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

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Background

What is IEPOX?

- Isoprene epoxydiols (IEPOX) are volatile organic compounds (VOCs) produced in the OH-initiated oxidation of isoprene in low-NO environments (Figure 1).[1]
- Two isomers of IEPOX form from isoprene: *trans*- and *cis*-β, in a ratio of 2:1.[2]
- Models suggest that 240 ± 120 Tg of IEPOX forms annually (Figure 2).

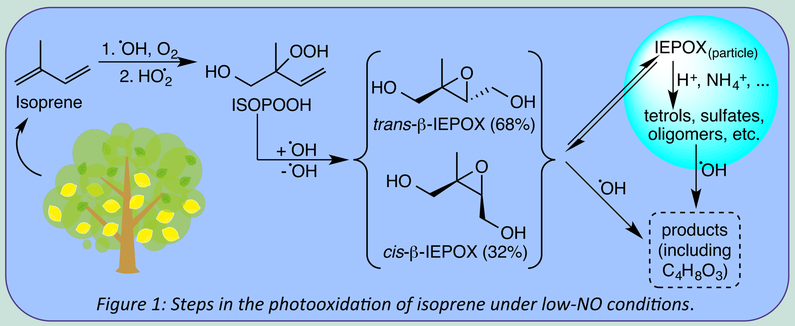

Figure 1: Steps in the photooxidation of isoprene under low-NO conditions.

Atmospheric Fate of IEPOX

- In the gas phase: IEPOX can be further oxidized by OH; previous measurements of rates and products have varied widely.[2-3]
- In particles: IEPOX undergoes efficient reactive uptake onto wet particles, especially acidic or ammonium-containing aerosol,[4-6] where it may form tetrols, organosulfates, and oligomers.[7] Subsequent oxidation of IEPOX-derived SOA is poorly understood; particle-phase reactions may lead to the production of highly oxidized SOA and/or gas-phase VOCs,[8] but these processes are difficult to reproduce in bulk experiments,[9-12] chamber studies,[13-14] and models.[15-17]

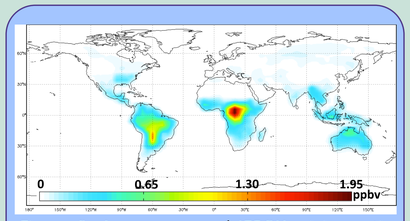

Figure 2: Average annual IEPOX mixing ratio (ppbv) at 0-1 km altitude, from a recently modified GEOS-Chem v9-02 mechanism.

In this study, we characterize the VOCs produced when IEPOX is oxidized in both the gas- and particle-phase. We show:

A: Product yields from the gas-phase oxidation of IEPOX by OH

B: Major products from the oxidation of IEPOX-derived SOA by OH

C: Oxidation rates of various $C_4H_8O_3$ isomers, the major products of IEPOX + OH

D: Results from a chemical transport model updated to include the chemistry in parts (A) and (C)

Results

A: Gas-Phase IEPOX + OH Products

Eight experiments were performed to examine the products of IEPOX oxidation by OH in the gas phase. CIMS sensitivities of products were estimated from ab initio calculations of dipole moment and polarizability.[22] Major products identified in these experiments and their first-generation yields are shown in Table 1. The yields reported in Table 1 are inverse-variance-weighted means of yields from each IEPOX isomer's experiments. $MVK(OH)_2$ and $MACR(OH)_2$, the two isomers of $C_4H_8O_3$, were distinguished by GC-CIMS, as shown in Figure 5.

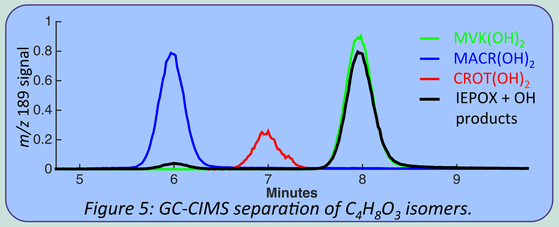

Figure 5: GC-CIMS separation of $C_4H_8O_3$ isomers.

C: $C_4H_8O_3$ + OH Rate Constants and Products

Eight experiments were performed on the three synthesized isomers of $C_4H_8O_3$ to investigate their rates of oxidation by OH. Rate coefficients were calculated relative to that of OH + propene (2.62×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 299 K),[23] which was injected into the chamber along with the compound of interest (Figure 7). Inverse-variance-weighted mean OH oxidation rate constants for the three $C_4H_8O_3$ isomers are shown in Table 2, along with rates estimated by a structure-activity relationship (SAR)[24] and those currently used in the Master Chemical Mechanism.[25]

Two additional experiments were performed to investigate the products of OH + $MVK(OH)_2$, the $C_4H_8O_3$ isomer produced in greatest abundance from IEPOX. As shown in Figure 8, the reaction produces compounds detected at *m/z* 187, likely $C_4H_6O_3{\bullet}CF_3O^-$, in quantitative yield. Proposed structures of these compounds are shown in Figure 9, along with yields estimated by SAR.[24]

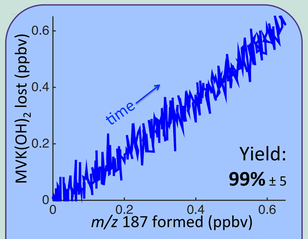

Figure 8: $MVK(OH)_2$ + OH produces a compound detected at m/z 187.

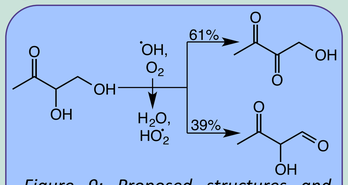

Figure 9: Proposed structures and yields of the $C_4H_6O_3$ compounds produced by $MVK(OH)_2$ + OH.

	% yields from: *cis*-β	*trans*-β
IEPOX + ˙OH → + H_2O + HO_2	20 ± 7	17 ± 2
+ CO + OH	43 ± 13	36 ± 4
+ CO + OH	5 ± 2	9 ± 1
+ HCHO + OH	8 ± 2	8 ± 1
hydroxyacetone + glyoxal + OH	8 ± 1	16 ± 1
glycolaldehyde + methylglyoxal + OH	16 ± 5	14 ± 7

Table 1: Major products, with yields, of the reaction of IEPOX and OH. A detailed mechanism can be found in Bates et al.[2]

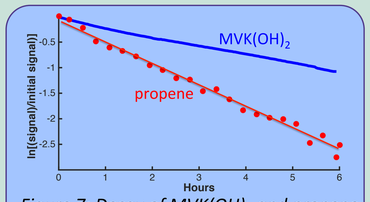

Figure 7: Decay of $MVK(OH)_2$ and propene over the course of photooxidation.

k_{OH} (10^{-11} cm^3 $molec^{-1}$ s^{-1})	This work	MCM[25]	SAR[24]
$MVK(OH)_2$	1.10 ± 0.12	1.88	1.067
$MACR(OH)_2$	3.0 ± 0.65	3.42	2.523
$CROT(OH)_2$	3.7 ± 0.63	7.01	3.582

Table 2: $C_4H_8O_3$ + OH rate coefficients.

B: IEPOX-derived SOA + OH Products

Four flow tube experiments were performed to investigate the gas-phase products of IEPOX-derived SOA oxidation, using both *cis*- and *trans*-β-IEPOX and three different inorganic salts. In each experiment, particle oxidation generated VOCs in high yields (Figure 6), which were largely the same across salt types and IEPOX isomers. As in gas phase oxidation, $C_4H_8O_3$ was the predominant product.

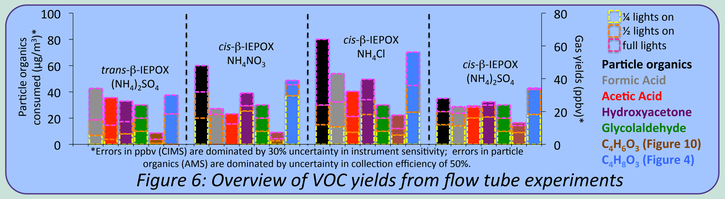

Figure 6: Overview of VOC yields from flow tube experiments

D: GEOS-Chem Modeling

Results from parts (A) and (C), as well as previously published IEPOX oxidation research,[2] were incorporated into GEOS-Chem v9-02, a chemical transport model. Further oxidative chemistry of the $C_4H_8O_3$ and $C_4H_6O_3$ isomers was predicted by structure-activity relationship.[24] Simulations were run at a resolution of 4° latitude × 5° longitude × 47 vertical layers, with a 1.5-year initialization period followed by a complete global simulation for the duration of 2012. Resulting global mixing ratios and production of $C_4H_8O_3$ and $C_4H_6O_3$ compounds are shown in Figure 10.

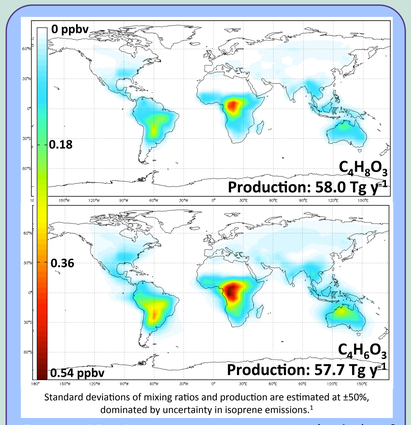

Figure 10: Average mixing ratio (ppbv) of $C_4H_8O_3$ (top) and $C_4H_6O_3$ (bottom) compounds at 0-1 km altitude in 2012, from a modified GEOS-Chem v9-02 mechanism.

Conclusions

- Two $C_4H_8O_3$ dihydroxycarbonyl isomers are the dominant products of gas-phase IEPOX oxidation by OH, and major products of IEPOX-derived SOA oxidation as well.
- Oxidation rates, and some products, of relevant $C_4H_8O_3$ dihydroxycarbonyl compounds have been experimentally determined.
- Chemical transport modeling suggests that cumulative global production of $C_4H_8O_3$ dihydroxycarbonyl compounds amounts to 58 Tg y^{-1}.

Methods

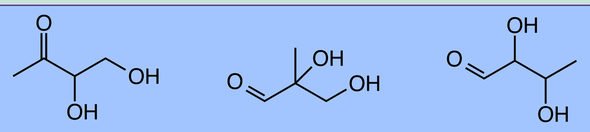

Figure 3: Isomers of $C_4H_8O_3$ synthesized and investigated in this study.

Synthesis

Three $C_4H_8O_3$ dihydroxycarbonyls (Figure 3) were synthesized for use in chamber studies. The synthetic route (Figure 4), adapted from previous literature,[18-20] was identical for the three isomers. *Trans*- and *cis*-β-IEPOX were also synthesized according to previously published methods.[2,21]

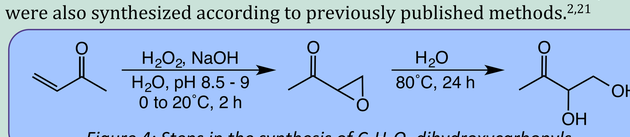

Figure 4: Steps in the synthesis of $C_4H_8O_3$ dihydroxycarbonyls.

Gas-Phase Chamber Studies

Experiments were conducted in a 0.85 m^3 Teflon-FEP chamber at 1 atm and 21-23 ˚C. H_2O_2 (2.5 ppm ±10%) provided the source of HO_x for oxidation upon photolysis under UV lights. For IEPOX oxidation experiments, 30 ppb ±50% of one IEPOX isomer was injected into the chamber before photooxidation. For $C_4H_8O_3$ oxidation experiments, propene was also injected (~100 ppb) for comparison of oxidation rates. Photooxidation lasted 1.5-6 h. The chamber's contents were monitored by time-of-flight CF_3O^- chemical ionization mass spectrometry (CIMS, Tofwerk/Caltech), gas chromatography with flame-ionization detection (GC-FID, Agilent 5890 II), and NO_x Monitor (Teledyne 200EU). Before and after photooxidation, chamber contents were also analyzed by gas chromatography with detection by CIMS (GC-CIMS), which allowed for separation of IEPOX and $C_4H_8O_3$ isomers.[2]

Particle-Phase Flow Tube Studies

Experiments were conducted in an 8 foot long, 6 inch diameter pyrex flow tube, operated at a 36 min residence time, 23-25 ˚C and 1 atm. Atomizing solutions were prepared by mixing one IEPOX isomer (0.019 M) with an inorganic salt (0.038 M), heating to 50 ˚C while stirring for 2 h, and finally adding H_2O_2 (50 μM) immediately before the experiment to provide particle-phase OH upon photolysis. Particles were generated by atomizing the resulting solution into the flow tube, where particles were photooxidized at three light levels for at least two hours each while being monitored by CIMS and high-resolution time-of-flight aerosol mass spectrometry (AMS). Temperature and RH was monitored throughout the experiments with a Vaisala HMM211 probe.

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. Jacobs, M. I.; Darer, A. I.; Elrod, M. J. Rate constants and products of the OH reaction with isoprene-derived epoxides. *Environ. Sci. Technol.* **2013**, *47*, 12868-76.
4. 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.
5. 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.
6. 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.
7. 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.
8. 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*.
9. 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.
10. 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.
11. 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.
12. 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.
13. 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*.
14. 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.
15. 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.
16. 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.
17. 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.
18. Antczak, K.; Kingston, J. F.; Fallis, A. G. Addition initiated ring closure: synthesis of substituted spiro[2.4]hepta-4,6-dienes via cyclopentadiene intermediates from fulvene precursors. *Can. J. Chem.* **1984**, *62*, 2451-5.
19. Payne, G. Reactions of hydrogen peroxide. V. Alkaline epoxidation of acrolein and methacrolein. *J. Am. Chem. Soc.* **1959**, *81*, 4901-4.
20. Wang, Z.; Cui, Y.-T.; Xu, Z.-B.; Qu, J. Hot water-promoted ring-opening of epoxides and aziridines by water and other nucleophiles. *J. Org. Chem.* **2008**, *73*, 2270-4.
21. 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*, 8529-35.
22. Su, T.; Chesnavich, W. J. Parameterization of the ion-polar molecule collision rate constant by trajectory calculations. *J. Chem. Phys.* **1982**, *76*, 5183-5.
23. Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103* (12), 4605-4638.
24. Kwok, E. S. C.; Atkinson, R. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update. *Atmos. Environ.* **1995**, *29*, 1685–1695.
25. Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* **2003**, *3*, 161-180.