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Peroxide Content of Secondary Organic Aerosol

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Abstract

Secondary organic aerosol (SOA) formed from the oxidation of monoterpenes can impact the Earth's radiation balance, act as cloud condensation nuclei and negatively affect human health. In the summer of 2015, the **S**econdary **O**rganic **A**erosol **F**rom **F**orest **E**mission **E**xperiment (SOAFFEE) laboratory campaign was launched in order to study the physical properties of SOA generated from the oxidation of α–pinene and Δ-carene. Both compounds are gas-phase monoterpenes emitted into the atmosphere via biogenic sources. In this study, the peroxide content of SOA was determined using an iodometric-spectrophotometric (IS) technique. It was found that the peroxide content of SOA generated during the SOAFFEE campaign was similar to that found in previous studies.

Possible SOA Reaction Mechanisms

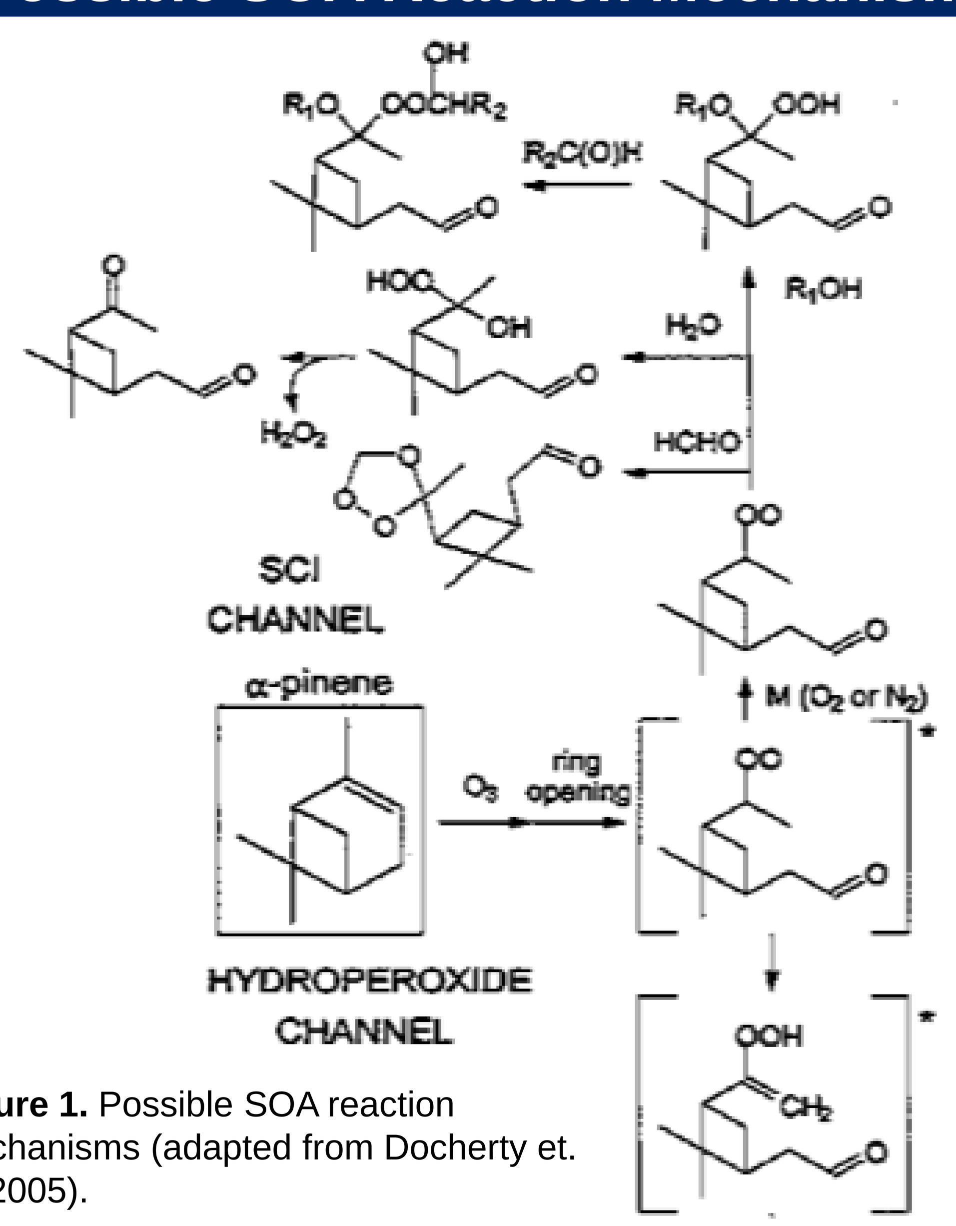

Figure 1. Possible SOA reaction mechanisms (adapted from Docherty et. al, 2005).

Environmental Chamber

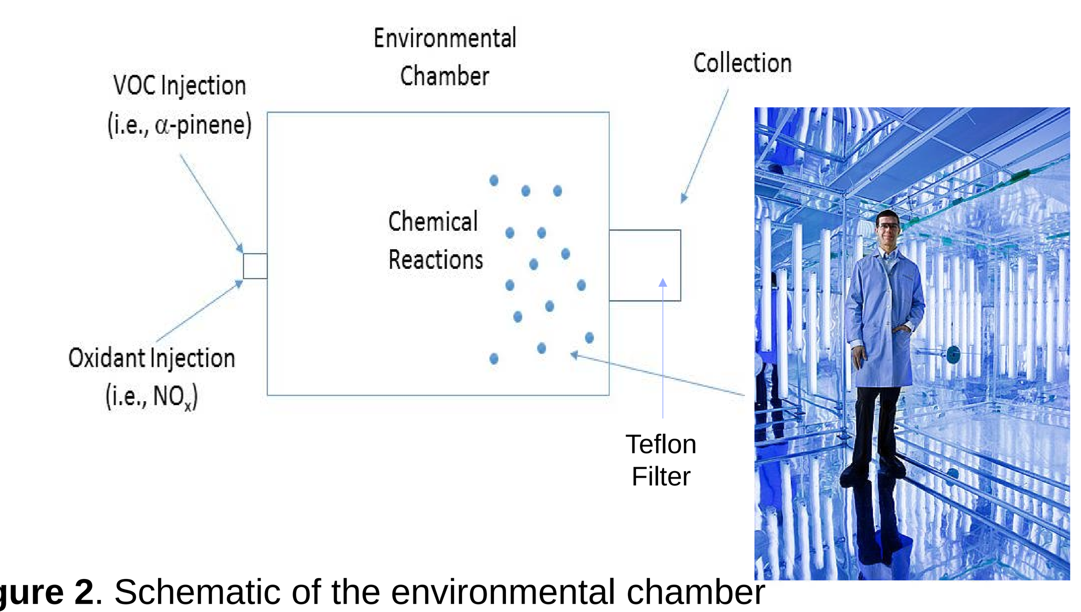

Figure 2. Schematic of the environmental chamber

Materials and Methods

$$2KI_{(aq)} + 2HCl_{(aq)} + H_2O_{2\,(aq)} \rightarrow I_{2\,(s)} + 2H_2O_{(l)} + 2KCl_{(aq)}$$

$$I_{2\,(s)} + KI_{(aq)} \rightarrow KI_{3\,(aq)}$$

Figure 3. Reactions used in the IS technique. Colorless H_2O_2 is converted into yellow colored I_3^- ions. The absorbance of the I_3^- ions is measured using a high resolution UV/Vis spectrometer.

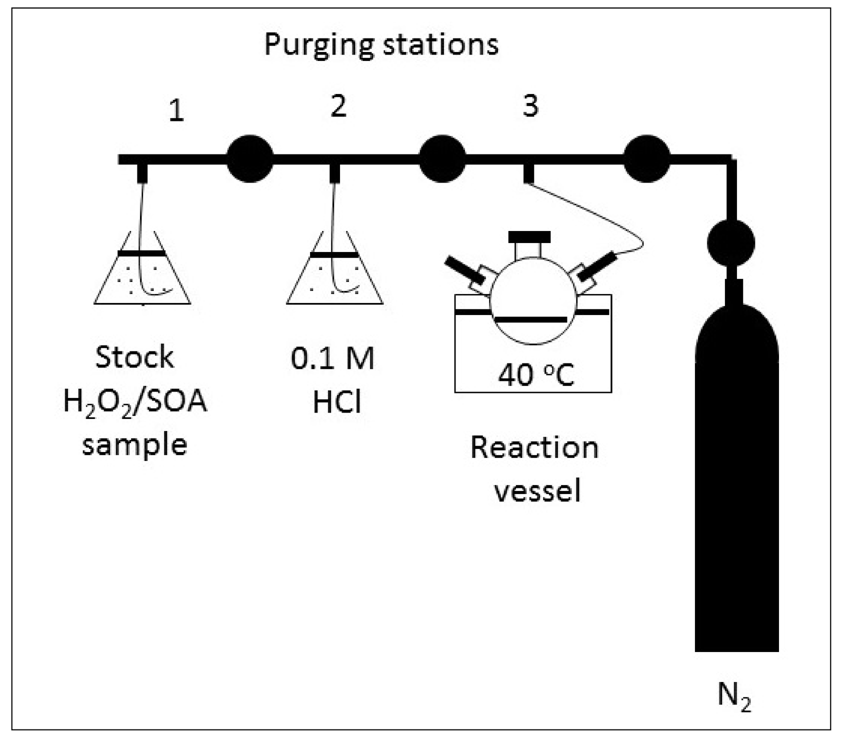

Figure 4. Experimental set-up used for the IS reactions.

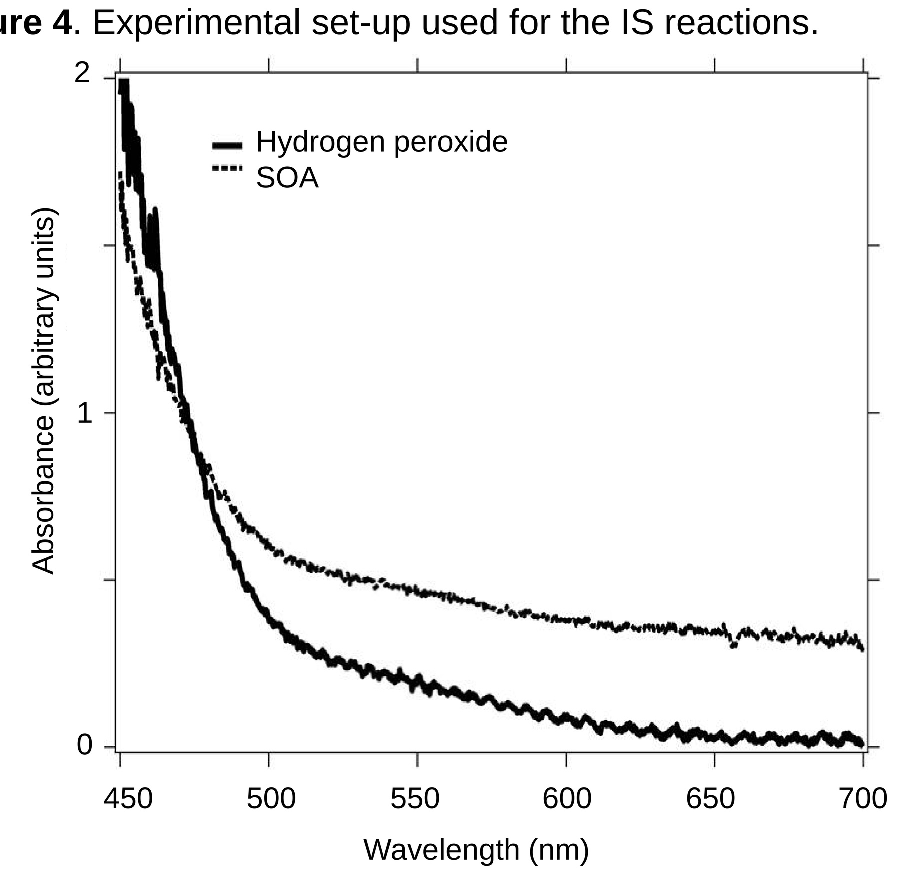

Figure 5. UV-Vis absorption spectrum of 15.62 μM H_2O_2 and SOA. The SOA was created using 10 ppb α-pinene, 1 ppm H_2O_2 and 5 ppb NO.

Results

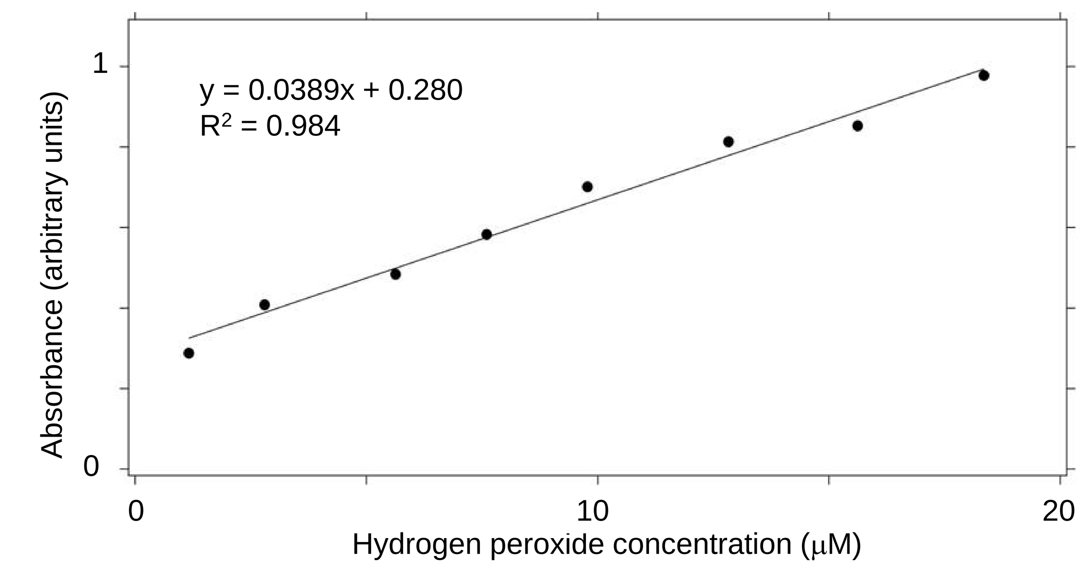

Figure 6. Hydrogen peroxide calibration curve ($A_{470} - A_{542}$)

VOC	VOC (ppb)	H2O2 (ppm)	O3 (ppb)	NO (ppb)	Cyclohexane/ MeOH (ppm)	Peroxide content (wt%), 300 g/mol
a-pinene	10	0	80	0	0	18.85
a-pinene	10	0	80	0	10	89.17
a-pinene	10	0	80	25	10	21.09
a-pinene	10	0	80	25	10	15.74
a-pinene	10	1	0	0	0	47.70
a-pinene	10	1	0	1	0	51.78
a-pinene	10	1	0	5	0	26.00
a-pinene	10	1	0	10	0	25.66
a-pinene	10	1	0	25	0	5.80
a-pinene	10	1	60	0	0	46.95
a-pinene	20	1	60	0	0	18.50
a-pinene	20	1	60	0	0	16.16
a-pinene	20	1	60	0	0	43.92
a-pinene	20	1	60	0	0	25.25
a-pinene	20	1	60	0	0	36.72
a-pinene	40	2	60	0	0	64.93
d-carene	10	0.25	0	0	0	47.49
d-carene	10	0.5	0	0	0	41.67
d-carene	10	1	0	0	0	26.24

Table 1. Estimated peroxide content in SOA generated during the SOAFFEE campaign.

Comparison With Literature

monoterpene	OH scavenger	RH (%)	$Y_{SOA/MT}$ [a] (%)	$Y_{OP/MT}$ [b] (%)	$Y_{OP/SOA}$ [c] (%)
α-pinene	cyclohexane	<0.5	48.7	4.6	28.6
		<0.5	45.2	7.5	49.8
		<0.5	50.6	5.2	30.8
		<0.5	39.5	7.3	55.5
		~50	51.9	7.1	41.3
		~50	41.5	7.9	57.3
	1-propanol	<0.5	48.8	7.0	43.0
		<0.5	47.1	10.1	64.5
	formaldehyde	<0.5	42.4	6.0	42.7
		<0.5	29.5	6.0	60.8
Δ-3carene	cyclohexane	<0.5	47.5	3.9	24.5
	1-propanol	<0.5	55.4	8.0	43.5
β-pinene	cyclohexane	<0.5	32.5	8.6	79.2
		<0.5	31.7	7.9	74.7
		~50	21.1	5.1	72.8
		~50	21.6	6.7	93.6
	1-propanol	<0.5	15.1	6.0	119.9
		<0.5	12.4	3.2	76.7
	formaldehyde	<0.5	10.2	3.0	88.3
		<0.5	8.3	2.1	77.1
sabinene	cyclohexane	<0.5	38.1	11.7	92.6
	1-propanol	<0.5	10.4	3.6	103.1

[a] Mass yield of SOA relative to reacted monoterpene [SOA (mass)/ reacted monoterpene (mass)] × 100. [b] Molar yield of SOA organic peroxides relative to reacted monoterpene [SOA peroxide (mol)/reacted monoterpene (mol)] × 100. [c] Mass yield of SOA organic peroxides relative to SOA [[SOA peroxide (mol) × MW (300 g mol^{-1})]/SOA mass (g)] × 100.

Table 2. Measured SOA and organic peroxide yields from reactions of monoterpenes with ozone (Docherty et. al, 2005).

Conclusions

The IS technique, used to measure the total peroxide content of SOA, was optimized. The hydrogen peroxide calibration curve constructed during the optimization process agreed well with the literature. SOA created during the SOAFFEE study were analyzed to determine their peroxide content. It was found that the SOA particles had similar amounts of peroxide as those created in previous experimental studies. The results presented here will aid in the determination of SOA composition and formation pathways. However, it is not sufficient to fully quantify the peroxide content of SOA. More UV/Vis absorbance measurements must be collected using SOA generated under different conditions. Furthermore, it is not clear if a hydrogen peroxide calibration curve is sufficient to predict total peroxide content in all types of SOA. Additional experimental methods can be used to validate the IS procedure.

References

1. Mertes, P., Pfaffenberger, L., Dommen, J., Kalberer, M., Baltensperger, U. (2012). Development of a sensitive long path absorption photometer to quantify peroxides in aerosol particles (Peroxide-LOPAP). Atmospheric Measurement Techniques, 5, 2339-2348.

2. Docherty, K.S., Wu, W., Lim, Y.B., and Ziemann, P.J. (2005). Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O_3. Environmental Science and Technology, 39, 4049-4059.

3. Xu, L., Kollman, M. S., Song, C., Shilling, J. E., & Ng, N. L. (2014). Effects of NO_x on the volatility of secondary organic aerosol from isoprene photooxidation. Environmental Science & Technology, 48(4), 2253-2262.

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