Effects of Selected Low Vapor Pressure –Volatile Organic Compounds (LVP-VOCs) on Atmospheric Photochemical Reactions

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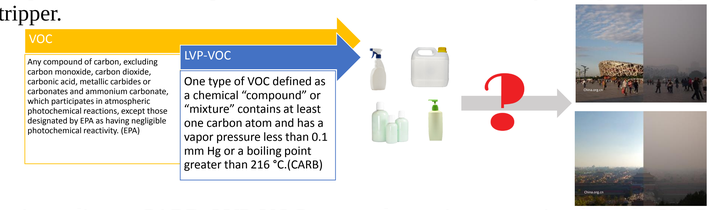
Background & Motivation

Volatile Organic Compounds (VOCs) play an important role in atmospheric photochemical oxidation, which results in the formation of Secondary Organic Aerosol(SOA) and ground-level ozone. Low Vapor Pressure Volatile Organic Compounds(LVP-VOCs) is a type of VOC with low volatility and it's an essential component in consumer products, like caulk remover, laundry detergent and paint stripper.



According to CARB, LVP-VOCs currently receive exemption from the VOC limits because of their relative lower vapor pressure and higher boiling point. However, recent study indicates that LVP-VOCs may have greater impacts on atmosphere that previous understood. Therefore, more qualitative and quantitative analysis of the availability of LVP-VOCs to atmospheric photochemical reactions should be conducted to provide more information on LVP-VOCs regulation.

Chemical Pathway of Ozone and SOA (Secondary Organic Aerosol) formation:

$$NO2 + h\nu \underset{k2}{\overset{J1}{\Rightarrow}} NO + O(3P)$$
$$O + O2 + M \underset{k3}{\Rightarrow} O3 + M$$
$$O3 + NO \Rightarrow O2 + NO2$$

$$[O3] = \frac{J1\,[NO2]}{K3[NO]}$$

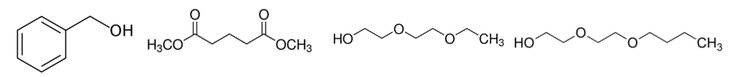
Fig 1. Photochemical reactions of NOx in atmosphere

Fig 2. SOA formation pathway from LVP-VOCs in atmoshphere

Methods & Facility

This research investigated atmospheric reactivity, SOA and ozone formation of LVP-VOCs. All photochemical reaction experiments were conducted with the advanced environmental chamber facility at University of California, Riverside(UCR) College of Engineering – Center for Environmental Research and Technology (CE-CERT).

The atmospheric reactivity of pure LVP-VOCs, **Benzyl Alcohol**, **DEGBE**, **DBE-5**, and **DEGEE**, were evaluated with the presence of an anthropogenic surrogate mixture, H2O2 and NOx (NO and NO2).



Benzyl Alcohol | Dimethyl Glutarate (DBE-5) | Di(ethylene glycol) ethyl ether DEGEE | Diethylene glycol butyl ether DEGBE

Gas and Particle phase Measurement		**Targets**
GC-FID	Agilent 6890 gas chromatography flame ionization dectector	Select hydrocarbons
SIFT-MS	SYFT Technologies Vocie200 Selected Ion Flow Tube Mass Spectrometer	Gas phase VOCs
Nox Analyzer	Thermoenvrionmental Model 42C	NO, NO2 and Nox concentrations
O3 Analyzer	Dasibi Model 1003-H	O3 concentration
SMPS	Home built scanning mobility particle sizer	Aerosol size distribution and concentration
APM-SMPS	Kanomax 3600 Aerosol Particle Mass Analyzer	Aerosol particle density
HR-ToF-AMS	Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer	Aerosol chemical composition

Table 1. Instruments used in UCR CE-CERT chamber

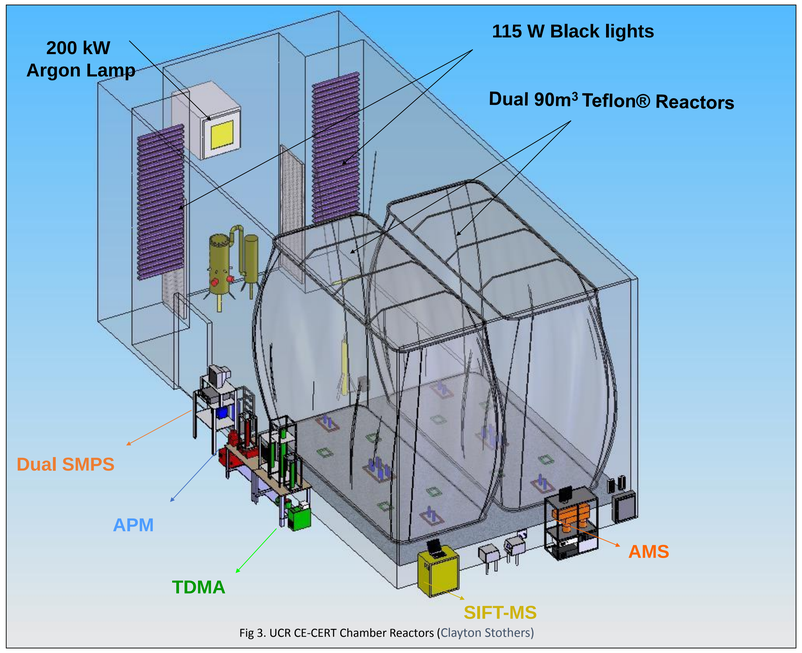


Fig 3. UCR CE-CERT Chamber Reactors (Clayton Stothers)

Experiments Results

All selected LVP-VOCs were injected with 1.1 ppm MOIR surrogate, 1.1 ppm H2O2 and 25 ppb NOx(NO and NO2 ratio is around 2) and reacted in the chamber reactors irradiated by UV.

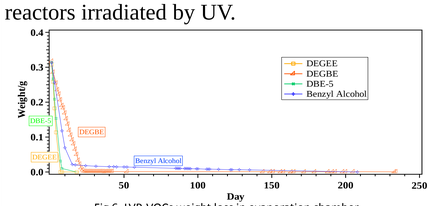


Fig 6. LVP-VOCs weight loss in evaporation chamber

The SOA formation from only experiments was $9\pm1\ \frac{um3}{cm3}$. Benzyl alcohol, DEGBE and DEGEE enriched the aerosol formation while DBE-5 showed no noticeable effect in forming SOA.

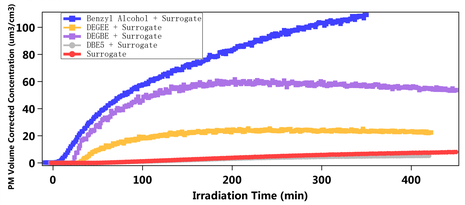


Fig 7. SOA formation from individual LVP-VOC with surrogate, H2O2 and NOx

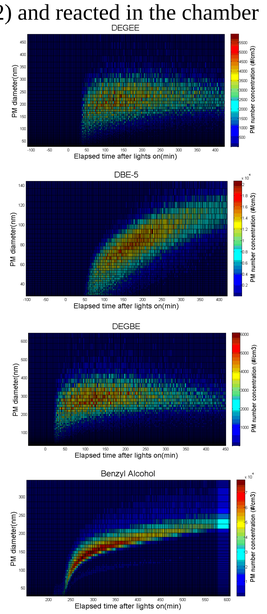


Fig 8. Real-time PM distribution

Run ID	Compound	Initial LVP-VOC	Initial NO	Initial NO2	ΔPM	Average Density	OSc
EPA2006(A)	Benzyl Alcohol + Surrogate	80	20.1	8.3	+	1.5	0.2
EPA2027(A)	DBE-5 + Surrogate	160	20.36	10.93	=	1.47	3.23
EPA2029(A)	DEGEE + Surrogate	40	21.92	9.49	+	1.4	0.39
EPA2030(A)	DEGBE + Surrogate	40	18,87	9.72	+	1.29	-0.26

Table 2. SOA characteristics

SOA Composition Analysis

Benzyl Alcohol in the chamber reactor forms significant amount SOA with the presence of surrogate and H2O2 compared to other LVP-VOCs or only surrogate. SOA(EPA2006) Chemical composition was characterized by High Resolution Time of Flight Aerosol Mass Spectrometer(HR-ToF-AMS).

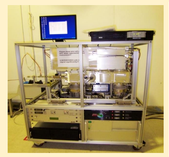


Fig 4. Aerodyne HR-ToF- AMS

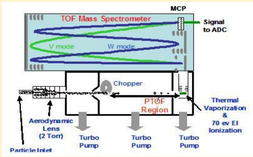


Fig 5. Schematic of the HR-ToF-AMS

AMS principle:

- Chamber air is sampled through an aerodynamic lens.
- Particle size is determined by flight time.
- Aerosol gets vaporized, ionized and then analyzed by mass spectrometer

[DeCarlo, et al, Anal Chem 2008]

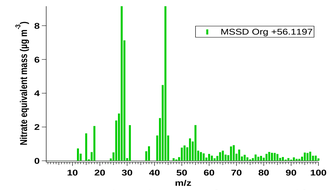


Figure 9. Mass-to-Charge distribution of organic aerosol fragment

m/z	Fragment to total organic	*formula*
44	16.31%	CO_2, C_2H_4O or C_3H_8
28	16.31%	CO
29	12.71%	CHO
43	8.00%	C_2H_3O or C_3H_7,
27	4.98%	C_2H_3
18	3.67%	H_2O
55	3.77%	C_3H_3O

Table 3. Possible decomposition ions

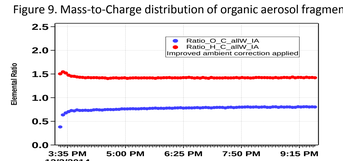


Figure 10. Atomic O/C and H/C ratios

$\overline{OS}_C$ indicates the oxidation state of organic particle, and can be obtained form the equation:

$$\overline{OS}_C = 2O/C - H/C$$ [DeCarlo et al. ACP2008]

The rise of $\overline{OS}_C$ could be caused by the breaking of CH bond or the formation of CO bond.

	O/C	*H/C*	$\overline{OS}_C$		*O/C*	*H/C*	$\overline{OS}_C$
Beginning	0.64	1.55	-0.27	*End*	0.81	1.42	0.20

Table 4. SOA parameters through the evolution of OA

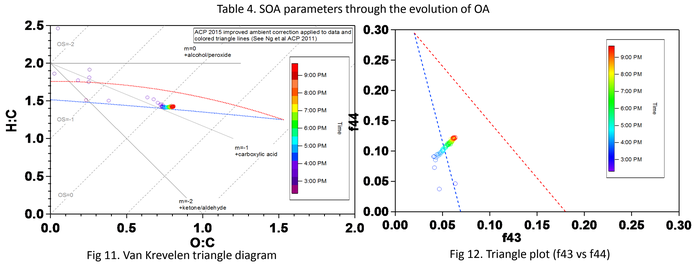


Fig 11. Van Krevelen triangle diagram

Fig 12. Triangle plot (f43 vs f44)

In fig 11, H:C vs O:C data levels off at OSc = 0, also consistent with the alcohol or peroxide addition group.

Benzyl alcohol SOA data falls into the lower part of the triangle in fig 12, suggesting that this SOA has large chance to be less oxidized or younger photo-chemically aged which is defined as SV-OA. [Ng et al. 2011]

Conclusion

- All four LVP-VOCs studied in this project evaporated (>95%) in less than a month;
- SOA formation from LVP-VOCs varies widely. Benzyl alcohol, DEGBE and DEGEE formed appreciable SOA while DBE-5 did not make much difference in SOA formation.

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