Henry's Law Partitioning and Setschenov Salting of 1,2-ISOPOOH in Aqueous Solutions Containing Ammonium Sulfate and Sodium Oxalate

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Motivation

Isoprene is the predominant biogenic emission from plants and contributes approximately 30% of global non-methane volatile organic carbon (VOC) emissions. [1] Isoprene hydroxyhydroperoxides (ISOPOOHs) are a first-generation product of isoprene oxidation in low-NOx conditions. In addition to forming secondary organic aerosol (SOA) precursors through further oxidation, ISOPOOHs can also directly contribute to particle growth by partitioning to the condensed phase.[1] The equilibrium between ISOPOOH in the gas and particle phases is governed by Henry's Law:

$$ISOPOOH_{(g)} \rightleftharpoons ISOPOOH_{(aq)}$$

For the partitioning process, we can write the equilibrium expression:

$$K_H = \frac{ISOPOOH_{(g)}}{ISOPOOH_{(aq)}}$$

where K_H is the Henry's Law constant. The presence of salts in the aqueous phase can exponentially affect the equilibrium constant, i.e.

$$K_{H,s} = K_{H,w} \times 10^{K_s[salt]}$$

where $K_{H,s}$ is the Henry's Law constant in the presence of a salt, $K_{H,w}$ is the Henry's Law constant in pure water, and K_s is known as the Setschenov constant. [2]

This Study

In this experiment, the K_S for 1,2-ISOPOOH is determined for ammonium sulfate and sodium oxalate, two major components of atmospheric aerosols. This is accomplished by measuring the gas phase concentrations of 1,2-ISOPOOH in the head space above aqueous solutions of 1,2-ISOPOOH with varying concentrations of ammonium sulfate and sodium oxalate. Gas-phase measurement was accomplished using iodine chemical ionization mass spectrometry (I^--CIMS). In addition, calibration of the CIMS, combined with quantification of the aqueous 1,2-ISOPOOH concentration by a colorimetric method[3], allowed for calculation of the value of the Henry's Law constant for 1,2-ISOPOOH.

References

[1] Rivera Rios, J.C.: Atmospheric Chemistry of Isoprene Hydroxyhydroperoxides (2018)

[2] Ruckenstein, E., Shulgin, I.: Salting-Out or –In by Fluctuation Theory. Ind. Eng. Chem. Res. 41, 4674-4680 (2002)

[3] Ranney, A.P., Ziemann, P.J.:: Microscale Spectrophotometric methods for Quantification of Functional Groups in Oxidized Organic Aerosol. Aerosol Science and Technology. 9, 881-892 (2016)

Acknowledgements

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Experimental Setup

Aqueous Phase 1,2-ISOPOOH Quantification

Aqueous phase 1,2-ISOPOOH measured by colorimetric method adapted from Ranney and Ziemann:

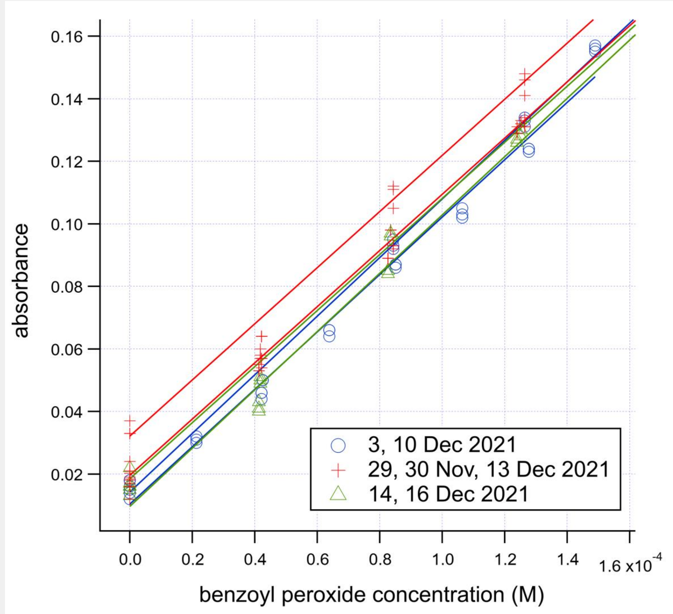
Peroxide/KI reaction produces equilibrium of I_2 and I_3^-.

(1) $R_1\text{-OO-}R_2 + 2I^- + 2H_2O \rightarrow R_1OH + R_2OH + I_2$

(2) $I_2 + I^- \rightleftharpoons I_3^-$

Absorption of I_2/I_3^- equilibrium mixture measured at 470 nm.

Benzoyl peroxide is used as a standard.

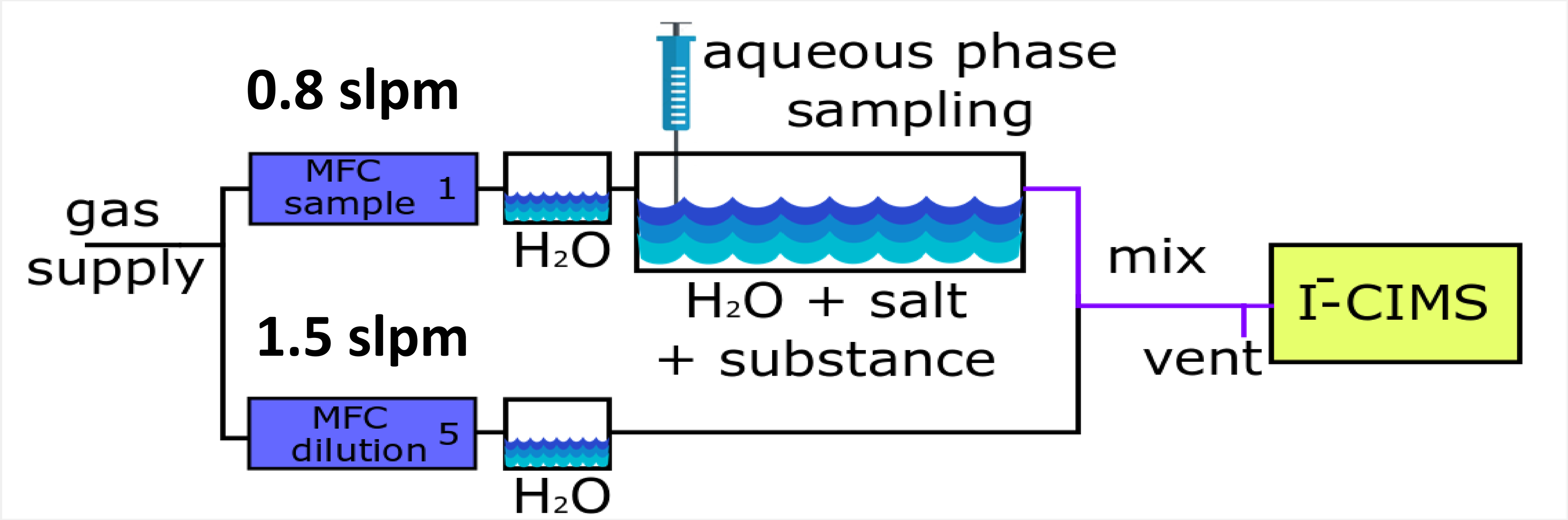


Contribution of aqueous phase analysis to the overall error budget is estimated to be 3%.

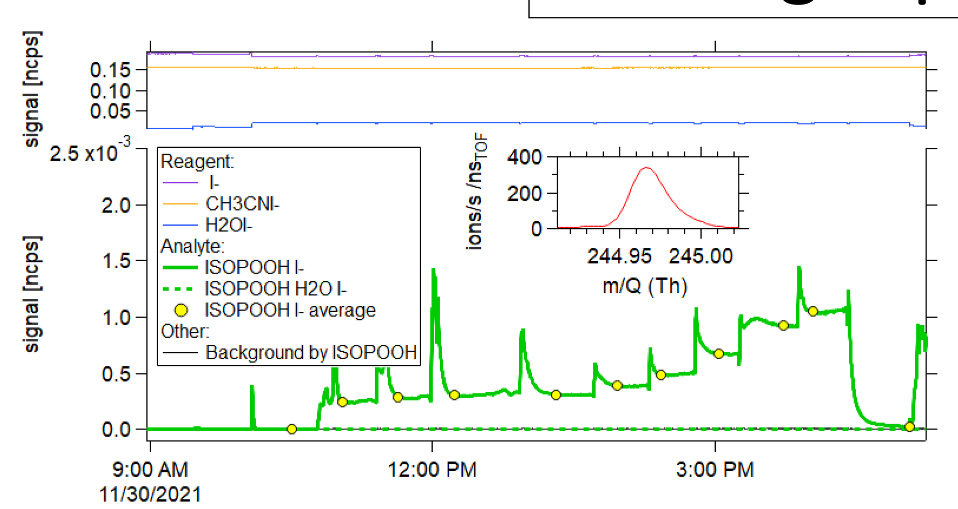
measurement day	16-Dec-21	18-Dec-21
standard concentration (M)	0.00413	0.00417
slope	932	896
intercept	0.00961	0.0184
n measurements	6	6
avg. measured concentration (M)	0.00301	0.00306
std dev. measurements (M)	0.00008	0.00003

Partitioning Experiments

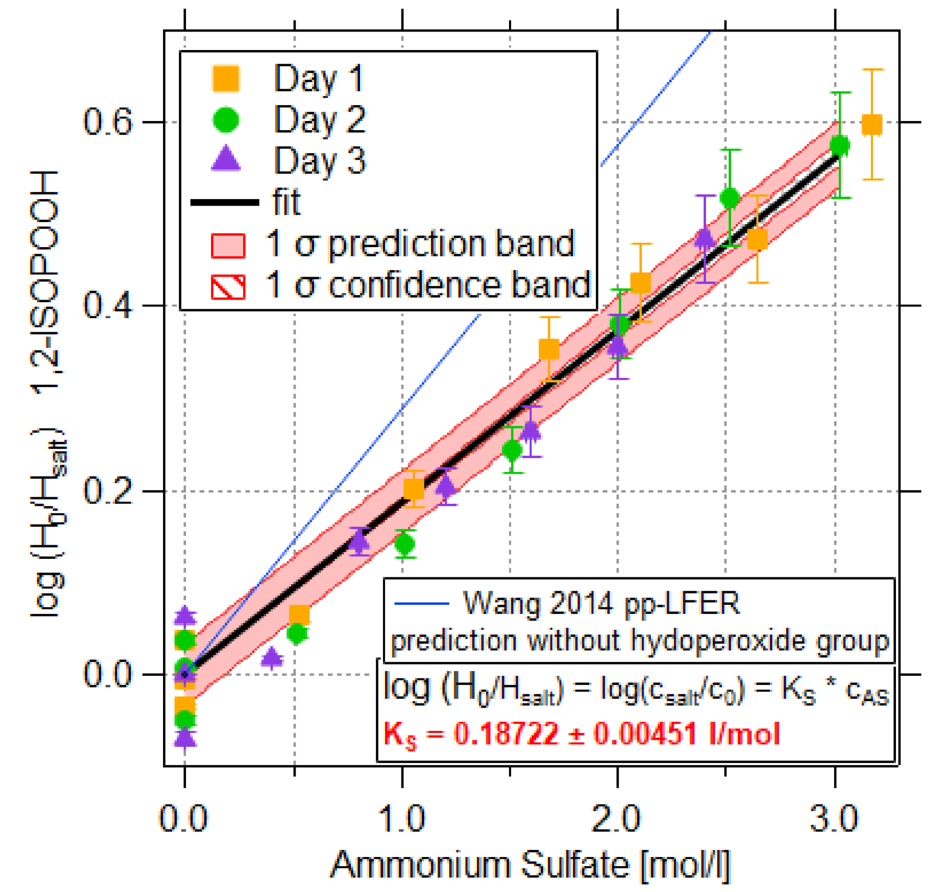
Samples were injected into a round-bottom flask and purified nitrogen was flowed through the head space. For each sample, partitioning and sampling lines came to equilibrium within ~8 minutes. The stable gas-phase signal was measured for an additional ≥20 minutes. Approximately 11 samples of varying salt concentrations were measured per day.

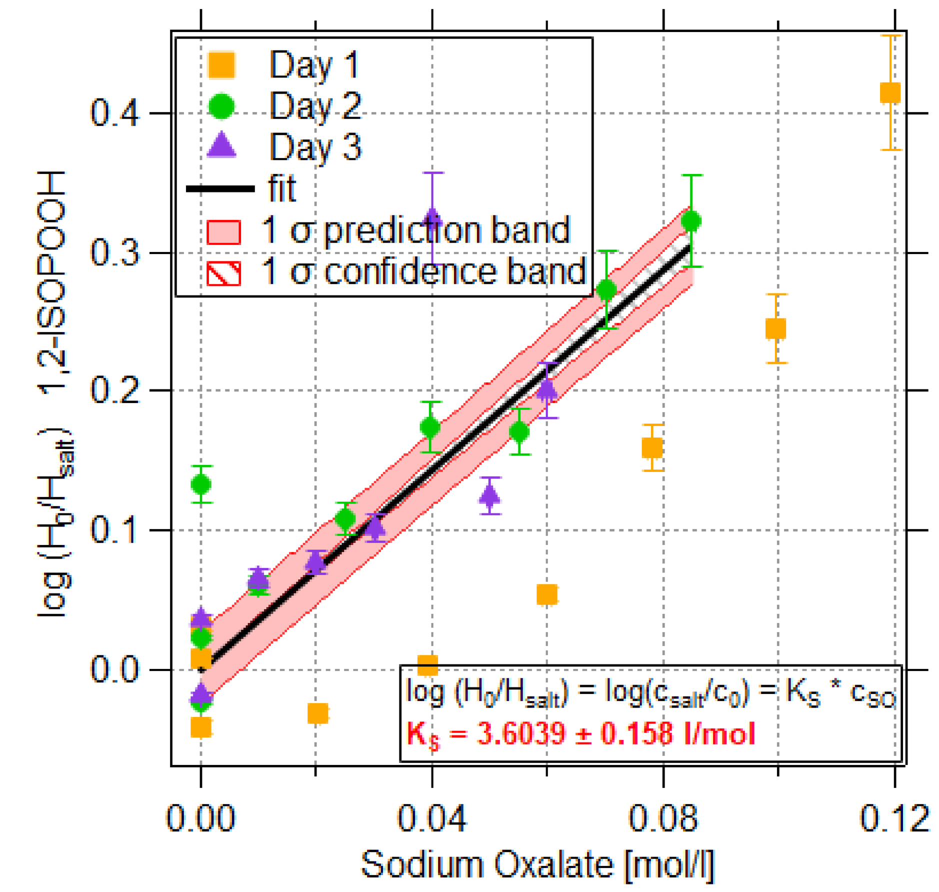


Salting Experiment Results



Gas-phase time series of a typical experiment (0.415 mmol/L 1,2-ISOPOOH). Samples were measured in order of increasing ammonium sulfate concentration (0 – 3M). Increasing gas-phase signal shows salting-out behavior.





$\log(K_{H,w}/K_{H,s})$ vs salt concentrations (M). K_S is determined from the slope.

Salting out is less than expected from parameterization without OOH group, so the OOH group decreases the salting effect.

Comparison of Measured Ks with Ammonium Sulfate		
Compound	This Study	pp-LFER model (Wang 2014)
1,2-ISOPOOH	0.189	0.288
Cumene Hydroperoxide	0.331	0.444

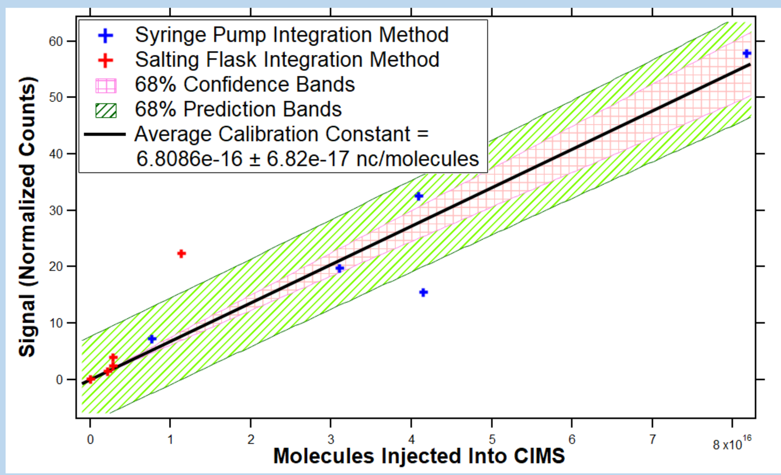
Ongoing work: Determination of mixing rules for salting effects of combined ammonium sulfate/sodium oxalate solutions.

Henry's Law Constant

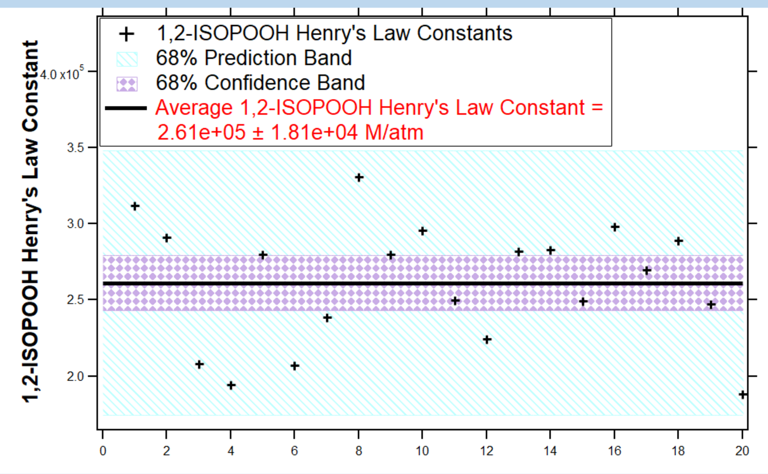
Calculation of K_H (Henry's Law constant without salt) requires quantification of both aqueous and gas phase concentrations. CIMS (gas phase) calibration was accomplished by integration of the total signals from injecting and completely evaporating known volumes of 1,2-ISOPOOH solutions.

Henry's Law Constant: From the gas-phase signal of the salt-free samples, the Henry's Law constant is determined by the following relation:

$$K_H = \frac{aq.\,conc.\,(M)}{partial\ pressure\ (atm)} = \frac{(aq.conc.)}{\dfrac{signal(ncps) * cal.const}{\frac{0.8\,L}{min} \times \frac{1\,min}{60\,sec} \times \frac{1000\,cm^3}{1\,L} \times dil.\,factor \times \frac{2.5\times10^{19} molec}{1\,cm^3}}}$$



Integrated signal vs number of molecules injected.



The measured 1,2-ISOPOOH Henry's Law constants.

Summary of 1,2-ISOPOOH Henry's Law Constants (M·atm−1)				
This Study KH 30°C	Rios KH 25°C	E + A 25 °C	Ranventos-Duran KH	GROMHE 25 °C
2.61E+05	1.18E+05	1.00E+05	7.53E+05	1.30E+06

Ongoing work: Determining ΔHsol from Arrhenius plot of temperature-dependent K_H measurements.