Photooxidation of Isoprene Epoxydiol (IEPOX)-Derived Secondary Organic Aerosol

Kelvin Bates*, Tran Nguyen, Matthew Coggon, Hanna Lignell, Xuan Zhang, Richard Flagan, Brian Stoltz, John Seinfeld, Paul Wennberg

California Institute of Technology, Pasadena, CA

*kelvin@caltech.edu Poster 2.AC.4

1. Background

What is IEPOX?

- Isoprene epoxydiols (IEPOX) are second-generation products of OH-initiated isoprene oxidation in low-NO environments (Figure 1).[1]
- Four IEPOX isomers can be formed from isoprene (Figure 2[2]).
- Chemical transport models suggest 239 ± 120 Tg is formed annually (Figure 3).
- IEPOX undergoes efficient reactive uptake onto wet particles, especially acidic or ammonium-containing aerosol,[3-5] where it forms tetrols and organosulfates.[6]

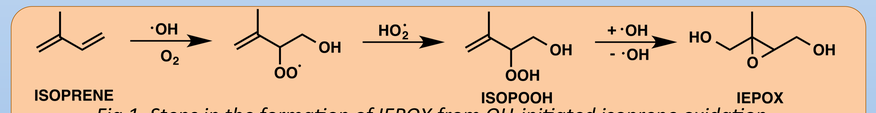


Fig 1. Steps in the formation of IEPOX from OH-initiated isoprene oxidation

Secondary Organic Aerosol (SOA) from IEPOX

- Subsequent oxidation of SOA is poorly understood; bulk-phase studies cannot replicate the liquid water content or gas-particle partitioning of aerosol.[7-10]
- Particle-phase oxidation is a potential route to gas phase compounds (e.g. acids) and highly oxidized SOA, which forms rapidly in the environment[11] but is difficult to mimic in chamber studies[12-13] and models.[14-16]
- IEPOX is generally assumed to stay in the particle while the O:C ratio increases.

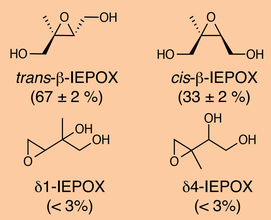


Fig 2. The isomers of IEPOX and their relative yields from ISOPOOH

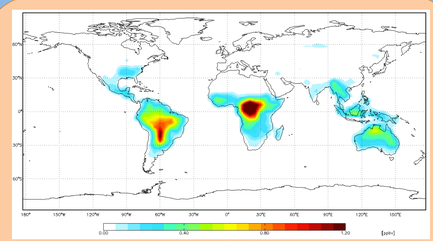


Fig 3. Average annual IEPOX concentration (ppbv), 0-1 km altitude, from a recently modified GEOS-Chem v.9-02 mechanism

In this study, we aim to investigate the oxidation of IEPOX in particles under atmospherically relevant conditions. We show that oxidation of IEPOX-derived SOA can be a significant source of highly oxygenated gas-phase compounds, especially organic acids, and that oxidation of organic material remaining in the particle phase proceeds most rapidly in sulfate-containing aerosol.

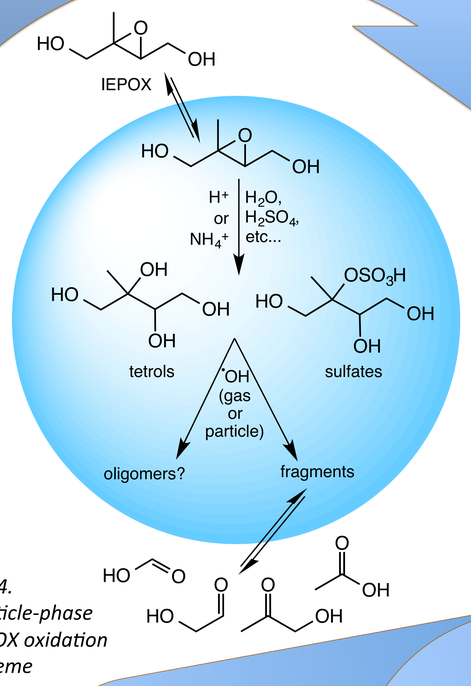


Fig 4. Particle-phase IEPOX oxidation scheme

2. General Methods

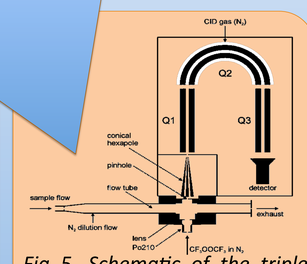


Fig 5. Schematic of the triple quadrupole chemical ionization mass spectrometer

Particle generation:

Trans- and *cis*-β-IEPOX were synthesized according to previously published methods.[17] Solutions of IEPOX (0.019 M) and a salt (0.038 M) were heated to 50 ˚C while stirring for 2 h prior to use. The resulting solution was introduced into the chamber or flow tube by atomization.

Oxidation:

Particles were oxidized by exposure to either gas-phase (chamber) or particle-phase (flow tube) OH radicals. OH was generated by photolysis of H_2O_2 under UV light.

Instrumentation:

- Gas-phase species were monitored with a triple quadrupole CF_3O^- chemical ionization mass spectrometer (**CIMS**; Varian/Caltech; Figure 5), alternating between scanning negative ions with *m/z* 50-250 and detecting specific fragmentation patterns from N_2-collision induced dissociation.
- Particle composition was monitored with a high-resolution time-of-flight aerosol mass spectrometer (**AMS**; Aerodyne Research Inc.; Figure 6), operated alternately in W mode (R≅3500 at *m/z* 200) and V mode (R≅2000 at *m/z* 200).
- Temperature and relative humidity of the chamber and flow tube were monitored throughout the experiments with a Vaisala HMM211 probe.

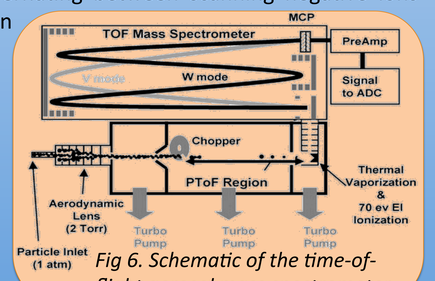


Fig 6. Schematic of the time-of-flight aerosol mass spectrometer

3a. Gas-phase OH

Methods:

Experiments were conducted in the 24 m^3 FEP-Teflon Caltech environmental chamber (Figure 7) at 23-25 ˚C. The chamber was first humidified to 50% RH, followed by atomization of the IEPOX/salt solution to ~35 μg/m^3 organics and introduction of 2 ppmv H_2O_2. Photooxidation lasted 6 hours and was monitored by CIMS and AMS.

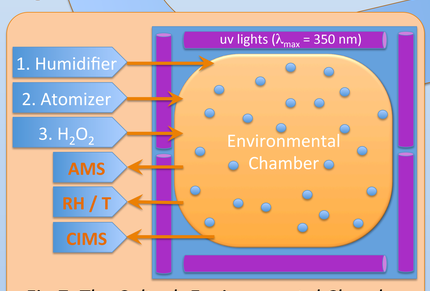


Fig 7. The Caltech Environmental Chamber

Table 1. Summary of chamber experiments.

Experimental Setup				Particle organics (μg/m³)*		Product yields (ppbv)*						
Expt #	Salt	IEPOX	H_2O_2	Initial	Consumed	Formic Acid	Acetic Acid	HAC	GLYC	PAA	*m/z* 187	*m/z* 189
1	$(NH_4)_2SO_4$	cis	gas	31.23	24.89	40.5	17.3	5.0	2.8	2.9	4.4	2.4
2	NH_4NO_3	cis	gas	44.47	24.48	54.1	18.1	4.6	2.8	2.6	2.8	0.1
3	NH_4Cl	cis	gas	50.69	21.96	78.7	22.0	6.5	4.2	2.7	4.5	0.0
4	$(NH_4)_2SO_4$	cis	gas	17.31	13.08	46.2	15.2	3.4	2.3	2.0	3.0	0.0
5	$(NH_4)_2SO_4$	trans	gas	45.39	34.14	59.8	24.0	8.6	4.7	4.1	6.6	8.9

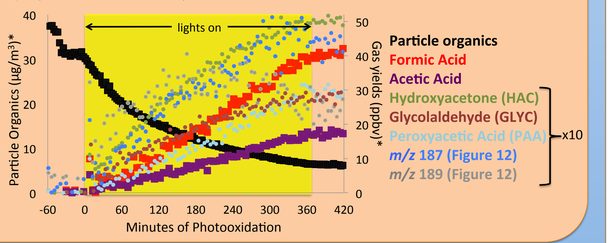
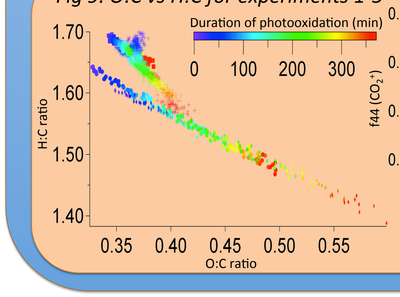


Fig 8. Particle organics & gas phase yields for experiment #1

Results: In each experiment, exposure to gas-phase OH caused significant loss of particle organic mass and generation of volatile organic compounds (VOCs) in the gas phase, especially acids (Figure 8, Table 1). Particle phase oxidation, measured in O:C and H:C ratios (Figure 9) and f43/f44 (Figure 10), was most prominent in ammonium sulfate particles.

Fig 9. O:C vs H:C for experiments 1-5



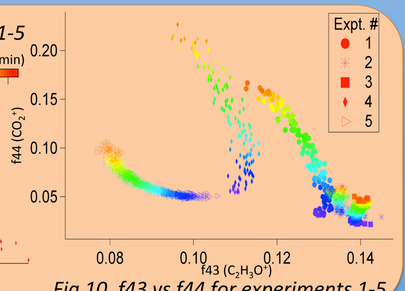


Fig 10. f43 vs f44 for experiments 1-5

3b. Particle-phase OH

Methods:

Experiments were conducted in an 8' long, 6" diameter pyrex flow tube, operated at a 36 min residence time (Figure 11). H_2O_2 (50 μM) was added to each IEPOX/salt solution immediately before atomization. Particles were photooxidized at three light levels for at least two hours each while being monitored by AMS and CIMS.

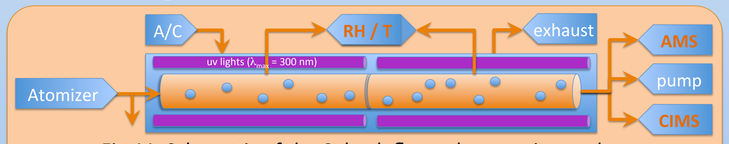


Fig 11. Schematic of the Caltech flow tube experimental setup

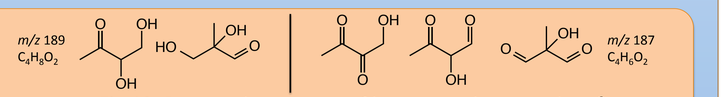


Fig 12. Proposed structures of large gas-phase products[2]

Results: Photooxidation with particle-phase OH generated substantial amounts of organic acids and other gas-phase VOCs, especially one detected at *m/z* 189 (Figure 12), all of which scaled positively with light exposure (Figures 13-14). As with gas-phase OH oxidation, major VOC products were the same across salt types and IEPOX isomers.

Fig 13. Overview of VOC yields from flow tube experiments.

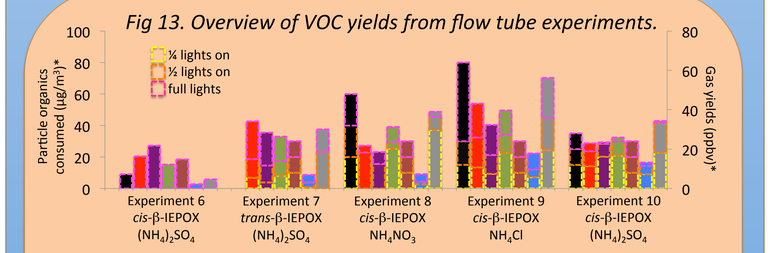
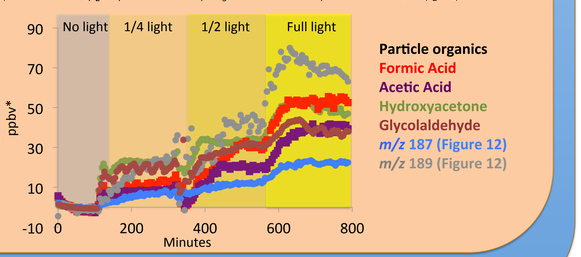


Fig 14. Particle organics & gas phase yields for experiment #9



*Errors in reported ppbv (CIMS) are dominated by 30% uncertainty in instrument sensitivity; errors in reported particle organics (AMS) are dominated by uncertainties in collection efficiency of 30% & 50% for chamber and flow tube respectively.

4. Discussion

- ★ Particle organic mass attributed to IEPOX-derived SOA cannot necessarily be assumed to remain in the particle phase under photooxidative conditions.
  - Incorporating this particle-to-gas transfer into models should be a high priority
- ★ Oxidation of IEPOX-derived SOA may provide a significant source of gas-phase oxidized VOCs, especially small organic acids.
  - This may help account for the poorly understood budget of gas-phase organic acids in remote areas
- ★ Oxidation of particle-phase organics proceeds more rapidly in ammonium sulfate particles than those with other anions.

5. Sources

1. Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kürten, A.; St Clair, J. M.; Seinfeld, J. H.; Wennberg, P. O. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science (New York, N.Y.)* **2009**, *325*, 730-3.
2. Bates, K. H.; Crounse, J. D.; St Clair, J. M.; Bennett, N. B.; Nguyen, T. B.; Seinfeld, J. H.; Stoltz, B. M.; Wennberg, P. O. Gas phase production and loss of isoprene epoxydiols. *J. Phys. Chem. A* **2014**, *118* (7), 1237-46.
3. Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D. Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed reactive uptake studies with authentic compounds. *Environ. Sci. Technol.* **2012**, *46*, 250-258.
4. Nguyen, T. B.; Coggon, M. M.; Bates, K. H.; Zhang, X.; Schwantes, R. H.; Schilling, K. A.; Loza, C. L.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds. *Atmos. Chem. Phys.* **2014**, *14*, 3497-3510.
5. Gaston, C. J.; Riedel, T. P.; Zhang, Z.; Gold, A.; Surratt, J. D.; Thornton, J. A. Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles. *Environ. Sci. Technol* **2014**, *48*, 11178-11186.
6. Surratt, J. D.; Chan, A. W. H.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6640-6645.
7. Daumit, K. E.; Carrasquillo, A. J.; Hunter, J. F.; Kroll, J. H. Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution. *Atmos. Chem. Phys. Disc.* **2014**, *14*, 13649-13680.
8. Ervens, B.; Turpin, B. J.; Weber, R. J. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field, and model studies. *Atmos. Chem. Phys.* **2011**, *11*, 11069-11102.
9. Ervens, B.; Volkamer, R. Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. *Atmos. Chem. Phys.* **2010**, *10* (17), 8219-8244.
10. Nguyen, T. B.; Coggon, M. M.; Flagan, R. C.; Seinfeld, J. H. Reactive uptake and photo-fenton oxidation of glycolaldehyde in aerosol liquid water. *Environ. Sci Technol.* **2013**, *47*, 4307-4316.
11. Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geophys. Res. Lett.* **2006**, *33*.
12. Heald, C. L.; Kroll, J. H.; Jimenez, J. L.; Docherty, K. S.; DeCarlo, P. F.; Aiken, A. C.; Chen, Q.; Martin, S. T.; Farmer, D. K.; Artaxo, P. A simplified description of the evolution of organic aerosol composition in the atmosphere. *Geophys. Res. Lett.* **2010**, *37*.
13. Kroll, J. H.; Donahue, N. N.; Jimenez, J. L.; Kessler, S. H.; Canagaratna, M. R.; Wilson, K. R.; Altieri, K. E.; Mazzoleni, L. R.; Wozniak, A. S.; Bluhm, H.; Mysak, E. R.; Smith, J. D.; Kolb, C. E.; Worsnop, D. R. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chemistry* **2011**, *3*, 133-139.
14. Dzepina, K.; Cappa, C. D.; Volkamer, R.; Madronich, S.; DeCarlo, P. F.; Zaveri, R. A.; Jimenez, J. L. Modeling the multiday evolution and aging of secondary organic aerosol during MILAGRO 2006. *Environ. Sci. Technol.* **2011**, *45*, 3496-3503.
15. Hodzic, A.; Jimenez, J. L.; Madronich, S.; Canagaratna, M. R.; DeCarlo, P. F.; Kleinman, L.; Fast, J. Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation. *Atmos. Chem. Phys.* **2010**, *10*, 5491-5514.
16. Lee-Taylor, J.; Madronich, S.; Aumont, B.; Baker, A.; Camredon, M.; Hodzic, A.; Tyndall, G. S.; Apel, E.; Zaveri, R. A. Explicit modeling of organic chemistry and secondary organic aerosol partitioning for Mexico City and its outflow plume. *Atmos. Chem. Phys.* **2011**, *11*, 13219-13241.
17. Zhang, Z.; Lin, Y.-H.; Zhang, H.; Surratt, J. D.; Ball, L. M.; Gold, A. Technical Note: Synthesis of isoprene atmospheric oxidation products: isomeric epoxydiols and the rearrangement products cis- andtrans-3-methyl-3,4-dihydroxytetrahydrofuran. *Atmos. Chem. Phys.* **2012**, *12*, 8529-8535.