Isoprene Oxidation Mechanisms and Secondary Organic Aerosol Formation Under HO_2-Dominated Conditions

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Kelvin Hamilton Bates

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Kelvin Hamilton Bates
ORCID: 0000-0001-7544-9580

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ABSTRACT

Isoprene, a volatile hydrocarbon emitted by plants, represents the single most abundant source of non-methane organic carbon to the atmosphere. After its rapid oxidation by OH radicals in the troposphere, isoprene may follow any of a number of complex reaction mechanisms to form more highly functionalized products, depending in large part on the relative abundance of reactive radicals such as HO_2 and NO; some of these products can be sufficiently water-soluble, non-volatile, and/or reactive to partition into atmospheric particles and contribute to the creation of secondary organic aerosol (SOA). In this work, I explore the gas-phase oxidation mechanisms and SOA formation potential of second- and later-generation products formed in the HO_2-dominated reaction cascade, which predominates in remote regions and is estimated to account for >40% of isoprene oxidation. Pure standards of significant isoprene products, such as isoprene epoxydiols (IEPOX) and C_4 dihydroxycarbonyl compounds, are synthesized, and the rates and product yields of their gas-phase reactions with OH are measured by CF_3O^- chemical ionization mass spectrometry in environmental chamber experiments. Results are compared to field observations from the Southern Oxidant and Aerosol Study in the Southeastern United States, where significant concentrations of these compounds were detected, and are integrated into a global chemical transport model to investigate their effects throughout the atmosphere. Further, the results from these and other gas-phase kinetic and product studies are incorporated into an explicit isoprene oxidation mechanism, designed to simulate the effects of isoprene chemistry on oxidant concentrations and to produce accurate representations of products known to be involved in condensed phase processes, including IEPOX. Finally, additional chamber experiments with synthetic IEPOX and inorganic seed aerosol are performed to derive particle uptake coefficients and examine the effects of particle pH, liquid water content, and chemical composition on IEPOX-SOA formation, using aerosol mass spectrometry and differential mobility analysis. The gas- and particle-phase reaction rates and product yields reported herein, along with the explicit model, provide important constraints on the fate of isoprene-derived carbon in the atmosphere and on the influence the HO_2-dominated isoprene oxidation pathway exerts on SOA and oxidant budgets.

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Liu, Y., J. Brito, M. R. Dorris, J. C. Rivera-Rios, R. Seco, K. H. Bates, P. Artaxo, S. Duvoisin, F. N. Keutsch, S. Kim, A. H. Goldstein, A. B. Guenther, A. O. Manzi, R. A. F. Souza, S. R. Springston, T. B. Watson, K. A. McKinney, and S. T. Martin (2016). “Isoprene photochemistry over the Amazon rainforest”. In: *Proc. Nat’l. Acad. Sci.* 113.22, pp. 6125–6130. DOI: 10.1073/pnas.1524136113.
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Nguyen, T. B., G. S. Tyndall, J. D. Crounse, A. P. Teng, K. H. Bates, R. H. Schwantes, M. M. Coggon, L. Zhang, P. Feiner, D. O. Milller, K. M. Skog, J. C. Rivera-Rios, M. Dorris, K. F. Olson, A. Koss, R. J. Wild, S. S. Brown, A. H. Goldstein, J. A. de Gouw, W. H. Brune, F. N. Keutsch, J. H. Seinfeld, and P. O. Wennberg (2016). “Atmospheric fates of Criegee intermediates in the ozonolysis of isoprene”. In: *Phys. Chem. Chem. Phys.* 18.15, pp. 10241–10254. DOI: 10.1039/C6CP00053C.
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St. Clair, J. M., J. C. Rivera-Rios, J. D. Crounse, H. C. Knap, K. H. Bates, A. P. Teng, S. Jorgensen, H. G. Kjaergaard, F. N. Keutsch, and P. O. Wennberg (2015). “Kinetics and products of the reaction of the first-generation isoprene hydroxy hydroperoxide (ISOPOOH) with OH”. In: *J. Phys. Chem. A* 120.9, pp. 1441–1451. doi: 10.1021/acs.jpca.5b06532.

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NOMENCLATURE AND ABBREVIATIONS

2MGA. 2-methylglyceric acid; an oxidation product of isoprene known to contribute to isoprene-derived SOA mass, with chemical formula $C_4H_8O_4$.

ABS. Ammonium bisulfate; $(NH_4)HSO_4$.

Aerosol. Fine solid or liquid particles suspended in a gas. The term aerosol can refer either to the particles themselves or the colloid of particles and gas.

AMS. Aerosol mass spectrometer; an instrument that measures the size and chemical composition of nonrefractory sub-micron particles in real time by coupling a particle time-of-flight separator, a filament to thermally vaporize particles and ionize their constituents *via* electron impact ionization, and a mass analyzer to determine the mass-to-charge ratios of the fragment ions.

APN. Acylperoxy nitrate; a class of compounds (including PAN and MPAN) containing the $C(=O)OONO_2$ moiety formed in the reaction of acylperoxy radicals with NO_2, which are often respiratory and eye irritants and a key component of photochemical smog. Also called peroxyacyl nitrate.

AS. Ammonium sulfate; $(NH_4)_2SO_4$.

BBOA. Biomass burning organic aerosol; primary or secondary organic particulate matter emitted from the combustion of living or dead vegetation.

BOAS. Biological and oceanic atmospheric study; an airborne atmospheric field campaign based in Marina, CA, that took place in July and August of 2015.

CCN. Cloud condensation nuclei; atmospheric particles onto which water vapor may condense to form cloud droplets.

CI*. Activated or excited Criegee intermediate; the energetic carbonyl oxide formed following the decomposition *via* retro 1,3 cycloaddition of a primary ozonide (POZ) during an ozonolysis reaction, which may have enough internal vibrational energy to rapidly isomerize or dissociate.

CIMS. Chemical ionization mass spectrometer; an instrument that ionizes analyte gases by colliding them with charged reagent gas molecules (*e.g* H_3O^+ in PTR-MS, or CF_3O^- in the Caltech CIMS) and then measures the mass-to-charge ratios of analyte ions.

CPC. Condensation particle counter; an instrument that counts particles by first growing them *via* supersaturated vapor condensation and then detecting them by laser scattering.

CTM. Chemical transport model; a numerical computer model used to simulated the stocks and fluxes of chemicals in the atmosphere.

DMA. Differential mobility analyzer; an instrument that separates charged particles based on their mobility in an electric field.

E-PEACE. Eastern Pacific Emitted Aerosol Cloud Experiment; an atmospheric field campaign based in Marina, CA, that took place in July and August of 2011, with airborne and ship-based measurements.

ELVOC. Extra low volatility organic compound; generally defined as any organic compound found in the atmosphere with a saturation vapor mass concentration $C^* \leq 10^{-3.5}$ μg m^{-3}.

ESI. Electrospray ionization; a soft ionization technique by which a solute is ionized in its passage through a charged capillary tip, then aerosolized into a spray of droplets that evaporate to form gaseous ions.

FIXCIT. Focused Isoprene eXperiment at the California Institute of Technology; an atmospheric chamber campaign that consisted of 26 environmental chamber experiments conducted over the course of January of 2014.

GC. Gas chromatography; an instrumental technique to separate gas-phase analytes by passing them through a column coated with a stationary phase with which the analytes interact, and generally increasing the column temperature to elute analytes.

GEOS-Chem. A 3-D chemical transport model that simulates atmospheric chemical composition using meteorological input from the Goddard Earth Observing System.

GLYC. Glycolaldehyde; a volatile organic compound with the chemical formula $C_2H_4O_2$, and a common oxidation product of larger VOCs, including isoprene.

GLYX. Glyoxal; a volatile organic compound with the chemical formula $C_2H_2O_2$, and a common oxidation product of larger VOCs, including isoprene.

GOAmazon. Green Ocean Amazon; an atmospheric field campaign based in various locations near Manaus, Brazil, that took place between January of 2014 and November of 2015, with airborne and ground-based measurements.

H/C. Hydrogen-to-carbon ratio, usually in reference to bulk organic aerosol as measured by aerosol mass spectrometry.

HAC. Hydroxyacetone; a volatile organic compound with the chemical formula $C_2H_4O_2$, and a common oxidation product of larger VOCs, including isoprene.

High-NO. Conditions under which organic peroxy radicals in the gas phase react primarily with nitric oxide. The exact NO concentration at which this occurs depends on a number of conditions, but is generally on the order of $\gtrsim$1 ppb in the troposphere.

HMML. Hydroxymethyl-methyl-α-lactone; a suspected product of MPAN photooxidation that may contribute to isoprene-derived SOA, with chemical formula $C_4H_6O_3$.

HO_2-dominated. Conditions under which organic peroxy radicals in the gas phase react primarily with the hydrogen dioxide radical.

HO_x. The hydrogen oxide radical family, defined as the sum of the hydroxyl (OH) and hydrogen dioxide (HO_2) radicals.

HPALD. Isoprene hydroperoxy aldehyde; a first-generation stable atmospheric product of isoprene photooxidation under low-NO conditions with chemical formula $C_5H_8O_3$. Two isomers of HPALD are known to form in the atmosphere from the isomerization of Z-δ-ISOPOO, while two others are expected to form as second-generation isoprene oxidation products from the reaction of ISOPOOH with OH.

HR. High resolution; in reference to mass spectrometry, refers to methods with mass resolving power $>10^4$ m/Δm.

ICN. Isoprene carbonylnitrate; a first-generation stable atmospheric product of isoprene's reaction with NO_3, followed by O_2 addition and reaction with NO or RO_2. Four isomers of ICN, with chemical formula $C_5H_7O_4N$, are known to form in the atmosphere.

IEPOX. Isoprene epoxydiol; a second-generation stable atmospheric product of isoprene photooxidation under HO_2-dominated conditions with chemical formula $C_5H_{10}O_3$, and a major SOA precursor in the low-NO isoprene reaction pathway. Four isomers of IEPOX can form in the atmosphere from the reaction of ISOPOOH or IHN with OH.

IHN. Isoprene hydroxynitrate; a first-generation stable atmospheric product of isoprene photooxidation under high-NO conditions with chemical formula $C_5H_9O_4N$, and a major contributor to NO_x transport and removal from isoprene oxidation. Eight isomers of IHN can form in the atmosphere from the reaction of ISOPOO with NO or the reaction of isoprene nitrooxy peroxy radicals with RO_2.

IHNE. Isoprene hydroxynitrooxyepoxide; a second-generation stable atmospheric product of isoprene's oxidation by NO_3 with chemical formula $C_5H_9O_5N$. Six isomers of IHNE can form in the atmosphere from the reaction of IPN with OH.

IPN. Isoprene hydroperoxynitrate; a first-generation stable atmospheric product of isoprene's reaction with NO_3, followed by O_2 addition and reaction with HO_2. Six isomers of IPN, with chemical formula $C_5H_9O_5N$, are known to form in the atmosphere.

ISOPN. Isoprene hydroxynitrate; see IHN.

ISOPOO. Isoprene hydroxyperoxy radical; a radical species formed following the addition of OH and O_2 to isoprene. Eight isomers of ISOPOO can form in the atmosphere, and their relative ambient abundance depends on the species' lifetime against isomerization and reaction with NO, HO_2, and RO_2.

ISOPOOH. Isoprene hydroxyhydroperoxide; a first-generation stable atmospheric product of isoprene photooxidation under HO_2-dominated conditions with chemical formula $C_5H_{10}O_3$. Eight isomers of ISOPOOH can form in the atmosphere from the reaction of ISOPOO with HO_2.

Isoprene. A volatile unsaturated hydrocarbon with chemical formula C_5H_8, emitted to the atmosphere primarily by deciduous trees in quantities exceeding 500 Tg y^{-1}.

IVOC. Intermediate volatility organic compound; generally defined as any organic compound found in the atmosphere with a saturation vapor mass concentration in the range of $10^{2.5}$ μg m^{-3} $\leq C^* \leq$ $10^{6.5}$ μg m^{-3}.

K_H. Henry's law constant; a measure of a compound's volatility, defined as the ratio of that compound's concentration in solution to its partial pressure in a parcel of air in equilibrium with that solution (mol L^{-1} atm^{-1}). Also commonly denoted H or H^{cp}.

Lifetime. The amount of time a chemical species lasts before being lost *via* such processes as reaction, deposition, or transport. The lifetime against a specific process refers only to the loss rate due to that process. Generally defined as the *e*-folding time, *i.e.*, the tame it takes to deplete a species to $1/e$ of its former amount.

LOD. Limit of detection; the analyte concentration below which a signal cannot be distinguished from noise.

Low-NO. Conditions under which organic peroxy radicals in the gas phase react primarily with compounds other than nitric oxide. The exact NO concentration at which this occurs depends on a number of conditions, but is generally on the order of $\lesssim$1 ppb in the troposphere.

LVOC. Low volatility organic compound; generally defined as any organic compound found in the atmosphere with a saturation vapor mass concentration in the range of $10^{-3.5}$ μg m^{-3} $\leq C^* \leq$ $10^{-0.5}$ μg m^{-3}.

***m/z*.** mass-to-charge ratio; usually in reference to an analyte ion detected by mass spectrometric methods.

MACR. Methacrolein; a volatile unsaturated aldehyde with chemical formula C_4H_6O, produced in the oxidation of isoprene by OH and O_3.

MAE. Methacrylic acid epoxide; a suspected product of MPAN photooxidation that may contribute to isoprene-derived SOA, with chemical formula $C_4H_6O_3$.

MGLY. Methylglyoxal; a volatile organic compound with the chemical formula $C_3H_4O_2$, and a common oxidation product of larger VOCs, including isoprene.

MPAN. Methacryloyl peroxynitrate; an acylperoxy nitrate with chemical formula $C_4H_5O_5N$ formed from the sequential reactions of methacrolein with OH, O_2, and NO_2, and an important SOA precursor in the high-NO oxidation pathway of isoprene.

MS. Mass spectrometry; an instrumental technique for measuring the mass-to-charge ratios of analyte ions.

MVK. Methyl vinyl ketone; a volatile unsaturated ketone with chemical formula C_4H_6O, produced in the oxidation of isoprene by OH and O_3.

MW. Molecular weight (g mol^{-1}).

NiCE. Nucleation in California Experiment; an airborne atmospheric field campaign based in Marina, CA, that took place in July and August of 2013.

NMHC. Non-methane hydrocarbons; volatile organic compounds found in the atmosphere that contain only hydrogen and carbon, excluding methane.

NMR. Nuclear magnetic resonance spectroscopy; an instrumental technique to determine the molecular structure and purity of a sample by measuring the effects of a strong magnetic field on the spin of atomic nuclei.

NO_3. Nitrate radical; the dominant oxidant in the troposphere at night, when NO_3 is typically present in concentrations on the order of 1-10 pptv.

NO_x. The nitrogen oxide radical family, defined as the sum of the nitric oxide (NO) and nitrogen dioxide (NO_2) radicals.

Nonrefractory. Used in conjunction with aerosol mass spectrometry to denote species that vaporize in 1 s or less at 600 °C under high vacuum, and can therefore be observed by AMS. This includes most secondary inorganic salts (*e.g* ammonium sulfate) and organic compounds. Also written non-refractory.

NSS. Non-sea-salt, referring to the portion of particle chemical constituents (*e.g* sulfate or chloride) that are not derived from primary emissions of sea salts.

O_3. Ozone; a major tropospheric oxidant, with typical concentrations on the order of 10 ppb. As a component of photochemical smog, tropospheric ozone also causes adverse health effects and contributes to greenhouse warming.

O/C. Oxygen-to-carbon ratio, usually in reference to bulk organic aerosol as measured by aerosol mass spectrometry.

OA. Organic aerosol, referring to the portion of particulate mass composed of organic compounds.

OC. Organic carbon, referring to the fraction of aerosol mass composed of carbon contained in organic molecules.

OH. Hydroxyl radical; the dominant oxidant in the troposphere, with typical daytime concentrations on the order of 1×10^6 molec cm^{-3}.

OM. Organic mass, used in reference to aerosol as a synonym for OA.

OOA. Oxidized organic aerosol; used in conjunction with aerosol mass spectrometry to refer to aerosol mass composed of oxygen-containing organic compounds.

PAN. Peroxyacetyl nitrate; the most abundant gaseous acylperoxy nitrate, with a chemical formula of $C_2H_3O_5N$, formed in the reaction of the peroxyacetyl radical with NO_2. PAN is a lachrymator and serves as a reservoir and transport mechamisn for NO_x.

PCASP. Passive cavity aerosol spectrometer probe; an instrument used to measure particle size distributions between 100 nm and 3 μm by light scattering.

PILS. Particle-into-liquid sampler; an aerosol sample acquisition method by which particles are grown *via* supersaturated water vapor condensation and collected by inertial impaction.

POA. Primary organic aerosol; particles emitted directly to the atmosphere.

POZ. Primary ozonide; the initial 5-member cyclic intermediate formed by the cycloaddition of ozone to a double bond during an ozonolysis reaction. Also called a molozonide or a 1,2,3-trioxolane.

PTR-MS. Proton transfer reaction mass spectrometry; a soft-ionization MS technique by which analyte gases are ionized by proton transfer from hydronium ions (H_3O^+).

RH. Relative humidity; water vapor concentration as a percentage of the concentration required for saturation at the same temperature.

RO_2. Any organic peroxy radical, where R represents an unspecified stable organic group.

SCI. Stabilized Criegee intermediate; the carbonyl oxide formed following the stabilization of an activated Criegee intermediate (CI*) *via* collisional energy transfer.

SEAC4RS. Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys; an airborne atmospheric field campaign based in Houston, TX, that took place in August and September of 2013.

SMPS. Scanning mobility particle sizer; an instrument consisting of a coupled differential mobility analyzer and condensation particle counter, used to measure particle size distributions.

SOA. Secondary organic aerosol; particle mass formed in the atmosphere from the condensation and reaction of gaseous species.

SOAS. Southern Oxidant and Aerosol Study; an atmospheric field campaign based in various locations throughout the Southeast United States that took place in June and July of 2013, with aiborne and ground-based measurements.

SVOC. Semi-volatile organic compound; generally defined as any organic compound found in the atmosphere with a saturation vapor mass concentration in the range of $10^{-0.5}$ μg m^{-3} $\leq$ C* $\leq$ $10^{2.5}$ μg m^{-3}.

ToF. Time-of-flight; a mass analysis technique in which an analyte ion's mass-to-charge ratio is measured by the time it takes to reach a detector after passing through an electric field.

UPLC. Ultra performance liquid chromatograph; a chemical separation technique utilizing a column with smaller beads (>2 μm in diameter) and higher flow rates and pressure to achieve greater resolution, speed, and sensitivity than other chromatographic techniques.

VOC. Volatile organic compound; generally defined as any organic compound found in the atmosphere with a saturation vapor mass concentration C* $\geq$ $10^{6.5}$ μg m^{-3}.

WSOC. Water-soluble organic carbon; particulate organic matter that dissolves into aqueous solution.

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ABOUT THE AUTHOR

Kelvin Hamilton Bates was born on January 9, 1990, in Seattle, Washington, to Tim Bates, an oceanographer, and Susan Hamilton, a biochemist. His parents' scientific backgrounds did not lead them to name their son after a unit of temperature – Kelvin was, instead, named after his grandfather – but did inspire them to invest heavily in his education. Kelvin's early schooling emphasized immersive cultural experiences, including travels to Japan, Vietnam, and the Dominican Republic, and instilled in him a profound love of learning. That passion helped him to thrive at Lakeside High School, where he first discovered his interests in organic chemistry and theater. In his eighteen years of childhood in the Pacific Northwest, Kelvin also gained an abiding appreciation for the splendor of the natural world.

In 2008 Kelvin matriculated at Davidson College, where he enjoyed the diversity of a liberal arts education and struggled to pick a major. He eventually settled on economics and chemistry, but not before taking a semester to study international politics in Geneva, Switzerland. While attending college, Kelvin spent two summers conducting biochemical research at pharmaceutical companies before being awarded a NOAA Hollings Scholarship, which led him to a summer research project with Dr. Chuck Brock at NOAA's facility in Boulder, CO, programming and calibrating an SMPS. Hooked on atmospheric research, he spent the following summer as an intern with NASA's Student Airborne Research Program, where he got his first taste of fieldwork under Prof. Don Blake at UC Irvine, investigating hydrocarbon emissions from California oil and gas infrastructure.

After graduating Summa cum Laude from Davidson, Kelvin came to Caltech on a Sharp Fellowship (and later an NSF Graduate Fellowship). As a graduate student in chemistry, Kelvin worked in a uniquely interdisciplinary collaboration between the labs of Profs. Brian Stoltz, Paul Wennberg, and John Seinfeld. While his main focus was to synthesize isoprene oxidation products and study their atmospheric fate in environmental chamber experiments, he also participated in a number of fieldwork and modeling projects. Kelvin will continue his studies in atmospheric chemistry at Harvard as a Harvard University Center for the Environment and NOAA Climate and Global Change postdoctoral fellow, in another collaboration between Profs. Daniel Jacob and Frank Keutsch.