

1 **Overview of the Focused Isoprene eXperiments at California Institute of Technology**
2 **(FIXCIT): mechanistic chamber studies on the oxidation of biogenic compounds**

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4 Tran B. Nguyen,¹ John D. Crouse,¹ Rebecca H. Schwantes,¹ Alexander P. Teng,¹ Kelvin H.
5 Bates,² Xuan Zhang,¹ Jason M. St. Clair,¹ William H. Brune,³ Geoffrey S. Tyndall,⁴ Frank N.
6 Keutsch,⁵ John H. Seinfeld,^{2,6} and Paul O. Wennberg^{1,6}

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- 8 1. Division of Geological and Planetary Sciences, California Institute of Technology,
9 Pasadena, California, USA
- 10 2. Division of Chemistry and Chemical Engineering, California Institute of Technology,
11 Pasadena, California, USA
- 12 3. Department of Meteorology, Pennsylvania State University, University Park,
13 Pennsylvania, USA
- 14 4. Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder,
15 Colorado, USA
- 16 5. Department of Chemistry, University of Wisconsin – Madison, Madison, Wisconsin,
17 USA
- 18 6. Division of Engineering and Applied Science, California Institute of Technology,
19 Pasadena, California, USA

20

1 **Abstract**

2 The Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT) was a
3 collaborative atmospheric chamber campaign that occurred during January 2014. FIXCIT is the
4 laboratory component of a synergistic field and laboratory effort aimed toward (1) better
5 understanding the chemical details behind ambient observations relevant to the Southeastern
6 United States, (2) advancing the knowledge of atmospheric oxidation mechanisms of important
7 biogenic hydrocarbons, and (3) characterizing the behavior of field instrumentation using
8 authentic standards. Approximately 20 principal scientists from 14 academic and government
9 institutions performed parallel measurements at a forested site in Alabama and at the
10 atmospheric chambers at Caltech. During the four-week campaign period, a series of chamber
11 experiments was conducted to investigate the dark- and photo-induced oxidation of isoprene, α -
12 pinene, methacrolein, pinonaldehyde, acylperoxy nitrates, isoprene hydroxy nitrates (ISOPN),
13 isoprene hydroxy hydroperoxides (ISOPOOH), and isoprene epoxydiols (IEPOX) in a highly-
14 controlled and atmospherically-relevant manner. Pinonaldehyde and isomer-specific standards of
15 ISOPN, ISOPOOH, and IEPOX were synthesized and contributed by campaign participants,
16 which enabled explicit exploration into the oxidation mechanisms and instrument responses for
17 these important atmospheric compounds. The present overview describes the goals, experimental
18 design, instrumental techniques, and preliminary observations from the campaign. This work
19 provides context for forthcoming publications affiliated with the FIXCIT campaign. Insights
20 from FIXCIT are anticipated to significantly aid in interpretation of field data and the revision of
21 mechanisms currently implemented in regional and global atmospheric models.

22

1 **Introduction**

2 **1.1. Background**

3 Biogenically-produced isoprenoids (hydrocarbons comprised of C₅H₈ units) have global
4 emission rates to the atmosphere surpassing those of anthropogenic hydrocarbons and methane
5 (Guenther et al., 1995; Guenther et al., 2012). The biogenic carbon emission flux is dominated
6 by isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆), which account for approximately 50% and 30%
7 of the OH reactivity over land, respectively (Fuentes et al., 2000). Further, it has been suggested
8 that the atmospheric oxidation of isoprene, in particular, can buffer the oxidative capacity of
9 forested regions by maintaining levels of the hydroxyl radical (OH) under lower nitric oxide
10 (NO) conditions (Lelieveld et al., 2008). Due to their large abundances, isoprene and
11 monoterpenes also dominate the global budget of secondary organic aerosol (SOA) (Henze et al.,
12 2008). Thus, the accurate representation of detailed chemistry for isoprene and monoterpene is
13 necessary for meaningful simulations of atmospheric HO_x (OH + HO₂), NO_x (NO + NO₂),
14 surface ozone (O₃), trace gas lifetimes, and SOA.

15 Unsaturated hydrocarbons like isoprene and monoterpenes are primarily oxidized by OH,
16 O₃, and the nitrate (NO₃) radical in the atmosphere. OH-oxidation is the dominant fate for
17 isoprene but O₃ and NO₃ oxidation can dominate reactivity for monoterpenes and sesquiterpenes.
18 Our understanding of the OH-initiated isoprene oxidation mechanism has significantly improved
19 during the last decade, following the first suggestion of the capacity of isoprene to produce SOA
20 (Claeys et al., 2004). The mechanistic developments have been propelled by technological
21 advancements in instrumentation (Hansel et al., 1995; Crounse et al., 2006; Jordan et al., 2009;
22 Junninen et al., 2010), enabling the detection of more-complex oxidation products derived from
23 isoprene and other biogenic hydrocarbons. However, the scientific understanding of these

1 biogenic oxidation mechanisms is far from complete. It is outside the scope of this overview to
2 describe comprehensively the isoprene and monoterpene oxidation mechanisms. Rather, we
3 provide a brief background of the oxidation of biogenic hydrocarbons, which includes a “state-
4 of-the-science” knowledge, to motivate the study. The mechanisms described here are illustrated
5 in Scheme 1.

6 **OH oxidation:** OH predominantly adds to either of the double bonds of isoprene,
7 followed by the reversible addition of O₂ (Peeters et al., 2009) to produce several isomers of
8 alkylperoxyl radicals (RO₂). In the atmosphere, these RO₂ react mainly with HO₂ and NO to form
9 stable products, although self-reaction can be non-negligible under certain conditions. The stable
10 products are often termed oxidized volatile organic compounds (OVOCs). In urban-influenced
11 areas, the “high-NO” pathway is more important and in more pristine environments, the “low-
12 NO” or HO₂-dominated pathway is more important. The high-NO pathway generates isoprene
13 hydroxy nitrates (ISOPN) that act as reservoirs for NO_x, as well as other products such as methyl
14 vinyl ketone (MVK), methacrolein (MAC), and hydroxyacetone (HAC) (Paulot et al., 2009a).
15 For conditions with sufficiently high NO₂-to-NO ratios, as is mainly the case in the atmospheric
16 boundary layer outside of cities, methacryloyl peroxyxynitrate (MPAN) is formed from the
17 photooxidation of MAC. Further oxidation of MPAN can generate SOA (Chan et al., 2010,
18 Surratt et al., 2010). The low-NO pathway generates isoprene hydroxy hydroperoxides
19 (ISOPOOH) in almost quantitative yields, and further OH-oxidation of ISOPOOH produces the
20 epoxydiols in an OH-conserving mechanism (Paulot et al., 2009b). In unpolluted atmospheres,
21 when the RO₂ lifetimes are sufficiently long (~ 100 s in a forest), isomerization of the RO₂
22 followed by reaction with O₂ becomes an important fate, producing the isoprene hydroperoxy
23 aldehydes (HPALDs) and other products (Peeters et al., 2009; Crouse et al., 2011). These RO₂

1 isomerization reactions are a type of rapid oxygen incorporation chemistry (Vereecken et al.,
2 2007; Crouse et al., 2013; Ehn et al., 2014) that is thought to be responsible for the prompt
3 generation of low-volatility SOA components. Further generations of OH-oxidation in isoprene
4 are currently being explored owing to recent success with chemical syntheses of important
5 OVOCs (Wolfe et al., 2012; Jacobs et al., 2013; Bates et al., 2014; Lee et al., 2014b). It has been
6 found that the OH-oxidation of IEPOX and ISOPN, surprisingly under both low-NO and high-
7 NO conditions, results primarily in fragmentation of the C₅ skeleton.

8 Despite extensive work on the isoprene + OH mechanism, large uncertainties persist,
9 some of which directly translate into uncertainties in atmospheric model predictions. These
10 uncertainties stem from, for example, the large range in reported yields for isoprene nitrates (4 –
11 15%) (Paulot et al., 2009a), disagreements up to 90% in reported MAC and MVK yields from
12 the low-NO pathway (Liu et al., 2013, and references therein), various proposed sources of SOA
13 from the high-NO pathway (Chan et al., 2010; Kjaergaard et al., 2012; Lin et al., 2013), missing
14 contributions to SOA mass from the low-NO pathway (Surratt et al., 2010), uncharacterized fates
15 of oxidized species like HPALDs (which may have isomer-dependence), incomplete
16 understanding of oxygen incorporation (Peeters et al., 2009; Crouse et al., 2013), and under-
17 characterized impact of RO₂ lifetimes on chamber results (Wolfe et al., 2012). The OH oxidation
18 of α -pinene (Eddingsaas et al., 2012) and other monoterpenes is less well-characterized than that
19 of isoprene, but in general, proceeds through analogous steps.

20 **Ozone oxidation:** Ozonolysis is a significant sink for unsaturated hydrocarbons and a
21 large nighttime source of OH, particularly in urban-influenced areas. Reaction with ozone is
22 more important for monoterpenes than isoprene, due to the faster rate coefficients (Atkinson and
23 Carter, 1984) and the nighttime emission profile for the monoterpenes. Further, monoterpene

1 ozonolysis is highly efficient at converting VOC mass to SOA (Hoffmann et al., 1997; Griffin et
2 al., 1999). There is a general consensus that ozonolysis occurs via the Criegee mechanism
3 (Criegee, 1975), wherein ozone adds to a hydrocarbon double bond to form a 5-member primary
4 ozonide that quickly decomposes to a stable carbonyl product and an energy-rich Criegee
5 intermediate (CI). In α -pinene oxidation, ozonolysis, NO_3 -initiated, and OH-initiated reactions
6 all produce pinonaldehyde ($\text{C}_{10}\text{H}_{16}\text{O}_2$) as a major product (Wängberg et al., 1997; Atkinson and
7 Arey, 2003), whereas major first-generation products from isoprene ozonolysis include MAC,
8 MVK, and formaldehyde. The “hot” Criegee can promptly lose OH (Kroll et al., 2001) while
9 ejecting an alkyl radical, or become stabilized by collision with atmospheric gases to form a
10 stabilized Criegee intermediate (sCI) with long enough lifetimes to react bimolecularly. The
11 subsequent reactions of sCIs produce both carbonyl products and non-carbonyl products such as
12 hydroperoxides. The *syn* and *anti* conformers of CIs and sCI can have substantially different
13 reactivities (Kuwata et al., 2010; Anglada et al., 2011), with *syn* conformers more likely to
14 decompose unimolecularly, possibly through a vinyl hydroperoxide intermediate (Donahue et al.,
15 2011).

16 It has been suggested that reaction with water molecules is a major (if not dominant)
17 bimolecular fate of sCI in the atmosphere due to the overwhelming abundance of atmospheric
18 water (Fenske et al., 2000). This suggestion is supported by observations of high mixing ratios
19 (up to 5 ppbv) of hydroxymethyl hydroperoxide (HMHP), a characteristic product of reactions of
20 the smallest sCI (CH_2OO) with water (Neeb et al., 1997), over forested regions and in biomass
21 burning plumes (Gäb et al., 1985; Lee et al., 1993; Lee et al., 2000; Valverde-Canossa et al.,
22 2006). Although HMHP and other hydroperoxides produced from ozonolysis are important
23 atmospheric compounds, their yield estimates are highly uncertain (Becker et al., 1990; Neeb et

1 al., 1997; Sauer et al., 1999; Hasson et al., 2001; Huang et al., 2013). This may be attributable to
2 the fact that hydroperoxide yields have mainly been determined by offline methods or under
3 conditions with highly-elevated hydrocarbon loadings. Further, little empirical data exist on the
4 humidity dependence of product branching in this reaction. Lastly, the rate coefficients for the
5 sCI+H₂O reaction, and other sCI reactions, are still uncertain by several orders of magnitude
6 (Johnson and Marston, 2008; Welz et al., 2012), precluding the assessment of their atmospheric
7 importance.

8 **Nitrate oxidation:** NO₃-oxidation also produces RO₂ radicals by addition to alkenes in
9 the presence of O₂. Owing to its high reaction rate coefficient coupled to atmospheric abundance,
10 α-pinene is expected to be an important sink for NO₃ in many areas. The NO₃-derived RO₂
11 radicals react with (a) NO₃ to form alkoxy radicals (RO) that lead primarily to the production of
12 nitrooxy carbonyls (b); with other RO₂ radicals to form RO radicals, nitrooxy carbonyls, hydroxy
13 nitrates, and nitrooxy peroxy dimers; and (c) with HO₂ to form nitrooxy hydroperoxides. Further
14 generation NO₃-oxidation produces dinitrates, amongst other products. As the NO₃ addition
15 initiates the reaction, the thermodynamically-preferred organic hydroxy nitrates produced
16 through nighttime oxidation may be structurally different than those produced in the daytime
17 through OH oxidation. During nighttime oxidation, tropospheric HO₂ mixing ratios often surpass
18 those of NO₃ (Mao et al., 2012), implicating HO₂ reaction to be a common fate for NO₃-derived
19 RO₂. However, previous studies of this reaction have maintained conditions where minimal HO₂
20 + RO₂ chemistry occurs and the dominant fate of RO₂ is reaction with NO₃ and RO₂ (Ng et al.,
21 2008; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012). This may be one of the
22 reasons why nitrooxy hydroperoxides (the RO₂ + HO₂ product) are observed with much higher
23 relative abundances in ambient air (Beaver et al., 2012) than in chamber studies.

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1.2. Scientific goals

The 2014 Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT) is a collaborative atmospheric chamber campaign focused on advancing the understanding of biogenic hydrocarbon oxidation in the atmosphere. The campaign was motivated by the communal need for a tight coupling of field and laboratory efforts toward understanding the mechanistic details responsible for ambient observations, exploring explicit chemistry as driven by the fate of RO₂ radicals through well-controlled experiments, and fully characterizing instrumental response to important trace gases using authentic standards to guide data interpretation. To accomplish these goals, a suite of instruments typically deployed for field missions was used to perform parallel measurements at a forested site in Alabama and then in the atmospheric chambers at Caltech. This overview provides an account of the goals and conditions for the experiments performed during the campaign. A key component of FIXCIT is the re-design of “typical chamber experiments” to recreate the ambient atmosphere with higher fidelity so that results from laboratory studies can be implemented in models and used to interpret ambient observations with higher confidence.

Understanding ambient observations: FIXCIT was designed as a sister investigation to the 2013 Southern Oxidant and Aerosol Study (SOAS). During SOAS (June – July 2013), a select sub-suite of instruments recorded ambient observations above the forest canopy on top of a metal walk-up tower 20 m in height. The sampling site, located in Brent, Alabama at the Centreville (CTR) SEARCH location managed by the Electric Power Research Institute (CTR, Latitude 32.90289 Longitude -87.24968), was surrounded by a temperate mixed forest (part of the Talladega National Forest) that was occasionally impacted by anthropogenic emission. CTR

1 was characterized by high atmospheric water content (2.4 – 3 vol. % typically), elevated
2 temperatures (28 – 30°C during the day), high SOA loadings (particulate organics ~ 4 – 10 $\mu\text{g m}^{-3}$;
3 sulfate ~ 2 $\mu\text{g m}^{-3}$), high isoprene mixing ratios (4 – 10 ppbv), high ozone (40 – 60 ppbv), low-
4 to-moderate nitrogen oxides ($[\text{NO}] \sim 0.3 - 1.5$ ppbv, $[\text{NO}_2] \sim 1 - 5$ ppbv), occasional plumes of
5 SO_2 from nearby power plants, and occasional biomass burning events during the SOAS
6 campaign.

7 The first goal of the chamber campaign was to further investigate the more interesting
8 observations at SOAS. Due to the ability of laboratory experiments to study the chemistry of a
9 single reactive hydrocarbon in a controlled setting, it was possible to test hypotheses during
10 FIXCIT in a systematic manner. Below we list some relevant questions from the SOAS
11 campaign that were explored during FIXCIT.

- 12 1. *Which reactions or environmental conditions control the formation and destruction of*
13 *OVOCs in the Southeast U.S.?*
- 14 2. *Are RO_2 isomerization and other rapid oxygen incorporation mechanisms of key*
15 *hydrocarbons important during SOAS?*
- 16 3. *How do anthropogenic influences, e.g., NO_x , O_3 , and $(\text{NH}_4)_2\text{SO}_4$, impact atmospheric*
17 *chemistry over the forest?*
- 18 4. *How much does the NO_3 -initiated reaction control nighttime chemistry during SOAS?*
- 19 5. *How do environmental conditions in the Southeast U.S. affect ozonolysis end*
20 *products, which are known to be water-sensitive?*
- 21 6. *Which reactions or environmental conditions most significantly impact SOA mass and*
22 *composition?*

23
24 **Updating the isoprene and monoterpene mechanisms:** Several experiments were
25 designed to “fill in the gaps” of the isoprene oxidation mechanisms by leveraging the

1 comprehensive collection of sophisticated instrumentation at FIXCIT. We targeted the following
2 acknowledged open questions.

- 3 7. *What are the products of the photochemical reactions stemming from OVOCs like*
4 *ISOPOOH, IEPOX, ISOPN, and pinonaldehyde?*
- 5 8. *What is the impact of photolysis vs. photooxidation for photolabile compounds?*
- 6 9. *What is the true yield of isoprene nitrates from the high-NO photooxidation*
7 *pathway?*
- 8 10. *What is the product distribution and true yield of nitrooxy hydroperoxides from the*
9 *NO₃-oxidation reaction of isoprene and monoterpenes under typical atmospheric*
10 *conditions?*
- 11 11. *How do products and yields change as RO₂ lifetimes in chamber studies approach*
12 *values estimated to be prevalent in the troposphere?*

13
14 **Instrument characterization:** A final goal of FIXCIT was to evaluate, compare, and
15 identify biases in field instrumentation by isolating one variable at a time. We focused on the
16 following objectives.

- 17 12. *Identify the causal factor(s) producing the “OH interference” (Mao et al., 2012)*
18 *that has been observed in various biogenically-impacted regions by some gas-*
19 *expansion laser-induced-fluorescence (LIF) techniques.*
- 20 13. *Characterize the performance of newly commercially-available CIMS*
21 *instrumentation with respect to the detection of OVOCs by using authentic*
22 *standards.*
- 23 14. *Compare similar measurements (e.g., OH reactivity, hydrocarbons, OVOCs) made*
24 *with different techniques.*

25 26 **2. Scope of the campaign**

27 **2.1. Facilities:** Experiments were performed in the Caltech Atmospheric Chamber Facility
28 within a one-month period in January 2014. The facility contains several in-house gas- and

1 aerosol-phase instruments and an 8 x 5 m insulated enclosure, housing two side-by-side Teflon
2 atmospheric chambers that are suspended from the ceiling. The chambers were manufactured
3 from Fluorinated Ethylene Propylene (FEP) Teflon. The chamber volume was measured
4 regularly by quantitative transfer of highly-volatile organics such as isoprene by an externally
5 calibrated GC-FID. Quantitative transfer was checked via injections of a measured quantity of
6 isoprene (checked by gravimetric, volumetric, and FT-IR methods) into a pillow bag with known
7 volume by timing a calibrated mass flow of air into the pillow bag. For most experiments, the
8 chamber volume was between 23 – 24 m³. The spatial configuration of instruments in the
9 chamber facility during FIXCIT is shown in Fig. 1. The instruments, contributors, and
10 identifying abbreviations used in this work are described in Table 1. A total of 320 UV black
11 lamps (broadband $\lambda_{\text{max}} \sim 350$ nm) are mounted on the walls of the enclosure. The lamps are
12 located behind Teflon films so that the heat produced from the operation of the lamps can be
13 removed by recirculating cool air. The interior of the enclosure is covered with reflective
14 aluminum sheets. Light intensities can be tuned to 100 %, 50 %, 10 %, and 1 %. J_{NO_2} was
15 measured to be $7 \times 10^{-3} \text{ s}^{-1}$ at 100 % light intensity. Light fluxes at several locations within the
16 chamber (e.g., center, corner, right, left, high, low) did not vary more than 15%. Temperature
17 controls in the chamber enclosure are tunable from 10 – 50 °C (typically set at 25°C) and did not
18 fluctuate more than 1°C except during periods when the temperature was explicitly changed or
19 during a 30 minute period immediately following a change in the light intensities (up to 2 °C
20 increase was observed from switching on 100 % lights.)

21 The chamber experiments were operated in batch mode throughout the campaign.
22 Temperature and RH were monitored continuously inside the chamber by a Vaisala HMM211
23 probe calibrated with saturated salt solutions in the RH range of 11 – 95%. In the range $\text{RH} <$

1 11%, water vapor measurements were provided by the TripCIMS. The chambers were flushed at
2 least 24 h before each use with ultra-purified air (purified in-house via a series of molecular
3 sieves, activated carbon, Purafil™ media, and particulate filters), at elevated temperature when
4 needed (~ 40 °C), so that the backgrounds on gas- and particle-phase instrumentation are at
5 baseline levels. As a reference, NO levels before each run were typically < 100 pptv (from NO-
6 CL measurements) and particle concentrations were < 0.01 µg m⁻³. Flushing rates, as balanced
7 by exhaust rates, were typically 250 std. L min⁻¹ (SLM) or ~ 0.6 chamber volumes per hour.
8 Chambers were mixed on the timescale of minutes by injecting high-pressure pulses of air during
9 the beginning of experiments.

10 Chamber 1 was reserved for low-NO experiments, so that the walls did not contact
11 elevated levels of nitric acid and organic nitrates during the lifetime of the chamber, while
12 Chamber 2 was reserved for moderate-to-high-NO experiments. Experiments were carried out
13 daily in alternating chambers to allow for the full flushing period of the previously-used
14 chamber. Each chamber was characterized separately prior to the campaign for vapor and
15 particle wall loss rates. Typically, wall loss rates for gas-phase species are slightly higher in the
16 high-NO chamber than the low-NO chamber due to the greater acidity of the walls. Particle wall
17 loss rates were not significantly different between chambers. Measurements of the particle wall
18 loss rates were performed by injecting ammonium sulfate (AS) seed aerosols into the chamber
19 and monitoring the decay over the course of 10 – 24 h. Particles were injected via atomization of
20 dilute salt solutions (e.g., AS 0.06 M) through a ²¹⁰Po neutralizer and water trap. Measurements
21 of vapor wall loss rates were performed by injecting OVOC standards (e.g., IEPOX, HMHP,
22 etc.) into the chamber. Both particle and vapor wall loss characterizations were performed at

1 several RH conditions (4 – 85 % RH). These characterizations have been described in more
2 detail previously (Loza et al., 2010; Nguyen et al., 2014).

3 Organic compounds were injected into the chamber by two methods: (1) For volatile
4 compounds, a measured volume was injected with a micro-syringe through a septum into a clean
5 glass bulb and the evaporated standard was quantitatively transferred into the chamber by dry
6 purified air. Gas introduction of VOCs (done for isoprene and methacrolein) by filling an
7 evacuated bulb with the chemical vapor, backfilling with nitrogen gas, and characterizing with
8 Fourier-transform infrared spectrometry before injecting did not produce significantly different
9 results than volume injection. (2) For semi-volatile compounds, the solid or liquid standard was
10 placed inside a two-neck flask, which was heated by a water bath (35 – 65°C), and the headspace
11 was carried into the chamber by dry purified air. The ToFCIMS or TripCIMS instruments
12 measured the gas-phase mixing ratio of the semi-volatiles in real time as the compounds entered
13 the chamber, and injection was halted when a satisfactory quantity was introduced. OVOCs were
14 calibrated by the ToFCIMS and TripCIMS by methods described earlier (Paulot et al., 2009a).
15 The desired RH inside the chamber was achieved by flowing dry purified air through a water-
16 permeable (Nafion) membrane humidifier (FC200, Permapure LLC), kept moist by recirculating
17 27 °C ultra-purified (18 MΩ, 3 ppb TOC) water (Milli-Q, Millipore Corp). Particles were
18 atomized into the chamber as described for particle wall loss experiments. When hydrated
19 particles were needed for experiments, particles were injected via an in-line, heated, wet-wall
20 denuder into a chamber that has RH above the efflorescence point of the particular salt (Martin,
21 2000).

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1 **2.2. Instrumentation and sampling modifications:** Instruments were connected via
2 sampling lines to both chambers through port holes in the enclosure as shown in Fig. 1. Sampling
3 lines were capped when not in use. Inlet and tubing material were instrument-specific and
4 included: stainless steel (GTHOS and ToF-AMS), heated stainless steel and quartz (TDLIF),
5 electro-polished steel and FEP Teflon (NO₃CIMS), polyetheretherketone (PEEK) and Teflon
6 (SRI-ToFMS), and perfluoroalkoxy polymer (PFA) Teflon (other instruments).

7 The duration of each experiment (i.e., the level of oxidation that can be probed) was
8 critically dependent on the net sampling flow rates at which air was withdrawn from the
9 chamber. Sampling strategies were developed to minimize the effective sampling flow rate from
10 each instrument, in such a way that instrument responses were not significantly different than
11 during field campaigns. In many cases, a common high-flow Teflon sampling line was used to
12 minimize the residence time of gases through tubing, and smaller flows were sampled
13 orthogonally by each instrument. In some cases, a duty cycle was used as needed.

14 Several modifications from field designs were utilized for chamber sampling. The
15 modifications included: (1) the GTHOS detection system was located between the chambers
16 inside of the enclosure to minimize the residence time of HO_x inside the instrument (Fig. 1). The
17 detection system was connected to the laser on the outside of the enclosure via a 3 m fiber optic
18 cable fed through the side port hole. The sampling flow rate was similar to field flows (6 SLM);
19 however, the fast-flow inlet was situated horizontally (~ 2 m height) instead of vertically. The
20 inlet was adapted to each bag directly, by attaching it to a Teflon plate that was in turn secured to
21 the chamber walls via a large o-ring. The GTHOS inlet switched from Chamber 1 to Chamber 2
22 as needed. Chemical zeroing was performed by releasing hexafluoropropene (C₃F₆) into the inlet
23 as an OH scrubber, and dark zeroing by measuring the difference between online and offline

1 signals. Chemical and dark zeroing methods were used to distinguish between OH present in the
2 chamber or atmosphere (chemical OH) and OH that may have been produced after the gas
3 stream enters the instrument, which is additional to the chemical OH signal; (2) LIF-OHR was
4 diluted a factor of 10 with nitrogen gas (effective flow 6 SLM); (3) NO₃CIMS was diluted a
5 factor of 5 with scrubbed zero air (effective flow 2 SLM); (4) GlyLIP and FormLIF both
6 operated at 5 SLM instead of the usual 17 and 10 SLM, respectively; and (5) SRI-ToFMS (1.5
7 SLM) and GCFID (0.1 SLM) occasionally sampled through a 0.125 – 0.25” OD PFA Teflon
8 tube that was submerged in a cold bath kept at – 40°C in order to remove interferences from
9 certain OVOC (see Section 2.3).

10 GC-ToFCIMS, first described in Bates et al (2014), is an extension of the ToFCIMS.
11 Analyte gas samples were focused with a cold trap onto the head of a RTX 1701 column
12 (Restek) and eluted with a temperature ramping program (30 – 130°C) in the oven before
13 reaching the ToFCIMS for mass spectrometry detection. GC-ToFCIMS recorded data only when
14 isomer separation was needed, because its operation took the standard scanning mode of the
15 ToFCIMS offline. All other instruments operated normally with the following sampling flows:
16 TDLIF (4 SLM), ToFCIMS and TripCIMS (2 SLM), CRM-OHR (0.5 SLM), NO-CL (1 SLM),
17 and IACIMS (2 SLM). Frequencies of zeroing (with dry N₂ or ultrazero air) and calibration
18 (various methods) were instrument-specific, with some instruments zeroing once per hour and
19 calibrating once per few hours and others performing zeroing/calibration between experiments.

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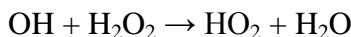
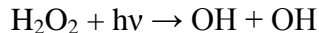
21 **2.3. Experimental design**

22 The experiments performed at FIXCIT can be divided into several categories, each
23 probing one or more specific science questions outlined in Section 1.2. Every experiment

1 included successful elements from past studies, but with a special focus on extending to
2 atmospheric conditions. One example is reducing the occurrence of RO₂ + RO₂ side reactions in
3 chamber experiments, which can lead to yields of atmospherically-relevant products that are
4 biased low. Enabled by the high sensitivity of field instruments, photooxidation was performed
5 with precursor mixing ratios as low as 12 ppbv. Certain instruments that required extensive
6 dilution in a chamber setting, e.g., LIF-OHR, had poorer-quality data for low-loading
7 experiments. Experimental durations were typically 4 – 6 h, with the exception of overnight runs
8 where the majority of instruments sampled briefly to establish starting conditions, then were
9 taken offline during the nighttime and resumed sampling in the morning. The typical reaction
10 time for an overnight experiment was ~ 15 h. Experimental details are reported in Table 2. OH
11 concentrations were derived from hydrocarbon decay data from GCFID, SRI-ToFMS, or
12 ToFCIMS, when available, using published rate coefficients (Atkinson et al., 2006; Lee et al.,
13 2014b; Bates et al., 2014). Otherwise, preliminary GTHOS chemical-zeroing data were used.
14 The following types of experiments were included in the study:

15 **a. Blank** (Exp. 4b and 5b): Blank experiments were designed to investigate background signals
16 present in experiments that may have sources other than gas-phase chemistry of the injected
17 hydrocarbon, e.g., from heterogeneous oxidation of residual organics on the chamber walls.
18 OH precursors, such as hydrogen peroxide, were added to each chamber, the UV lamps were
19 turned on, and sampling occurred as usual. Further, the temperatures inside the chambers
20 were ramped from 25 to 35° C to explore the extent to which elevated temperatures change
21 the chamber background signals due to increased volatilization of organics. Blank
22 experiments were performed under dry conditions. Common background compounds
23 produced from heterogeneous wall reactions are formic acid and acetic acid.

1 **b. Low-NO photooxidation** (Exp. 2, 10, 17, 19, and 25): The “low-NO” experiments that have
2 been extensively investigated in atmospheric chamber studies were designed to be relevant to
3 the pristine troposphere, and certain conditions at SOAS, where HO₂ reactions dominate the
4 RO₂ fate. Experiments were initiated by H₂O₂ photolysis as a NO_x-free source of OH and
5 HO₂:



6
7
8 The execution of these experiments requires precise engineering to closely simulate the
9 troposphere. One outstanding challenge of “low-NO” experiments is the variation in initial
10 NO levels across different chamber settings and on different days. Because typical HO₂
11 levels in a chamber environment do not typically exceed ~ 200 pptv from the self-limiting
12 HO₂ recombination, NO should be ~ 40 pptv during the reaction (a factor of 5 less abundant)
13 in order for the C₅ RO₂ reactions to be dominated by HO₂ by a factor of 10 ($k_{\text{RO}_2+\text{HO}_2} \sim 1.6 \times$
14 10^{-11} and $k_{\text{RO}_2+\text{NO}} \sim 8.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298K (Atkinson et al., 2006)). Thus,
15 experimental variations in NO that can lead to discrepancies in “low-NO” kinetics typically
16 elude quantification by commercially-available NO chemiluminescence instruments, owing to
17 their high limits of detection (~500 pptv).

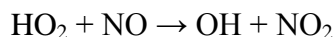
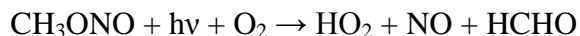
18 NO levels in the Caltech chambers were suppressed by continually flushing with filtered
19 air on the inside and outside the chamber walls. Initial NO levels of < 40 pptv were typically
20 achieved during experiments. The NO-CL instrument available during FIXCIT (Table 1) has
21 a limit of detection better than 25 pptv, and the GTHOS instrument provided online HO₂
22 quantification at the pptv-level. Another common challenge for “low-NO” experiments (even
23 when [NO] < [HO₂]) is that homogeneous or cross RO₂ + RO₂ reactions may dominate the

1 RO₂ reactivity ($k_{\text{RO}_2+\text{RO}_2} \sim 10^{-15} - 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298K (Atkinson et al., 2006)).
2 These experiments may be more correctly characterized as “low-NO, high-RO₂”. For
3 experiments using [H₂O₂] as an OH precursor, RO₂+RO₂ reactions were largely minimized
4 by using reaction conditions that ensures [HO₂] > [RO₂] (e.g., [H₂O₂]₀/[ISOP]₀ ~ 10⁵ and
5 $J[\text{H}_2\text{O}_2] \sim 4 - 5 \times 10^{-6} \text{ s}^{-1}$). Thus, the peroxy radical self-reaction channels are minor
6 compared to RO₂+RO₂ chemistry. We estimate that the “low-NO” experiments were HO₂-
7 dominated by at least a factor of 10 in RO₂ reactivity by monitoring tracers of chemistry
8 stemming from high-NO (isoprene nitrates), high-RO₂ (C₅ diols and other products), and
9 low-NO (ISOPOOH and IEPOX) pathways. The molar yield of the low-NO products
10 ISOPOOH + IEPOX (measured within the first 15 minutes of reaction) was estimated to be
11 95%, supporting the dominance of RO₂ + HO₂ chemistry over other channels. The
12 structurally isomeric ISOPOOH and IEPOX that were formed from the HO₂-dominated
13 isoprene photooxidation were distinguished by TripCIMS, and the sum was measured by
14 ToFCIMS, IACIMS, and NO₃CIMS. These experiments were performed with isoprene, α -
15 pinene, 4,3-ISOPOOH and MAC precursors.

16 **c. High-NO photooxidation** (Exp. 3, 11, 22, and 24): “High-NO” experiments are also
17 commonly performed in chamber studies. These experiments were designed to be relevant to
18 the urban-influenced troposphere, such as some cases at SOAS, where NO can dominate RO₂
19 reactions. Experiments were typically initiated by H₂O₂ with added NO during FIXCIT, but
20 have been performed using HONO or other precursors elsewhere. It is easier to ensure that
21 reaction with NO is the main fate of RO₂, even with higher hydrocarbon loadings, because
22 NO mixing ratios are typically in excess of both HO₂ and RO₂ by hundreds of ppbv. Hydroxy
23 nitrate products were measured by TDLIF, IACIMS, ToFCIMS, and GC-ToFCIMS.

1 Functionalized carbonyl products were measured by SRI-ToFMS and ToFCIMS. Glyoxal
2 and formaldehyde, also important high-NO products, were measured by the GlyLIP and
3 FormLIF, respectively. This well-studied experiment was important for multiple reasons,
4 including calibration, diagnostics, and for determining the hydroxy nitrate yields from
5 alkenes within the first few minutes of photooxidation. However, it should be noted that the
6 experimental result represents a boundary condition that may not fully represent NO-
7 influenced reactions in the atmosphere due to the extremely short RO₂ lifetimes (< 0.01 s at
8 500 ppbv NO). These experiments were performed with isoprene, α-pinene, and the 4,3-
9 ISOPN standard synthesized by the Caltech group.

10 **d. “Slow chemistry” photooxidation** (Exp. 7, 16, 18, and 27): The slow chemistry experiment
11 is designed to extend RO₂ lifetimes closer to atmospheric values when both NO and HO₂
12 impact RO₂ reactivity (~ 3 - 30 s, assuming 1500 – 100 pptv NO and 40 pptv HO₂). This was
13 achieved by employing low radical mixing ratios. With relevant RO₂ lifetimes, the RO₂
14 isomers may be closer to their equilibrium distribution because of the reversible addition of
15 oxygen (Peeters et al., 2009). Figure 2 shows the progress of a representative slow chemistry
16 experiment. The “slow” portion of experiments was performed under a low light flux ($J_{\text{NO}_2} \sim$
17 $4 \times 10^{-5} \text{ s}^{-1}$) with methyl nitrite as the OH precursor (Atkinson et al., 1981):



20 These reactions produce a steady-state OH concentration of $[\text{OH}]_{\text{ss}} \sim 0.4 - 1 \times 10^5 \text{ molec cm}^{-3}$
21 and an atmospherically-relevant ratio of NO/HO₂ (2 – 3) that is stable throughout the
22 majority of the experiment. Further, we aimed to simulate the summer conditions at SOAS,
23 where RO₂ isomerization is competitive with RO₂ + HO₂ and RO₂ + NO chemistry. Thus,

1 most experiments of this type were performed at elevated temperatures ($T \sim 40 - 45^\circ\text{C}$) to
2 facilitate the isoprene RO_2 isomerization to HPALDs (Crouse et al., 2011), as measured by
3 ToFCIMS. The atmospheric RO_2 fates were qualitatively deduced by observations of their
4 respective products during SOAS (forthcoming papers) and during other campaigns (Paulot
5 et al., 2009b; Wolfe et al., 2011; Beaver et al., 2012).

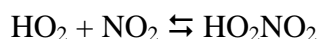
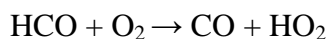
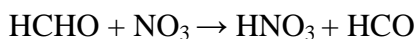
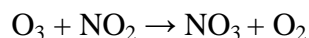
6 The fate of HPALDs is not known, but has been suggested to be strongly influenced by
7 photolysis based on reactions of chemical analogues (Wolfe et al., 2012). After the slow
8 chemistry period, 20 – 100% lights were turned on in order to diagnose the effects of direct
9 photolysis and OH-oxidation on the product compounds, which is especially instructive when
10 coupled with photochemical modeling. Table 2 reports conditions only for the $\leq 1\%$ light
11 period and the 20% light period due to availability of hydrocarbon decay data. When
12 CH_3ONO experiments were performed with higher light flux from the start, the NO-to- HO_2
13 reactivities were still competitive but the OH mixing ratios were higher. These experiments
14 were performed with isoprene, α -pinene, and *trans* β -IEPOX precursors.

15 **e. Ozonolysis** (Exp. 6, 14, 23, and 29): Ozonolysis reactions were performed in the dark, with
16 and without the use of excess cyclohexane (50 ppmv) as a scavenger for OH (Atkinson,
17 1995). Ozone reacts with isoprene and α -pinene with rate coefficients of $k_{\text{ISO}+\text{O}_3} = 1.3 \times 10^{-17}$
18 molec cm^{-3} and $k_{\alpha\text{-PIN}+\text{O}_3} = 9.0 \times 10^{-17} \text{ molec cm}^{-3}$ at 298 K, respectively (Atkinson et al.,
19 2006). After the first few steps of the reaction, however, little agreement exists in the
20 literature for product yields, product distribution, or rate coefficients stemming from
21 reactions of stabilized Criegee intermediates (sCI). This may be due to the large differences
22 among studies in the hydrocarbon loadings ($[\text{ISO}]_i = 40 - 10000 \text{ ppbv}$), ozone-to-isoprene
23 ratios (< 0.5 to > 100), water vapor content ($< 10 - 20000 \text{ ppmv}$), reaction pressures (4 –

1 760 torr), analytical methods used for product analysis (GC, HPLC, FTIR, direct OH vs.
2 scavenging, etc.), and methods used to generate sCI ($\text{CH}_2\text{I}_2 + \text{h}\nu$ vs. gas-phase ozonolysis)
3 (Simonaitis et al., 1991; Neeb et al., 1997; Sauer et al., 1999; Hasson et al., 2001; Kroll et al.,
4 2002; Johnson and Marston, 2008; Drozd and Donahue, 2011; Welz et al., 2012; Huang et
5 al., 2013).

6 We designed the ozonolysis experiments to have similar ozone-to-isoprene ratios to those
7 observed during SOAS ($\sim 5 - 7$), and performed the experiments under dry ($\text{RH} \sim 4\%$) and
8 moderately-humid ($\text{RH} \sim 50\%$) conditions. The ozonolysis experiments at FIXCIT primarily
9 focused on studying unimolecular and bimolecular chemistry of sCI that affects the yields of
10 OH, hydroperoxides, organic acids, and aldehydes/ ketones under humid vs. dry conditions.
11 These experiments represent the first coupling between direct OH observations from
12 GTHOS, aldehyde/ketone measurements from GCFID and SRI-ToFMS, online
13 formaldehyde measurements from FormLIF, and online hydroperoxide measurements from
14 the various CIMS instruments present to provide the most comprehensive picture thus far on
15 the humidity-dependent ozonolysis of isoprene.

16 **f. Competitive- HO_2 nitrate (NO_3) oxidation (Exp. 9 and 13):** The NO_3 -initiated experiments
17 during the campaign were performed in the dark, under dry conditions. Excess formaldehyde
18 ($[\text{HCHO}]_i \sim 4 - 8$ ppmv) was used as a dark HO_2 precursor in order to elevate the
19 contributions of $\text{RO}_2 + \text{HO}_2$ reactions in the NO_3 chemistry:





2 This process produces an HO₂/NO₃ ratio of approximately 2 (determined by photochemical
3 modeling from the mechanism described in Paulot et al (2009)), a ratio more relevant to the
4 troposphere during nighttime oxidation. As α-pinene has a higher NO₃ loss rate compared to
5 isoprene, a factor of 2 greater mixing ratio of initial formaldehyde was used. The
6 consequence of the experimental design is that the isoprene nitrooxy hydroperoxide (INP)
7 and monoterpene nitrooxy hydroperoxide (MTNP) are major products, in contrast to
8 experiments performed under RO₂ + RO₂ or RO₂ + NO₃ dominated conditions (Ng et al.,
9 2008; Perring et al., 2009; Kwan et al., 2012). The focus of these experiments was the
10 quantification of INP and MTNP with the various CIMS and with TDLIF, and further
11 exploration of their loss channels to OH oxidation (simulating sunrise) or to dry AS seed
12 particles by measuring organic aerosol growth on the ToF-AMS. These experiments were
13 performed with isoprene and α-pinene precursors.

14 **g. High NO₂/NO photooxidation** (Exp. 26 and 30): The high NO₂-to-NO ratios in the lower
15 troposphere in most regions of the globe favor the production of acylperoxy nitrates (APNs)
16 from the OH-initiated reaction of aldehydes like methacrolein and pinonaldehyde (Bertman
17 and Roberts, 1991; Nozière and Barnes, 1998). Unlike the APN from methacrolein (MPAN),
18 the APN from pinonaldehyde has never been measured in the atmosphere (Nouaime et al.,
19 1998; Roberts et al., 1998; Wolfe et al., 2009). The OH oxidations of aldehydes were
20 performed with an NO₂/NO ratio > 10, and NO₂ was replenished as it was reacted away.
21 These reactions were initiated by CH₃ONO photolysis under higher light flux, producing
22 [OH] > 3 x 10⁶ molec cm⁻³. Certain APNs were monitored with ToFCIMS, and total peroxy
23 nitrates (ΣPNs) were monitored with TDLIF. A major focus of the high-NO₂ experiments

1 was to investigate the SOA-formation potential and mechanisms from atmospherically-
2 relevant APNs, which is expanded in **h**.

3 **h. SOA-formation chemistry** (Exp. 19, 24, 26, and 30): Experiments aimed specifically at
4 studying chemistry leading to SOA formation have overlapping goals with those described
5 above. One focus was the evaluation of the SOA-formation route from APNs by the
6 proposed dioxo ketone, lactone, and epoxide mechanisms (Chan et al., 2010; Kjaergaard et
7 al., 2012 ; Lin et al., 2013), none of which have yet been validated by independent studies.
8 However, the proposed epoxide chemistry has been integrated into some studies published
9 soon after the proposal by Lin et al. (2013) (Worton et al., 2013; Pye et al., 2013). After
10 MPAN was formed from the high-NO₂ reaction of MAC + OH, a synthesized standard of
11 methacrylic acid epoxide (MAE, provided by the UNC group), the proposed epoxide
12 intermediate, was added to discern the SOA-forming potential of MAE vs. other reactive
13 intermediates in the MPAN reaction. Following the injection and stabilization of MAE, water
14 vapor was added until the reaction mixture reached ~ 40% RH. Then wet AS seeds were
15 injected to investigate any SOA mass growth, as quantified by ToF-AMS.

16 SOA formation from ISOPN high-NO photooxidation and isoprene low-NO
17 photooxidation products were investigated in the presence of wet AS seeds (40 – 50%
18 particle liquid water by volume), meant to simulate the high particle liquid water and sulfate
19 quantities during SOAS. For these experiments, the chambers were humidified to 40 – 50%
20 RH, and hydrated AS particles were injected through a wet-wall denuder so that the seed
21 particles retain liquid water above the efflorescence point of AS (Biskos et al., 2006). In the
22 ISOPN high-NO photooxidation, the potential for forming organics that will likely condense
23 onto seed particles, e.g., dinitrates and IEPOX, was recently suggested (Lee et al., 2014b;

1 Jacobs et al., 2014). The dinitrate pathway was investigated as a potential source of particle-
2 phase organic nitrogen. In the low-NO isoprene photooxidation, IEPOX reactive uptake onto
3 acidic Mg₂SO₄ particles (Lin et al., 2012) and non-acidified AS particles (Nguyen et al.,
4 2014), both with non-zero liquid water content, were recently demonstrated. We focused on
5 AS particles with no added acid. The impact of the partitioning of IEPOX on the gas-phase
6 mixing ratios was examined as a potential reason for the differences in observed IEPOX in
7 dry and humid regions.

8 **i. Cross-calibrations** (Exp. 4a, 5a, 24, 27, and 30): Newly commercially-available negative-
9 ion CIMS (Junninen et al., 2010; Lee et al., 2014a) may become common tools for
10 monitoring complex OVOCs in the atmosphere, similarly to the widespread adoption of
11 positive ion CIMS (PTR-MS based instruments). Some of the new negative ion CIMS
12 instruments were deployed for the first time in field campaigns occurring in recent years.
13 During FIXCIT, synthesized standards of 8 isomer-specific compounds were available for
14 cross calibrations with different CIMS in order to better understand the chemical sources of
15 ambient signals during SOAS and in other field campaigns. Table 3 shows the structures,
16 abbreviations, and contributors of the synthesized chemicals. The TripCIMS and the GC-
17 ToFCIMS separated structural isomers through collision-induced dissociation (CID) and
18 through chromatography, respectively. Figure 3 shows a GC-ToFCIMS separation of isomers
19 of the ISOPN synthesized standards, as well as ISOPNs present in a complex photooxidation
20 mixture. SRI-ToFMS and IACIMS tested the switchable reagent ion sources for preferential
21 detection of one or more isomers of compounds with the same molecular formula.

22 For certain cross-calibrations experiments, standards were injected into an inflatable
23 pillow bag (~ 0.2 – 0.3 m³) that was filled with dry N₂ to a known volume. The purities of the

1 standards were quantified by nuclear magnetic resonance (NMR) or Fourier-transform
2 infrared spectrometry (FT-IR). The injected material was measured by vapor pressure,
3 quantitative volume transfer, or by ToFCIMS and TripCIMS that were calibrated using
4 techniques described elsewhere (Garden et al., 2009; Paulot et al., 2009a; Lee et al., 2014b;
5 Bates et al., 2014). Some experiments, such as the IEPOX photooxidation experiment, also
6 served a dual purpose for cross-calibration. For example, *trans* β -IEPOX was injected into a
7 clean chamber and instruments were allowed to sample for ~ 1 h to cross-calibrate before an
8 oxidant precursor was injected. Both LIF-OHR and CRM-OHR were able to measure the OH
9 reactivity of these OVOC compounds individually, which aids in determining the known and
10 unknown OH reactivity in ambient environments.

11 **j. GTHOS test experiments:** The OH interference in GTHOS, and possibly other gas-
12 expansion LIF techniques, has been shown to systematically bias OH measurements high in
13 some biogenically-influenced areas unless chemical zeroing was performed (Mao et al.,
14 2012). The excess OH was demonstrated not to be produced by the GTHOS laser itself (308
15 nm) but rather, more likely, in the low-pressure flow zone within the nozzle of the
16 instrument. During FIXCIT, several hypotheses proposed by Mao et al (2012), and some
17 original proposals based on field observations, were tested. The interference precursor
18 candidates were: (i) ozonolysis intermediates – tested with ozonolysis experiments and with
19 ozone injection into the GTHOS inlet; (ii) biogenic peroxides like ISOPOOH or HMHP –
20 tested with synthesized standards; (iii) background chemistry such as $\text{NO}_2 + \text{O}_3$ – tested by
21 the nitrate-oxidation experiment and by sequential injection of NO_2 and O_3 separately; (iv)
22 dry and humid $\text{HO}_2 + \text{O}_3$ reaction – tested by formaldehyde photolysis with ozone injection
23 during a separate experiment (2/1/14, not shown in Table 2); (v) beta-hydroxy RO_2 radicals

1 formed from OH + alkene – tested with the photooxidation of 2-methyl-2-butanol and
2 compared with 2,2-dimethylbutane (2/2/14 and 1/31/14, not shown in Table 2); and (vi) heat-
3 mediated decomposition of thermally-unstable species – tested by temperature ramping to 35
4 – 40 °C inside the chamber. Often, single variables (like ozone or heat) were isolated by
5 incremental additions toward the end of an experiment.

6 The experiments not described in Table 2 (to test iv and v) were performed after the
7 formal experiments; thus, not all investigators were present. Only GTHOS, ToFCIMS,
8 TripCIMS, ToF-AMS, GCFID, O₃ monitor and NO_x monitor were collecting data. The HO₂
9 + O₃ test experiment (2/1/14) was performed by injecting ~ 600 ppbv of ozone, then ~ 50
10 ppbv of cyclohexane as an OH tracer for CIMS (monitored by the formation of cyclohexyl
11 hydroperoxide). UV lights were turned on and then 4 ppmv of formaldehyde was injected,
12 which photolyzed to produce 550 pptv of HO₂. The HO₂ reaction with formaldehyde
13 produced a small yield of HMHP (Niki et al., 1980). Water vapor was injected to diagnose
14 the effect of humidity. Experiments to test the effects of RO₂ structure utilized CH₃ONO to
15 oxidize ~ 50 ppbv of either 2-methyl-2-butanol and 2,2-dimethylbutane with OH. Ozone (~
16 600 ppbv), water vapor (until RH ~ 30 – 40%), and NO₂ (400 ppbv) were added sequentially
17 at toward the end of the photooxidation. Finally severally hundred ppb of NO was added to
18 titrate away the ozone.

19 20 **2.4. Analytical challenges**

21 Throughout the campaign, several sources of analytical interferences or systematic
22 biases were discovered. Some challenges resulted from the integration of field instruments to
23 a chamber setting, where high concentrations of certain chemicals were used to engineer

1 extremely specific conditions. Thus, these issues do not affect ambient sampling. For
2 example: (1) High NO₂ levels in some experiments affected the normal operation of TDLIF
3 because the ΣANs and ΣPNs measurements were determined by subtraction of NO₂. When
4 NO₂ is much higher than ΣANs and ΣPNs, the measurement by difference contains large
5 uncertainties; (2) High H₂O₂ for low-NO conditions affected the operation of some CIMS
6 instruments because the ppmv mixing ratios of H₂O₂ depleted a non-negligible quantity of
7 reagent ions. In order to correct for this, the CIMS instruments needed to calibrate as a
8 function of H₂O₂ in addition to traditional methods, or account for the true reagent ion signal
9 (which was anti-correlated with H₂O₂ concentration). High H₂O₂ also affected GTHOS due to
10 photolysis-derived OH production by the laser. GTHOS corrected for this effect by removing
11 the OH background that was determined by sampling when only H₂O₂ was present; (3) High
12 formaldehyde, cyclohexane, or H₂O₂ dominated the OH reactivity for certain experiments. In
13 experiments where ppmv levels of volatile compounds were used, LIF-OHR and CRM-OHR
14 did not operate. In contrast, high ozone and NO levels did not appear to affect the operation
15 of any instruments. Temperature and humidity effects on ion sensitivities have been
16 corrected for by ToFCIMS and TripCIMS as standard procedure. Other CIMS are actively
17 characterizing these effects for analytes of interest.

18 Yet other analytical challenges were not unique to laboratory studies. It was found
19 that chemical artifacts were produced from the decomposition of multifunctional OVOC
20 (e.g., ISOPN, ISOPOOH, IEPOX, and pinonaldehyde) under normal operating conditions in
21 some instruments; thus, possibly affecting ambient sampling and field data interpretation.
22 Scheme 2 shows the proposed decomposition pathways of certain isomers of isoprene-
23 derived OVOC to form MAC and MVK. We are aware of MAC and MVK interference only

1 from the 1,2- and 4,3- isomers of ISOPOOH, the 1,2- and 4,3- isomers and ISOPN, and the
2 beta isomers of IEPOX (i.e., the peroxide, nitrate, and epoxide groups are secondary or
3 tertiary). Unfortunately, these isomers are expected to be the most abundant in the
4 atmosphere, e.g., the beta IEPOXs are estimated to represent > 97% of atmospheric IEPOX
5 (Bates et al., 2014). The extent of decomposition and product distribution may also vary
6 based on the operating conditions of the particular analytical method. In general, the
7 decomposition was exacerbated by instruments with harsher sampling conditions, i.e., high
8 ionization energy (e.g., the standard H_3O^+ mode of SRI-ToFMS), high temperatures, and/or
9 materials incompatible with organics (e.g., the hot stainless steel sample loop and inlet of
10 GCFID). OVOCs from the low-NO isoprene photooxidation have been shown to decompose
11 to MAC and MVK in commercial PTRMS instruments (Liu et al., 2013), but the exact
12 identities of the compounds were unclear. During FIXCIT, it was observed that ISOPOOH,
13 IEPOX, and pinonaldehyde were detected at m/z 71.050 in the SRI-ToFMS in PTR mode
14 (the sum of MAC+MVK). Switchable reagent ions show promise for removing certain
15 biases, but more work is needed to characterize the chemistry that forms interfering ions.
16 Further, we observed that the decomposition interference also affected GCFID, the other
17 commonly-used detection method for MAC and MVK in ambient samples. ISOPOOH,
18 IEPOX, and ISOPN were detected as either MAC or MVK in the GCFID, depending on the
19 specific isomer. The interferences may not be localized to this particular GCFID, and a more
20 detailed account is forthcoming (Rivera et al., 2014). Conversion efficiencies of OVOCs to
21 the C_4 carbonyls in the Caltech GCFID range in order of ISOPOOH > IEPOX > ISOPN, and
22 can be almost quantitative for ISOPOOH because of the facile cleavage of the weak O-O

1 bond. Lastly, ISOPN were found to be converted to NO with a small yield in the NO-CL and
2 a larger yield in commercial NO_x analyzers.

3 All decomposition-derived artifacts can be avoided by collecting the air sample through a
4 length of tubing submerged in a cold bath (– 40 °C), which trapped OVOCs that are less
5 volatile than authentic MAC and MVK. Liu et al (2013) implemented this technique
6 successfully in their laboratory study using SRI-ToFMS, resulting in a lower yield than
7 previously reported for MAC and MVK in the low-NO oxidation of isoprene. Field
8 application may prove more challenging, however, as the trapping is labor-intensive and
9 requires careful humidity control to avoid ice buildup and blockage. During FIXCIT, both
10 GCFID and SRI-ToFMS employed trapping techniques at various times to avoid biases in
11 the detection and interpretation of MAC and MVK data.

12 **3. Preliminary results and atmospheric implications:** Forthcoming papers will discuss
13 campaign results in detail. Here, we summarize a few interesting observations that appeared
14 to be robust based on preliminary data analysis of the laboratory and field work.

- 15 • *Nighttime chemistry of alkenes, as controlled by the NO₃ radical, leads to several*
16 *organic nitrates that are unique compared to daytime high-NO photooxidation. A*
17 *significant product is the nitrooxy hydroperoxide, the atmospheric importance of*
18 *which has likely been significantly underestimated in past chamber studies. The*
19 *nitrooxy hydroperoxide reacts further in the daytime through a currently-unknown*
20 *mechanism.*
- 21 • *The high-NO hydroxy nitrate yield from isoprene is closer to the high end of the*
22 *spectrum (range 4 – 15%), important for the accurate simulations of volatile nitrogen*
23 *in the atmosphere.*

- 1 • *Observed mixing ratios of isoprene low-NO photooxidation products are impacted by*
2 *heterogeneous chemistry that appears to be mediated by aqueous processes, which*
3 *has implications for the interpretation of IEPOX observations in dry vs. humid areas*
4 *of the world.*
- 5 • *Environmental conditions in many locations, including within a biomass burning*
6 *plume, are favorable for the H-shift RO₂ isomerization chemistry that produces*
7 *compounds like HPALDs and very low-volatility oxygenates. The atmospheric fate of*
8 *HPALDs is highly impacted by direct photolysis that recycles OH, as well as other*
9 *complex chemistry and physical processes.*
- 10 • *The ozonolysis reaction of isoprene produces a high yield of C₁ compounds that are*
11 *also observed with considerable abundance during ambient sampling. The*
12 *hydroperoxide and acid yields appear to be underestimated by previous studies that*
13 *detected these compounds via offline techniques. The OH yield may not follow the*
14 *same trend with RH as the hydroperoxide and acid yields.*
- 15 • *APNs are efficient SOA precursors. SOA formation was prompt, and organic mass*
16 *growth occurred quickly without the addition of inorganic seeds, i.e., the SOA*
17 *intermediate(s) from APN+OH condensed onto predominantly-organic SOA*
18 *material. Injections of the MAE standard did not increase the SOA mass growth.*
- 19 • *Several experiments produced significant amounts of excess OH, as measured by the*
20 *GTHOS instrument, providing further avenues for investigation. These experiments*
21 *also ruled out several candidates for the OH interference. More work is underway to*
22 *comprehensively characterize the phenomenon.*

- *Calibrations with several synthesized standards of OVOC (Table 3) significantly aid in data interpretation from OHR and new CIMS instruments. Sampling these OVOC through standard instrumentation may interfere with some routine field and chamber measurements (depends on the run conditions and instrument setup), but may be mediated by cold-trapping methods. This is likely a contributing factor in the high discrepancies in MAC and MVK yields from low-NO isoprene photooxidation previously reported. For example, we find the preliminary low-NO yields of MVK ($6 \pm 3\%$) and MAC ($4 \pm 2\%$), determined by GC-FID, from photooxidation of isoprene are consistent with Liu et al (2013) when cold-trapping methods were employed (Exp #21). However, the low-NO “yields” of MVK and MAC are each $> 40\%$ when sampled directly by the GC-FID from the chamber (Exp #2) due to interferences by isomers of ISOPROOH (Rivera et al., 2014) and possibly other OVOCs.*

Final data from the FIXCIT campaign will be made publicly available on archives hosted by the U.S. National Oceanic and Atmospheric Administration (NOAA, <http://esrl.noaa.gov>) in January 2016. Data will be submitted in the ICARTT format, standardized by the U.S. National Aeronautics and Space Administration (NASA, <http://www-air.larc.nasa.gov/missions/etc/IcarttDataFormat.htm>).

4. Summary

Although data analysis is ongoing, the goals of the FIXCIT campaign appear to have been met during the campaign period. The insights gained from experimental observations under well-controlled laboratory conditions have already proved valuable for understanding ambient observations from SOAS. The community effort to pursue atmospherically-important chemistry with sensitive ambient techniques and custom-synthesized chemicals

1 has elevated our understanding of atmospheric oxidation for a number of biogenic
2 compounds. Novel mechanistic information obtained during FIXCIT will be helpful to
3 update chemical mechanisms currently implemented in large-scale chemistry-coupled
4 transport models. Instrumental inter-comparisons, an important aspect of the campaign, have
5 demonstrated that a thorough characterization of new and standard ambient sampling
6 techniques using authentic standards is necessary for accurate data interpretation.

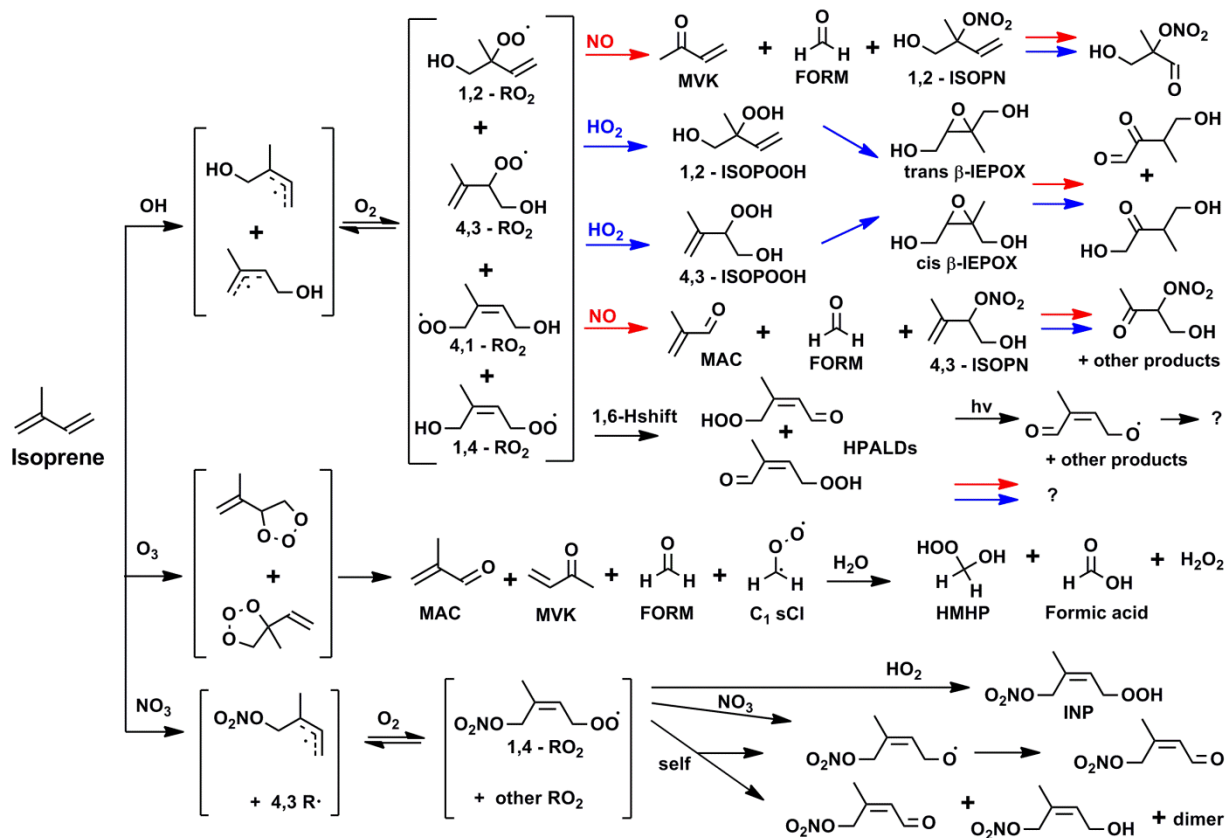
7 Chamber experiments are clearly invaluable to the field of atmospheric chemistry, as
8 the results feed directly into models that are used to ascertain regional and global climate and
9 chemistry feedbacks. Further, chamber data aid in the interpretation of complex results
10 obtained from field studies. Yet, it can be difficult to decipher the conditions under which
11 chamber experiments are most relevant, and a standard protocol for data reporting may be
12 needed. For example, best estimates of oxidation conditions in chambers (i.e., if reactions are
13 HO₂-dominated, low-NO but RO₂-dominated, high-NO, high-NO_x but low-NO, and so on)
14 would greatly aid in comparisons of these experiments and others. The experiments in this
15 campaign were fundamentally focused on the fate of the RO₂ radical as a delineation between
16 chemical regimes. FIXCIT experiments (Table 2) can be further improved or tailored to the
17 specific needs of the scientist. It has been demonstrated, here and elsewhere, that chamber
18 studies that include chemistry representative of the atmosphere and well-characterized
19 instrumental methods can accurately reproduce observations in the ambient environment.
20 The results from FIXCIT make a case for future synergistic integration of laboratory studies
21 with field campaigns, which maximizes the level of mechanistic understanding and data
22 confidence obtained from the combination of both types of studies.

23

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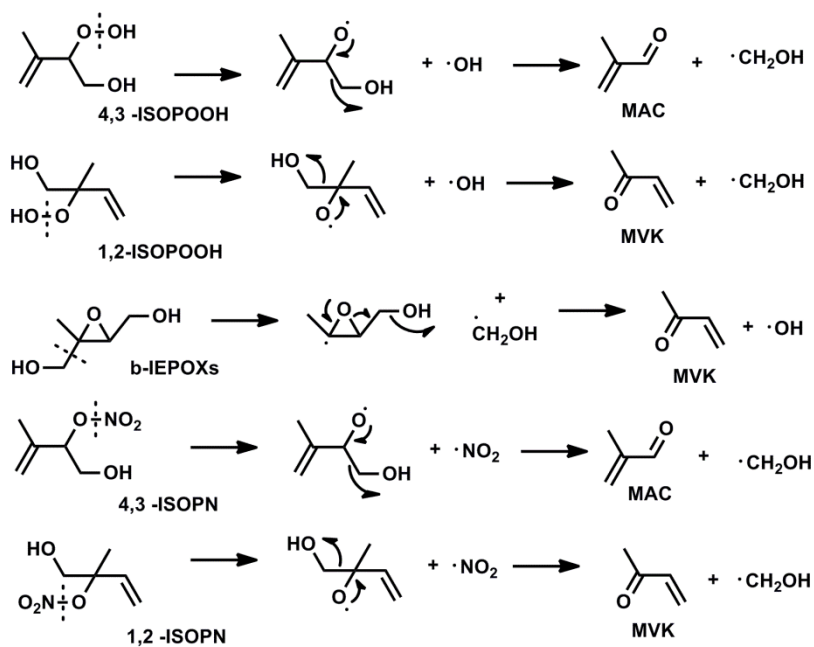
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1 Schemes



2
3 **Scheme 1:** Representative mechanism from the OH-, O₃- and NO₃-initiated oxidation of isoprene.
4 The most abundant isomers of a particular pathway are shown. Red and blue arrows in the OH-
5 oxidation scheme denote the NO-dominated and HO₂-dominated RO₂ reactions, respectively. For
6 the ozonolysis reaction, only the C₁ sCI and its reaction with water are shown as further-
7 generation chemistry. For the NO₃-oxidation pathway, only one isomer each of R and RO₂
8 radicals is shown for brevity. Abbreviations are defined in the text.

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10



1

2 **Scheme 2:** Select proposed mechanism for the decomposition of OVOCs to carbonyls on contact

3 with metal surfaces or high ionization energies within instrumentation. Other decomposition

4 pathways likely exist and the branching ratios are dependent on instrument operation conditions.

5 Cleavage sites are indicated by dashed lines.

6

7

1 **Table 1:** List of participating instruments, principle investigators (PIs), and institutions. Key
 2 acronyms: laser-induced fluorescence (LIF), laser-induced phosphorescence (LIP), high-
 3 resolution time-of-flight (HRTof), compact time-of-flight (CTof), MS (mass spectrometer), and
 4 CIMS (chemical ionization mass spectrometer).

Instrument	Instr. ID	PI(s)	Institutions	Measurements	Ref.
Ground-based Hydrogen Oxides Sensor	GTHOS	W.H. Brune	Pennsylvania State University (PSU)	OH, HO ₂ , RO ₂	Brune et al., 1995
LIF OH reactivity monitor	LIF-OHR	W.H. Brune	PSU	OH reactivity by decay of OH	Mao et al., 2009
Thermal dissociation LIF NO ₂ monitor	TDLIF	R.C. Cohen	University of California, Berkeley (UCB)	NO ₂ , sum of organic nitrates (ΣANs), sum of peroxy nitrates (ΣPNs), particulate org. nitrates (pANs)	Day et al., 2002
Switchable iodide and acetate ion HRTof-CIMS	IACIMS	D.K. Farmer	Colorado State University (CSU)	Oxidized VOCs (organic nitrates, organic acids, etc.)	Lee et al., 2014a
NO ₃ ⁻ HRTof-CIMS	NO ₃ CIMS	M.R. Canagaratna, D.R. Worsnop, J.L. Jimenez	Aerodyne Research, Inc. (ARI) and Univ. of Colorado, Boulder (CUB)	Low-volatility organic compounds	Junninen et al., 2010
LIP glyoxal monitor	GlyLIP	F.N. Keutsch	University of Wisconsin, Madison (UWM)	Glyoxal	Huisman et al., 2008
LIF formaldehyde monitor	FormLIF	F.N. Keutsch	UWM	Formaldehyde	Hottle et al., 2008; DiGangi et al., 2011
Comparative rate method OH reactivity monitor	CRM-OHR	S. Kim, A.B. Guenther	Univ. of California, Irvine (UCI) and Pacific NW National Lab (PNNL)	OH reactivity by decay of hydrocarbons	Sinha et al., 2008
Switchable reagent ion (H ₃ O ⁺ /NO ⁺ /O ₂ ⁺) HRTof-MS	SRI-ToFMS	A.B. Guenther, J.E. Mak, A.H. Goldstein	PNNL, SUNY Stonybrook (SUNY), and UCB	Hydrocarbons, carbonyls, alcohols, etc.	Jordan et al., 2009
Chemical luminescence NO monitor	NO-CL	G.S. Tyndall, D.D. Montzka, A.J. Weinheimer	National Center for Atmospheric Research (NCAR)	NO (> 25 pptv)	Ridley and Grahek, 1990
CF ₃ O ⁻ triple quadrupole CIMS	TripCIMS	P.O. Wennberg	California Institute of Technology (Caltech)	ISOPOOH, IEPOX, glycolaldehyde, acetic acid, methyl hydroperoxide	St. Clair et al., 2010

CF ₃ O ⁻ CTof-CIMS	ToFCIMS	P.O. Wennberg	Caltech	Oxygenated VOCs (hydroperoxides, organic nitrates, multifunctional compounds)	Crouse et al., 2006
Gas chromatograph with ToFCIMS	GC-ToFCIMS	P.O. Wennberg	Caltech	Isomers for oxygenated VOCs	Bates et al., 2014
HRTof- aerosol mass spectrometer	ToF-AMS	J.H. Seinfeld	Caltech	Aerosol composition and size distribution	DeCarlo et al., 2006; Canagaratna et al., 2007
Gas chromatograph with flame-ionization detector	GCFID	J.H. Seinfeld	Caltech	Isoprene, methacrolein, methyl vinyl ketone, cyclohexane	N/A
Thermocouple and membrane probe	T/RH probe	J.H. Seinfeld	Caltech	Temperature and relative humidity	N/A
UV-absorption ozone monitor	O ₃ monitor	J.H. Seinfeld	Caltech	O ₃ (> 1000 pptv)	N/A
Chemical luminescence NOx detector	NOx monitor	J.H. Seinfeld	Caltech	NO (> 500 pptv), and NO ₂ (catalytic conversion to NO)	N/A

1

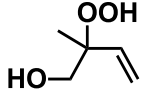
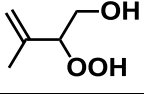
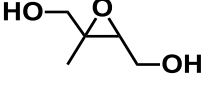
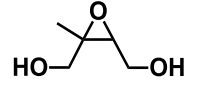
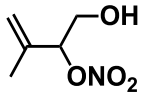
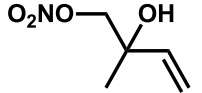
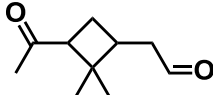
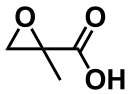
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1 **Table 2:** Formal experiments and reaction conditions during the campaign. Chemical
2 abbreviations are defined in Table 3. Other abbreviations are: C1 = Chamber 1, C2 = Chamber 2,
3 ISOP=isoprene, α -PIN = α -pinene, HP = hydrogen peroxide, MN = methyl nitrite, CHX =
4 cyclohexane, HCHO = formaldehyde, AS = ammonium sulfate seeds. Exp. types are defined in
5 the text. Exp. # corresponds to the date in Jan. 2014 when the experiment was performed.

#	Exp. type	HC precursor	[HC] (ppb)	Ox	Ox source	[OH] _{ss} (# cm ⁻³)	[O ₃] _i (ppb)	[NO] _i (ppb)	[NO ₂] _i (ppb)	[NO] [HO ₂]	Add'l Inj.	Rxn T (°C)	RH (%)
2	b	ISOP	45	OH	HP + hv	1.5 x 10 ⁶	< 5	< 0.04	< 2	1/7	–	27	< 5
3	c	ISOP	100	OH	HP + hv	2.4 x 10 ⁶	< 5	500	15	> 100	–	26	< 5
4a	i	ISOPOOHs	250	–	–	–	–	–	–	–	–	24	< 3
4b	a	Blank C1	0	OH	HP + hv	2.0 x 10 ⁶	< 5	< 0.04	< 3	1/6	–	27 – 33	< 5
5a	i	ISOPNs	< 13	–	–	–	–	–	–	–	–	24	< 3
5b	a	Blank C2	0	OH	HP + hv	2.0 x 10 ⁶	< 5	< 0.04	< 2	1/5	–	27	< 5
6	e	ISOP	91	O ₃	O ₃ rxn	[OH] _i ~ 1 x 10 ⁶	615	< 0.04	< 3	–	–	25	< 5
7*	d	ISOP	30	OH	MN + hv	4.1 x 10 ⁴ , 4.8 x 10 ⁶	< 5	0.08	45	2, 6	–	40, 40	< 5
9	f	ISOP	18	NO ₃	NO ₂ /O ₃	3.8 x 10 ⁸	55	0.10	100	2 – 3	HCHO	26	< 5
10	b	α -PIN	30	OH	HP + hv	2.0 x 10 ⁶	< 5	< 0.04	< 2	1/10	–	27	< 5
11	c	α -PIN	30	OH	HP + hv	2.5 x 10 ⁶	< 5	85	10	> 100	–	26	< 5
13	f	α -PIN	30	NO ₃	NO ₂ /O ₃	4 x 10 ⁸	75	0.17	150	1.5 – 8	HCHO	25	< 5
14	e	ISOP	100	O ₃	O ₃ rxn	[OH] ~ 0	605	< 0.04	< 3	–	CHX	25	< 5
16*	d	α -PIN	30	OH	MN + hv	6 x 10 ⁴ , 4 x 10 ⁶	< 5	0.08	< 3	2 – 3, 10	–	40, 40	< 5
17	b, i	4,3- ISOPOOH	60	OH	HP + hv	1.2 x 10 ⁶	< 5	< 0.04	< 3	1/5	–	26	< 5
18*	d	ISOP	28	OH	MN + hv	1.0 x 10 ⁵ , 4.3 x 10 ⁶	< 5	0.08	< 3	2 – 3, > 100	–	25, 26	< 5
19	b, h	ISOP	60	OH	HP + hv	1.0 x 10 ⁶	< 5	< 0.04	< 4	1/5	wet AS	28	51
21	b	ISOP	22	OH	HP + hv	2.0 x 10 ⁶	< 5	< 0.04	< 2	1/10	–	27	< 5
22	c	ISOP	100	OH	HP + hv	2.3 x 10 ⁶	< 5	430	15	> 100	–	27	< 5
23	e	ISOP	90	O ₃	O ₃ rxn	[OH] _i ~ 1 x 10 ⁶	600	< 0.04	< 3	–	–	25	50
24	c, h, i	4,3 - ISOPN	12	OH	HP + hv	3 x 10 ⁶	7	115	55	> 100	wet AS	26	52
25	b	MAC	43	OH	HP + hv	3 x 10 ⁶	< 5	< 0.03	< 3	1/10	–	28	< 5
26	g, h	MAC	45	OH	MN + hv	2 x 10 ⁷	< 5	3.5	50	10 – 20	MAE, wet AS	26	< 5, 40
27	d, i	<i>trans</i> β - IEPOX	60	OH	MN + hv	7.3 x 10 ⁶	< 5	0.25	< 3	2 – 5	–	25	< 5
29	e	ISOP	91	O ₃	O ₃ rxn	[OH] ~ 0	610	< 0.04	< 4	–	CHX	25	58
30	g, h, i	Pinonald.	15	OH	MN + hv	3.5 x 10 ⁶	< 5	0.50	< 3	4 – 8	–	26	< 5

* 1% lights, 20% lights, then 100% lights

1 **Table 3:** List of contributed synthesized chemical standards for experiments and calibration.

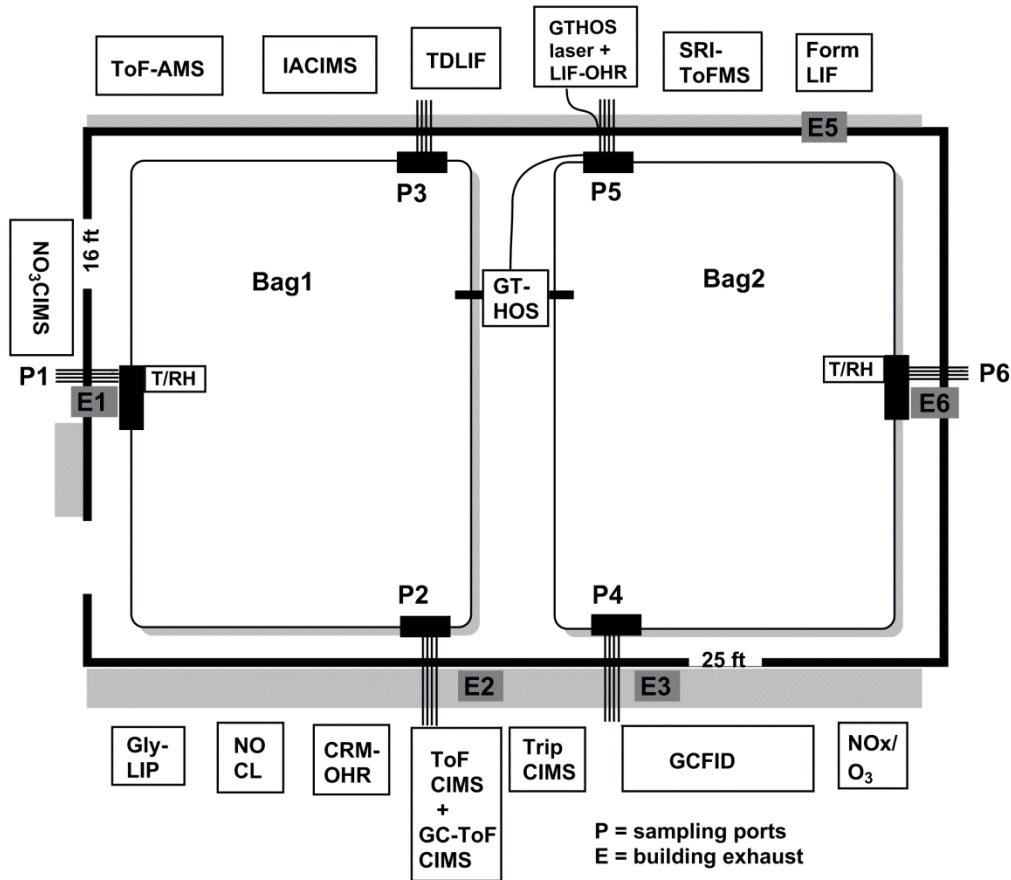
Synthesized standard	PIs	Institutions	Molecular structure	Atmos. Relevance	Synthesis Ref.
Isoprene 1-hydroxy 2-hydroperoxide (1,2 – ISOPOOH)	F.N. Keutsch	UWM		Major 1 st gen low-NO Isoprene + OH product	Rivera et al., 2014
Isoprene 3-hydroxy 4-hydroperoxide (3,4 – ISOPOOH)	F.N. Keutsch	UWM		Major 1 st gen low-NO Isoprene + OH product	Rivera et al., 2014
<i>trans</i> Isoprene 2-epoxydiol (<i>trans</i> β-IEPOX)	P.O. Wennberg and J.H. Seinfeld	Caltech		Major 2 nd gen low-NO Isoprene + OH product	Bates et al., 2014
<i>cis</i> Isoprene 2-epoxydiol (<i>cis</i> β-IEPOX)	P.O. Wennberg and J.H. Seinfeld	Caltech		Major 2 nd gen low-NO Isoprene + OH product	Bates et al., 2014
Isoprene 4-hydroxy 3-nitrate (4,3 – ISOPN)	R.C. Cohen, P.B. Shepson, A.S. Hasson, and P.O. Wennberg	UCB, Purdue Univ, CSU Fresno (CSUF), and Caltech		Major 1 st gen high-NO Isoprene + OH product	Lee et al., 2014b
Isoprene 2-hydroxy 1-nitrate (2,1 – ISOPN)	A.S. Hasson	CSUF		Minor 1 st gen high-NO Isoprene + OH product	N/A
Pinonaldehyde	P.O. Wennberg and J.H. Seinfeld	Caltech		Major 1 st gen α-Pinene + OH and O ₃ product	Griesbaum et al., 1997
Methacrylic acid epoxide (MAE)	J.D. Surratt and A. Gold	Univ. of NC Chapel Hill (UNC)		Minor product and possible SOA precursor from MAC + OH + NO ₂ reaction	Lin et al., 2013

2

1 **Figures**

2

3

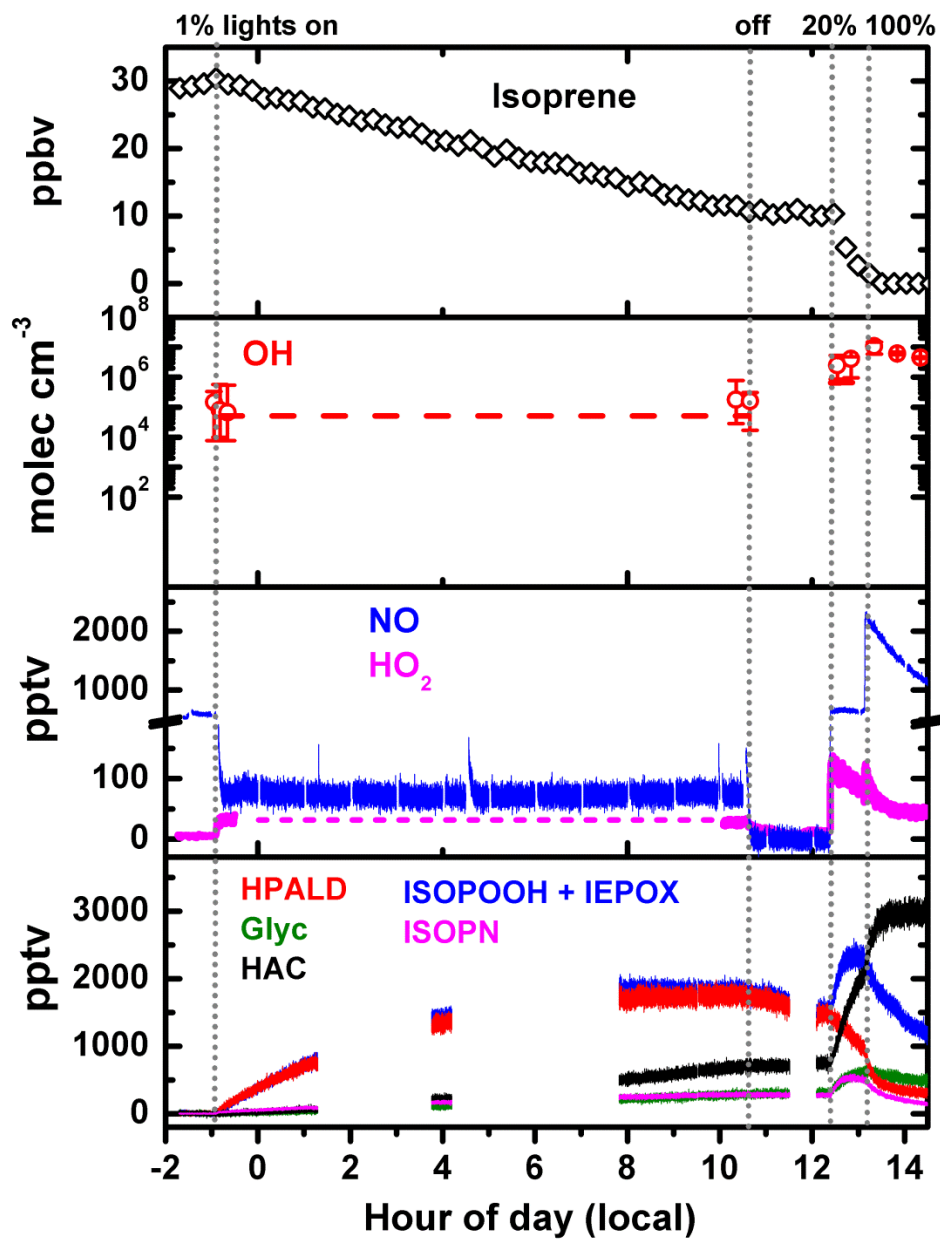


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5 **Figure 1:** Arrangement of instruments at the Caltech Atmospheric Chamber Facility during the
6 campaign. Instrument IDs are in Table 1.

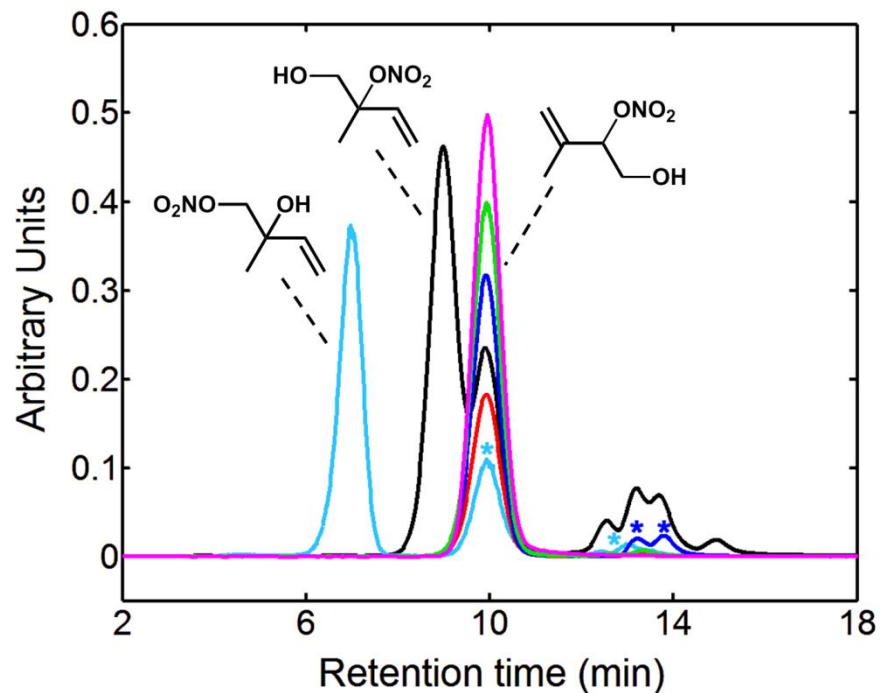
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 2 **Figure 2:** Progress of the slow chemistry experiment performed on 1/7/14. Isoprene data were
 3 provided by GCFID. The red dashed line in the OH plot is the steady-state OH concentration
 4 derived from the decay of isoprene as monitored by GCFID. OH and HO₂ preliminary data were
 5 provided by GTHOS, using chemical zeroing, although the steady-state value of $(0.4 - 1) \times 10^5$
 6 molec cm⁻³ was below the detection limit of GTHOS. OH preliminary data were averaged to
 7 reduce noise. NO data were provided by NO-CL and OVOC data were provided by ToFCIMS.

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1
 2 **Figure 3:** GC-ToFCIMS chromatogram of ISOPNs from an isoprene high-NO photooxidation
 3 experiment (black), and from the introduction of 2,1-ISOPN standard synthesized by CSUF
 4 (cyan) and 4,3-ISOPN standards synthesized by Caltech (magenta), CSUF (green), UCB (blue),
 5 and Purdue (red). The rightmost four peaks apparent in the photooxidation chromatogram are
 6 preliminarily identified as the *cis* and *trans* 1,4-ISOPN and *cis* and *trans* 4,1-ISOPN, although
 7 the elution order is not clear. Asterisks (*) denote impurities in synthesized samples of
 8 corresponding color.

9

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