EPR studies of Reactive Oxygen Species (ROS) and the pH Effect on the Iron Catalytic Cycles

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Introduction

- Reactive oxygen species (ROS) such as OH, HO_2, O_2^-, or RO_2 radicals as well as peroxides occur in the tropospheric multiphase system both in the gas phase and in the aqueous phase (e.g., clouds, fog, and deliquescent aerosols). [1,2,3,4]
- Peroxides and short-lived ROS are important drivers of secondary organic aerosol (SOA) formation in the troposphere. [1,5]
- An important source of ROS in the aqueous phase is the Fenton reaction, in which dissolved iron, e.g. from dust emissions, reacts with peroxides such as hydrogen peroxide (H_2O_2) to form OH radicals. [6,7,8]
- The different acidity (pH) in the aqueous phase influences numerous processes, such as reactivity and the nature of chemical reactions. [6]
- While many studies have been conducted on the mechanism of the Fenton reaction and the fate of ROOHs, only a few studies have investigated the effects of pH under atmospheric conditions on the system. [6,7,9]

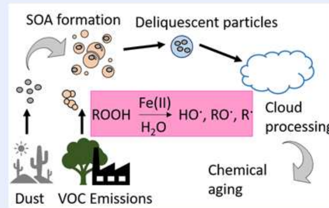

Fig. 1: ROS formation by Fenton reaction in the atmosphere, adopted from Tong et al., 2017 [5].

EPR experiment

Scavenging of OH and quantification by EPR method

- Formed ˙OH scavenged by DMPO spin-trap, which forms a stable radical adduct (Fig. 2). [10]
- DMPO-OH adduct generates EPR-detectable signal.
- The Fenton reagent of 5×10^{-6} M Fe(II) is mixed with up to 9×10^{-5} M H_2O_2 in a 1 mL flask in the presence of 2×10^{-2} M DMPO.

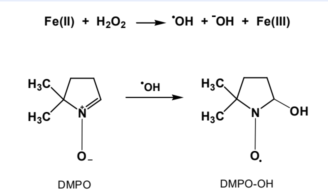

Fig. 2: Adduct formation from the Fenton reaction.

Aqueous phase bulk reactor experiment

Scavenging of OH and quantification by GC-MS method

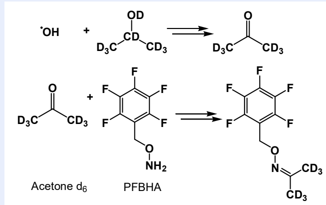

Fig. 3: OH scavenging and derivatization reaction.

- The ˙OH formed reacts in the presence of 1×10^{-2} M propanol-d_8 to form acetone-d_6.
- Acetone-d_6 was derivatized by 2×10^{-2} M (o-(pentafluorobenzyl)-hydroxylamine) and analyzed by GC-MS. [11]
- The Fenton reagent of 5×10^{-6} M Fe(II) is mixed with 2.5×10^{-5} M H_2O_2 in a 150 mL batch reactor.

Results

pH-dependent measurements using the EPR

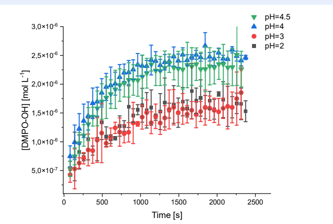

Fig. 4: Measured concentration-time-profiles of DMPO-OH adduct at different pH values using EPR technique.

- In the Fenton reaction between H_2O_2 and Fe(II), lowering the pH from 4.5 to 2, results in a weaker EPR signal.
- The change in the detected DMPO-OH adduct concentration due to a lower pH limits its use for the rate constant determination.
- To verify the obtained data by EPR, a GC-MS method was applied for comparison.

pH-dependent measurements using the GC-MS

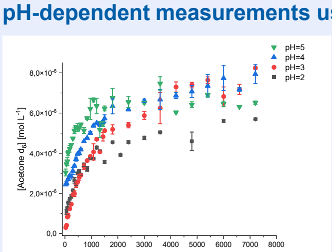

Fig. 5: Measured concentration-time-profiles of acetone-d_6 at different pH values using GC-MS technique.

- Increasing the pH value in the Fenton reaction shows also a difference in the OH radical yield.

pH	k_{1st} / s^{-1}	R^2
2	$1.9 \pm 0.02 \times 10^{-3}$	0.93
3	$2.4 \pm 0.01 \times 10^{-3}$	0.99
4	$2.5 \pm 0.01 \times 10^{-3}$	0.99
5	$7.0 \pm 0.07 \times 10^{-3}$	0.71

- The k_{1st} rate constants show a similar change when increasing the pH between 2 and 4.
- Further detailed studies on pH dependence are required.

Kinetic study of the classical Fenton reaction by EPR

- The k_{1st} for the classic Fenton reaction were calculated using the slope of DMPO-OH concentration-time profiles at constant Fe(II) and DMPO concentrations with the different H_2O_2 concentrations.

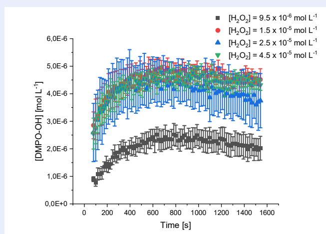

Fig. 6: Measured concentration-time-profiles of DMPO-OH adduct at different H_2O_2 concentration at pH = 4.5.

$[H_2O_2]$/ M	k_{1st} / s^{-1}	R^2
9.5×10^{-6}	$5.2 \pm 0.1 \times 10^{-3}$	0.96
1.5×10^{-5}	$9.8 \pm 0.1 \times 10^{-3}$	0.93
2.5×10^{-5}	$1.2 \pm 0.1 \times 10^{-2}$	0.94
4.5×10^{-5}	$8.9 \pm 0.1 \times 10^{-3}$	0.94

- Applying the k_{1st} values against the H_2O_2 concentration yields the second-order rate constant:

$$k_{2nd} = 67 \pm 297 \ \text{L mol}^{-1} \text{s}^{-1}$$

First measurements on organic hydroperoxides by EPR at TROPOS

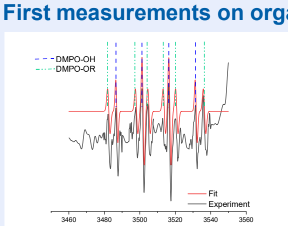

Fig. 7: EPR spectra of radical adducts from reaction of ISOPOOH with Fe(II) in the presence of the spin-trapping agent DMPO.

- A more complex spectrum was obtained by using an organic hydroperoxide (ISOPOOH) instead of H_2O_2 (Fig. 7).

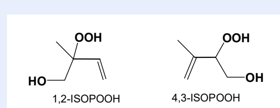

Fig. 8: Two isomers of isoprene hydroxyhydroperoxide (ISOPOOH).

- The dashed vertical lines show the DMPO-OH adduct (blue) and the DMPO-OR adduct from a carbon-centered radical (green).

Summary & Outlook

- The decomposition of peroxides such a H_2O_2 and 1,2-ISOPOOH through the Fenton reaction in the aqueous phase was investigated.
- The kinetic behaviour of the Fenton-type reactions was studied by EPR and by GC-MS for pH values between 2 and 5.
- A pH dependence was found with both analytical techniques.
- The rate constant k_{2nd} of the Fenton reaction at pH 4.5 was calculated from the EPR data.

References

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