (D) naphthalene SOA, (E) 180–320 nm size field particles, (F) 180–320 nm size field particles mixed with Fe^{2+} , (G) tert-Butyl hydroperoxide solution, and (H) H_2O_2 solution with Fe^{2+} . The four peaks (dotted lines) are characteristic for BMPO-OH adducts.

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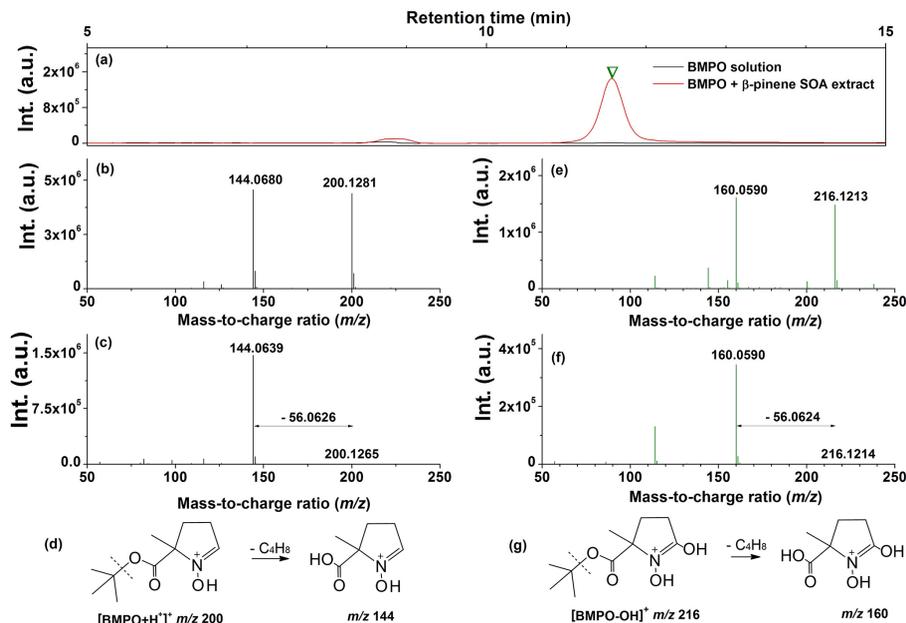


Figure 3. LC-MS/MS analysis. **(a)** LC-MS chromatogram of aqueous BMPO solution (black line) and BMPO mixed with β -pinene SOA water extracts (red line). The downward triangle indicates the retention time of m/z 216 (BMPO-OH). **(b)** MS spectrum of $[\text{BMPO}+\text{H}^+]^+$ with nominal m/z 200. **(c)** MS^2 spectrum of m/z 200, with the characteristic fragment ion m/z 144.0639 ($[\text{BMPO}+\text{H}^+]^+ - m/z$ 56.0626). **(d)** Proposed fragmentation pathway for m/z 200. The most abundant fragment ion present in **(c)** corresponds to the loss of C_4H_8 from $[\text{BMPO}+\text{H}^+]^+$. **(e)** MS spectrum of $[\text{BMPO}-\text{OH}]^+$ with m/z 216. **(f)** The MS^2 spectrum of m/z 216, with the characteristic fragment ion m/z 160.0590 ($[\text{BMPO}-\text{OH}]^+ - m/z$ 56.0624). **(g)** Proposed fragmentation pathway for m/z 216. The observed loss of C_4H_8 is characteristic for the fragmentation of the *t*-butoxycarbonyl function of BMPO.

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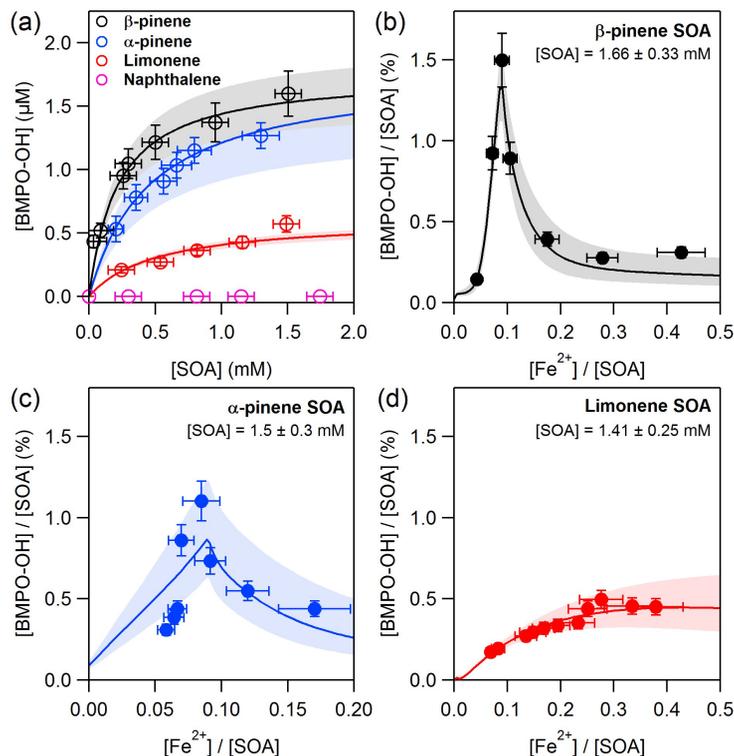


Figure 4. OH formation efficiency by SOA. **(a)** Concentrations of OH radicals formed in water extracts of SOA of β -pinene (black), α -pinene (blue), limonene (red), and naphthalene (pink) as a function of SOA concentrations in the aqueous phase. The formation efficiency of OH (molar concentration ratio of OH to SOA: $[\text{BMPO-OH}] / [\text{SOA}]$, in %) in iron containing SOA water extracts against molar concentration ratios of FeSO_4 and SOA ($[\text{Fe}^{2+}] / [\text{SOA}]$) by **(b)** β -pinene, **(c)** α -pinene, and **(d)** limonene. The markers are experimental data and the solid curves with shaded area are modelled with uncertainty.

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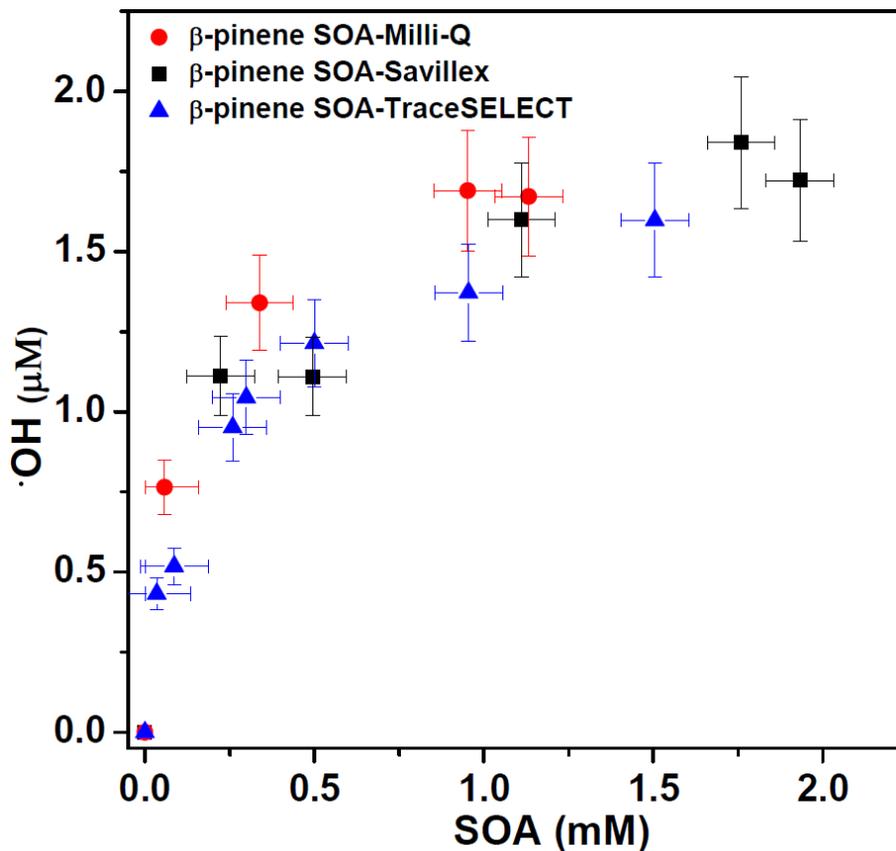


Figure 5. OH yield of β -pinene SOA in three different kinds of pure water: Savillex (black squares), Milli-Q (red solid balls), and TraceSELECT (Sigma, blue triangles).

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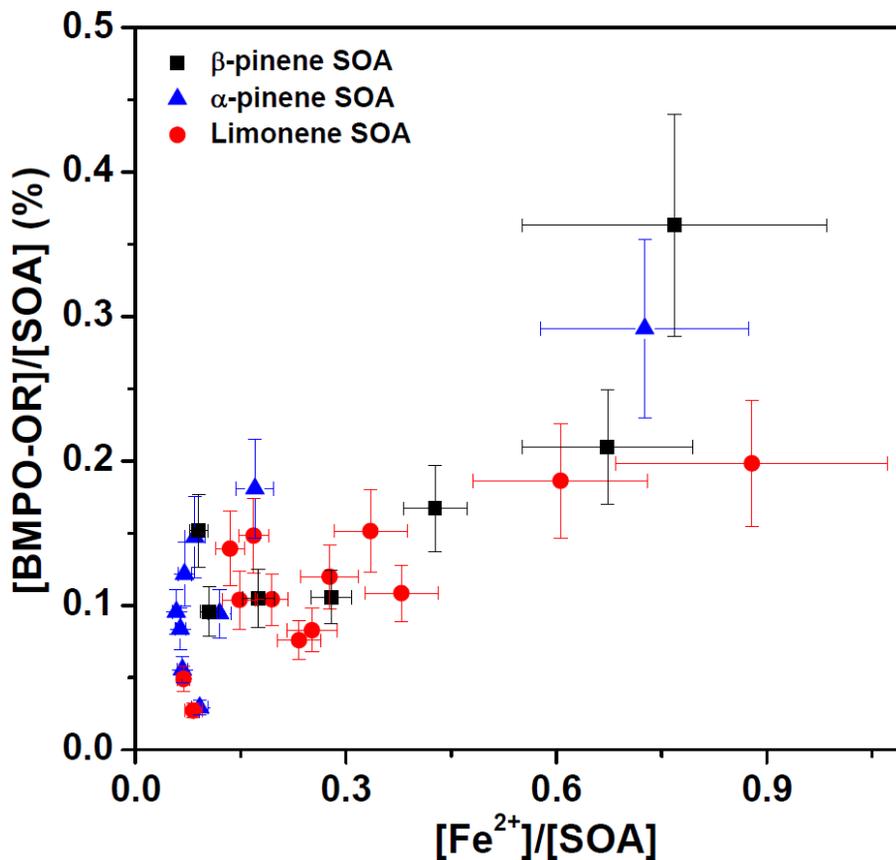


Figure 6. Formation efficiency of organic radicals. Molar concentration ratio of organic radicals to SOA ($[BMPO-OR]/[SOA]$, in %) in mixtures of Fe^{2+} and SOA solutions.

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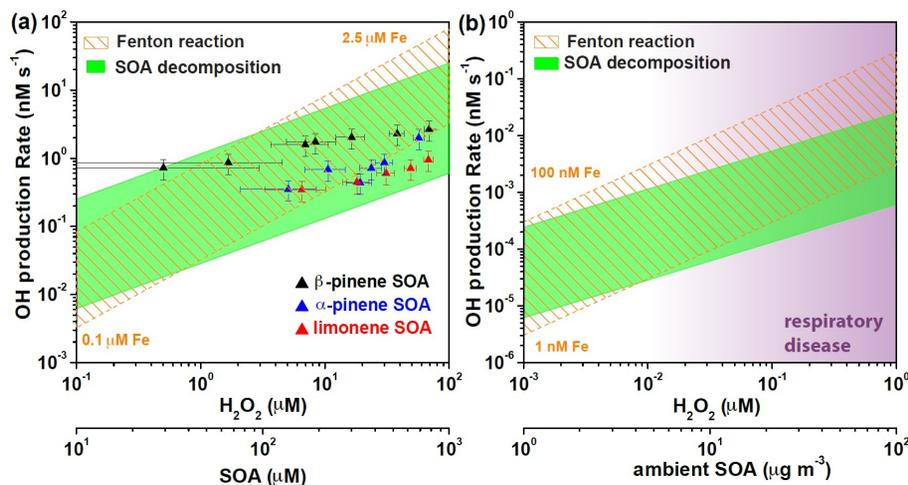


Figure 7. OH production rate in cloud droplets and lung lining fluid. **(a)** The OH production rate in cloud droplets by SOA decomposition compared to the classical Fenton reaction. The data points were measured in the absence of Fe^{2+} for different precursors of β -pinene (black), α -pinene (blue), and limonene (red), and the shaded green area represents the possible range in the presence of iron as a function of SOA concentration in the aqueous phase. The dashed lines represent OH production rates due to the Fenton reaction from H_2O_2 with typical dissolved iron concentrations ($\text{Fe}^{2+} : \text{Fe}^{3+} = 1 : 1$) of 0.1 and $2.5 \mu\text{M}$. **(b)** The OH production rate in lung lining fluid by SOA decomposition as a function of ambient SOA concentrations, and by the classical Fenton reaction as a function of H_2O_2 concentrations with typical dissolved iron concentrations ($\text{Fe}^{2+} : \text{Fe}^{3+} = 1 : 1$) of 100 and 1 nM . The purple shaded area represents patients with respiratory disease exhibiting high H_2O_2 concentrations in the bronchoalveolar lavage (Corradi et al., 2008).

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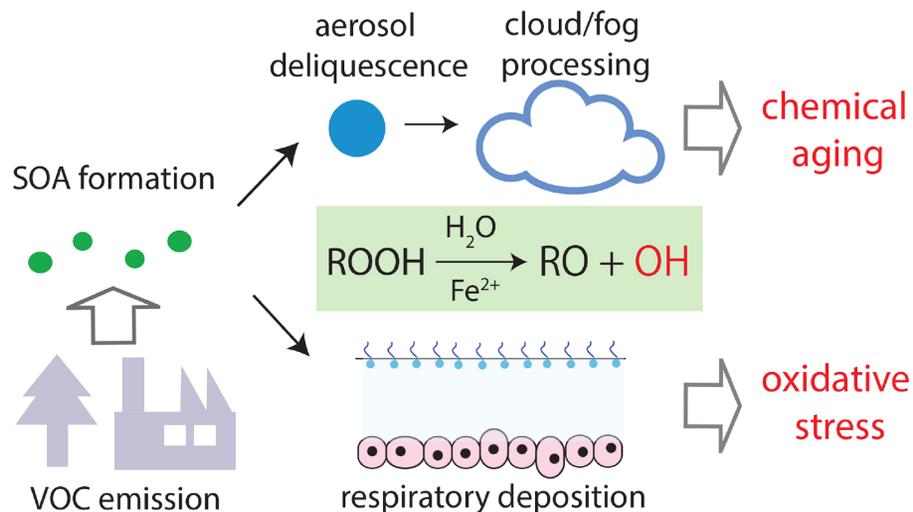


Figure 8. Implications of OH formation by SOA. Formation of OH radicals upon decomposition of organic hydroperoxides (ROOH) in secondary organic aerosol leads to rapid chemical aging of SOA particles upon deliquescence and cloud or fog processing in the atmosphere as well as oxidative stress upon inhalation and deposition in the human respiratory tract. Mixing and Fenton-like reactions of iron with ROOH from SOA can occur both in atmospheric particles and in the lung lining fluid.