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# Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: Observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry

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**Abstract** Atmospheric volatile organic compound (VOC) oxidation mechanisms under pristine (rural/remote) and urban (anthropogenically-influenced) conditions follow distinct pathways due to large differences in nitrogen oxide ($NO_x$) concentrations. These two pathways lead to products that have different chemical and physical properties and reactivity. Under pristine conditions, isoprene hydroxy hydroperoxides (ISOPOOHs) are the dominant first-generation isoprene oxidation products. Utilizing authentic ISOPOOH standards, we demonstrate that two of the most commonly used methods of measuring VOC oxidation products (i.e., gas chromatography and proton transfer reaction mass spectrometry) observe these hydroperoxides as their equivalent high-NO isoprene oxidation products – methyl vinyl ketone (MVK) and methacrolein (MACR). This interference has led to an observational bias affecting our understanding of global atmospheric processes. Considering these artifacts will help close the gap on discrepancies regarding the identity and fate of reactive organic carbon, revise our understanding of surface-atmosphere exchange of reactive carbon and SOA formation, and improve our understanding of atmospheric oxidative capacity.

## 1. Introduction

Atmospheric oxidation of volatile organic compounds (VOCs) is driven by catalytic cycles of hydrogen oxides ($HO_x \equiv OH + HO_2$) and nitrogen oxides ($NO_x \equiv NO + NO_2$). These oxidation reactions are coupled to the formation of secondary pollutants, e.g., ozone and secondary organic aerosol (SOA), which affect climate, human health, and the environment. VOC reactivity can also impact the atmospheric oxidative capacity, which is dominated by the OH radical, thereby controlling the lifetime of many atmospheric trace constituents, including important greenhouse gases such as methane and hydro(chloro)fluorocarbons.

This work focuses on isoprene, the predominant biogenic emission from vegetation which contributes about one third of global nonmethane VOC emissions (i.e., reactive carbon) [*Guenther et al.*, 2006]. The peroxy radical ($RO_2$) formed in the first step of (O)VOC oxidation (OVOC = oxidized VOC) primarily reacts with either $HO_2$ or with NO (Figure 1), the latter of which is largely anthropogenic in origin. Reactions with $HO_2$ dominate the fate of $RO_2$ under pristine conditions [*Crounse et al.*, 2011]. The pristine reaction products of isoprene, i.e., the hydroxy hydroperoxides (ISOPOOHs) have very different chemical and physical properties than their urban counterparts. The pathways have different radical chain propagation properties, which directly impacts secondary pollutant production and oxidative capacity [*Crounse et al.*, 2013]. Modeling work demonstrates that only 30% of isoprene $RO_2$ reacts with NO globally, highlighting the importance of pristine products [*Crounse et al.*, 2011]. In the western and southeastern United States, ISOPOOH concentrations over 1 ppb [*Worton et al.*, 2013] have been observed with the California Institute of Technology (Caltech) $CF_3O^-$ triple-quadrupole chemical ionization mass spectrometer (CIT-3Q-MS), [*Paulot et al.*, 2009; *St Clair et al.*, 2010],
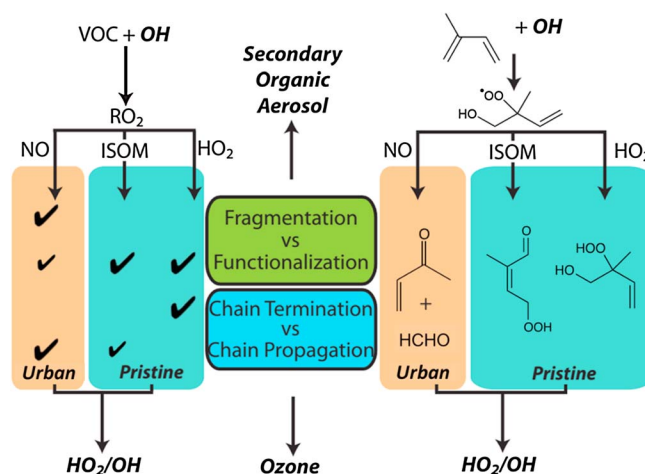
**Figure 1.** (left) General VOC oxidation scheme under urban and pristine conditions. The reaction of peroxy radicals (RO$_2$) with NO under urban conditions results in different first-generation oxidation products than the reaction with HO$_2$ or unimolecular isomerization, which dominate under pristine conditions and are important even under intermediate conditions. (right) OH radicals react with isoprene to form hydroxy-peroxy radicals (RO$_2$). Differences in chemical and physical properties of products, e.g., the degree of functionalization and fragmentation, impact SOA formation potential. Differences in the degree of radical propagation impact ozone formation and oxidative capacity.



**Figure 2.** (bottom) The gas-chromatogram from an isoprene oxidation experiment under high-NO$_x$ (urban) conditions shows the characteristic elution times of isoprene, MACR, and MVK, sampled through 0.91 m of 1/8 OD PFA Teflon tube submerged in a −40°C cold trap to remove lower volatility contaminants that would interfere with authentic MACR and MVK determinations [*Liu et al.*, 2013]. The traces are from experiments without the cold trap in which authentic (middle, red) 1,2-ISOPOOH and (top, blue) 4,3-ISOPOOH standards were introduced, respectively. Conversion yields of greater than 70% were obtained for the ISOPOOH isomers demonstrating that pristine products are detected as their urban counterparts.

rivaling concentrations of urban products. Due to regulations on NO$_x$ emission, most of the U.S., including the Southeast, is experiencing decreasing NO$_x$ concentrations [*Russell et al.*, 2012]. As a result, pristine products are increasing in importance. Accurate understanding of the chemistry and contribution of pristine VOC oxidation products is central to the capabilities of models to predict secondary pollutant concentrations, oxidative capacity, and the role of anthropogenic influence. Accurate atmospheric model results are particularly important for making informed regulatory decisions.

We describe here work that uses synthesized standards of the two main isomers of ISOPOOH, the dominant hydroperoxides derived from nonmethane VOCs, for detailed characterization of the most widely used instrumentation for monitoring VOC oxidation products: gas chromatography (GC) and proton transfer reaction–mass spectrometry (PTR-MS). We find that the peroxy bond in ISOPOOH is sufficiently weak that fragmentation is facile, leading to misidentification of ISOPOOH.

## 2. Experiment

Characterization of ISOPOOH isomers and instrument details are described in the supporting information. At Caltech, we introduced 1,2- and 4,3-ISOPOOH standards (see supporting information for structures) into an Agilent 6890N commercial GC with flame ionization detector. The resulting chromatograms included signals at the elution times of methyl vinyl ketone (MVK) and methacrolein (MACR), respectively (Figure 2). The conversion rates for both isomers are greater than 70%. The observation was reproduced with the NOAA GC-MS field instrument under standard field operating conditions (Figure S3 in the supporting information). The mass to charge ratios (*m/z*) in the GC-MS were consistent with those from MVK/MACR standards. The results show that
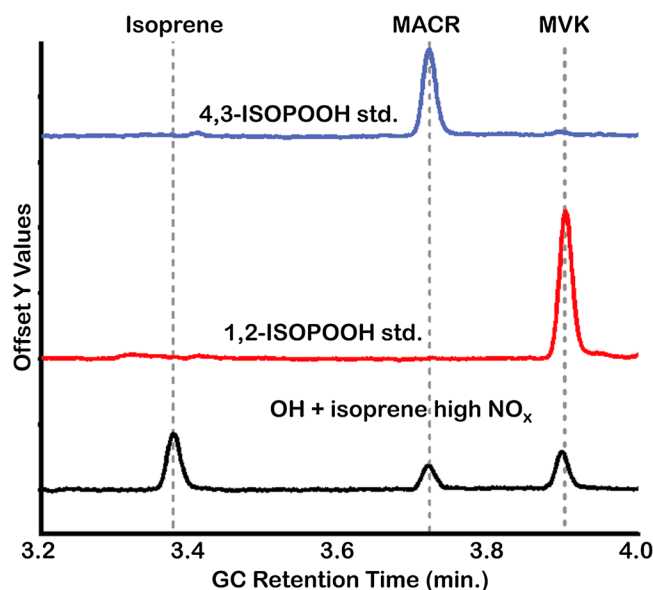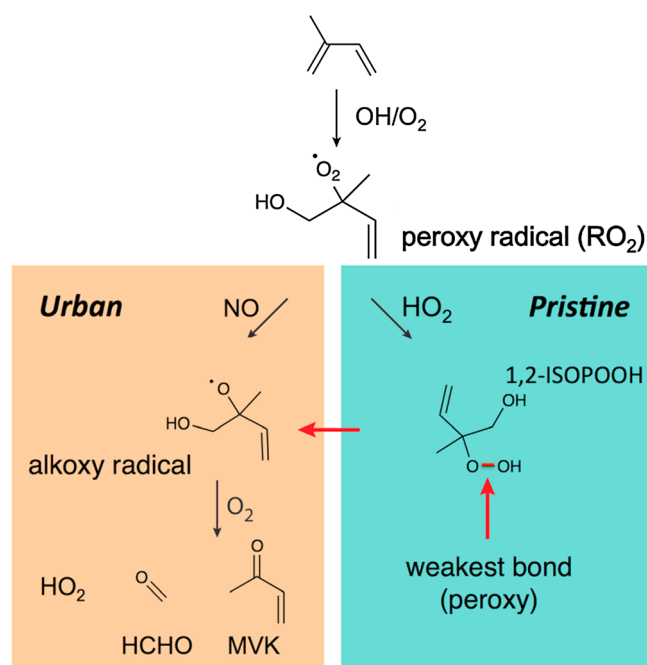
**Figure 3.** Proposed interference mechanism: Under high-NO$_x$ conditions, peroxy radicals react with NO to form alkoxy radicals that fragment rapidly to form carbonyls, e.g., MVK and formaldehyde, and hydroperoxy radical (HO$_2$), which is recycled to OH via reaction with NO. The reaction of the peroxy radical with HO$_2$ under pristine conditions forms a hydroperoxide. Breaking of the O–O bond, the weakest molecular bond, produces the alkoxy radical that is formed under urban (high NO$_x$) conditions.

ISOPOOH is detected with significant conversion efficiency as MVK and MACR in GC instrumentation used in both laboratory and field studies.

While sampling with the (quadrupole) PTR-MS (Ionicon Analytik), 1,2-ISOPOOH was detected as a product ion with $m/z$ of 71, consistent with C$_4$H$_7$O$^+$ (MVK/MACR) with an efficiency of 44% (+21/−12%) of the sensitivity of MVK based on the 1,2-ISOPOOH mixing ratio determined with the CIT-ToF-MS (California Institute of Technology–time of flight–mass spectrometry). Both ISOPOOH isomers produced significant C$_4$H$_7$O$^+$ ($m/z$ of 71.050) signals in the H$_3$O$^+$ mode of the switchable reagent ionization–time of flight–MS (SRI-ToF-MS, University of Innsbruck). Using NO$^+$ as reagent ion confirmed that C$_4$H$_7$O$^+$ observed from 1,2- and 4,3-ISOPOOHs correspond to MVK and MACR, respectively. The results with NO$^+$ also unambiguously demonstrate the fact that the decomposition of ISOPOOH occurs before any interactions with the reagent ions. These results are consistent with a recent study that observed MACR/MVK (C$_4$H$_7$O$^+$) in low-NO$_x$ isoprene oxidation experiments [Liu et al., 2013]. The authors proposed that the observed signal is an analytical interference by ISOPOOH but could not prove this due to lack of standards. Our work unambiguously confirms that ISOPOOH results in this interference in PTR-MS and SRI-ToF-MS but does not rule out other products as precursors to the C$_4$H$_7$O$^+$ signal.

Overall, experiments demonstrate that in both GC and PTR instrumentations, 1,2- and 4,3-ISOPOOHs are detected with high conversion efficiency as MVK and MACR, respectively. Although whole air sampling methods were not tested, it is likely that these are also impacted by ISOPOOH decomposition upon sampling. Previous instrument intercomparisons of PTR-MS, online GC, and whole air samples with off-line GC analysis may not be aware of the analytical challenges posed by ISOPOOH [de Gouw et al., 2003; de Gouw and Warneke, 2007], possibly because the interference has a common effect among these methods.

## 3. Interference Mechanism

Knowledge of the interference mechanism can guide experimental advances that allow distinct detection of ISOPOOH and MVK/MACR. Mechanistic understanding is also required to assess the implications beyond ISOPOOH-MVK/MACR. Organic hydroperoxides are inherently unstable species and are susceptible to a variety of decomposition mechanisms. A common reaction is homolytic cleavage of the weak peroxy bond (O–OH). This reaction can be catalyzed by metals [Fenton, 1894; Weiss, 1935; Chevallier et al., 2004]. Based on our work, we propose that the initial step of the ISOPOOH decomposition occurs via homolytic peroxy bond cleavage on metal surfaces in the GC and PTR-MS instrumentations (Figure 3 and the supporting information). This produces the isomer-specific alkoxy radicals, analogous to those formed under high-NO$_x$ conditions in the gas phase, which immediately decompose to MVK and MACR, and formaldehyde. This suggestion rationalizes the production of MVK from 1,2-ISOPOOH and MACR from 4,3-ISOPOOH.
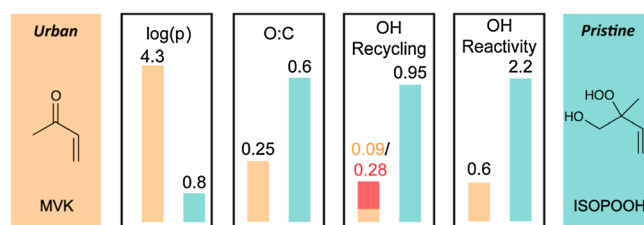
**Figure 4.** Urban (orange and red, represented by MVK) and pristine oxidation products (green, represented by 1,2-ISOPOOH) have important differences in their chemical and physical properties. The vapor pressure (log(p)) of MVK/MACR is much higher than that of ISOPOOH due to differences in functional groups (carbonyl in MVK/MACR, alcohol, and hydroperoxide for ISOPOOH) and due to the fact that ISOPOOH has a higher number of carbons since the isoprene carbon skeleton does not fragment in the first step of the pristine oxidation pathway. The oxygen to carbon ratio (O:C) of ISOPOOH is also much higher since the hydroperoxide group contributes two extra oxygen atoms when compared to MVK/MACR. Under pristine conditions, the reaction of OH with ISOPOOH returns OH efficiently after formation of IEPOX. The direct recycling of OH is much lower for the urban products since it depends on significantly slower 1,4 or 1,5 hydrogen shifts. Finally, for a given OVOC concentration, the OH reactivity ($s^{-1}$) of ISOPOOH is much higher than that of MVK/MACR due to the difference in their OH reaction rate constants. The values shown in this figure are for the isomeric mixture, but for simplicity, only MVK and 1,2-ISOPOOH are shown (see Text S6 in the supporting information).

These findings highlight that our observationally based understanding of VOC oxidation in the atmosphere may be influenced by an observational bias toward the urban, high-NO products. The source of this bias was not diagnosed previously due to a lack of standards of pristine oxidation products, which has prevented fundamental mechanistic studies of their physical and chemical properties [*Liu et al.*, 2013]. In addition, there have been few ambient observations of these compounds [*Paulot et al.*, 2009; *Worton et al.*, 2013] resulting from a combination of limitations in instrumentation to specifically observe these products and no standards to calibrate and characterize instrument performance.

## 4. Implications

The chemical and physical properties of the pristine products are very different from those of the urban products. Due to the aforementioned observational bias, important aspects of our understanding of tropospheric chemistry may need to be revisited, in particular, those involving the budget and surface-atmosphere exchange of reactive carbon, oxidative capacity, and SOA formation. First, we discuss the implications arising from the difference in physical and chemical properties of ISOPOOH and MVK/MACR and then the broader context. It should be noted that the extent of this interference depends on the conversion efficiency, as stated in the previous section.

After the initial attack of the OH radical, the reaction of the resulting $RO_2$ radical with $HO_2$ to form ISOPOOH retains the $C_5$ carbon backbone; i.e., there is no fragmentation, and the oxygen to carbon (O:C) ratio is higher than for the $C_4$ fragmentation products from the reaction of $RO_2$ with NO (Figure 4) [*Jenkin et al.*, 1997, 2003; *Saunders et al.*, 2003]. Furthermore, ISOPOOH contains polar alcohol and hydroperoxide functional groups that are capable of strong hydrogen bonding. The greater polarity and mass of ISOPOOH explain why its vapor pressure is more than 3 orders of magnitude lower than that of MVK and MACR, calculated using SIMPOL [*Pankow and Asher*, 2008]. Thus, partitioning to surfaces and the condensed phase, e.g., dry and wet deposition, is much more important for ISOPOOH than MVK/MACR.

Studies using PTR-ToF-MS have unexpectedly highlighted high-deposition fluxes of VOC oxidation products, in particular of MVK/MACR, in pristine conditions that are expected to be influenced by high ISOPOOH concentrations [*Karl et al.*, 2010; *Misztal et al.*, 2011]. Although it is unclear how much, if any, ISOPOOH contributed to the observed signals at the *m/z* of MVK/MACR, larger than expected deposition fluxes are consistent with a nonnegligible interference. Overall, the interference mechanism suggests that surface-atmosphere exchange of reactive carbon should generally be revisited with respect to the identity and O:C ratio of reaction products.

For ISOPOOH, reactive partitioning to aerosol needs to be considered, whereas it is unimportant for MVK/MACR. The functional groups of ISOPOOH allow numerous condensed phase reactions, such as esterification, breaking of the peroxy bond, and addition to the double bond. The lower vapor pressure and the largely unexplored,but likely high-condensed-phase reactivity of ISOPOOH make it a potential SOA precursor via reactive uptake. Further, in contrast to MVK and MACR, ISOPOOH is an SOA precursor via formation of isoprene epoxydiols, which have half the vapor pressure of ISOPOOH as calculated with SIMPOL and which have been shown to form SOA via reactive uptake [*Nguyen et al.*, 2014].

Observations of MVK and MACR have also been used to estimate OH concentrations [*Karl et al.*, 2007; *Kuhn et al.*, 2007]. For an observed compound with concentration [OBS], the observed or inferred loss rate from reaction with OH is given by

$$\frac{d[\text{OBS}]}{dt} = -k_{\text{OBS}+\text{OH}}[\text{OBS}][\text{OH}]$$

where $k_{\text{OBS}+\text{OH}}$ is the reaction rate of the observed compound, and [OH] is the OH radical concentration. For an observed OVOC loss rate, OH will be a factor of 3.75 lower if the observed compound is ISOPOOH compared to MVK/MACR due to the difference in $k_{\text{OBS}+\text{OH}}$.

The implications for studies that use OVOC/isoprene ratios to infer [OH] are complicated due to the fact that the reaction rate of ISOPOOH is much closer to that of isoprene than that of MVK/MACR, and importantly, the isoprene oxidation yields of MVK/MACR and ISOPOOH are significantly different. In addition, the conversion efficiency, which can vary between instruments, has to be considered. Figure S4 in the supporting information shows a study in which the vertical profile of these ratios is modeled following the method of *Karl et al.* [2007]. Clearly, OH concentrations inferred by this method will depend on the identity of the observed compound. Hence, conclusions drawn on oxidative capacity from MVK/MACR observations have to be carefully reconsidered. Finally, studies that have used MVK/MACR to infer details about reaction mechanisms [*Fuchs et al.*, 2013] need to be revisited as MVK/MACR and ISOPOOH are formed by different mechanisms.

The implications for radical chain propagation are complex. The formation of ISOPOOH from isoprene is a much stronger $HO_x$ sink than the formation of MVK/MACR. ISOPOOH formation is radical chain terminating, as it converts one molecule of OH, isoprene, and $HO_2$ into one molecule of ISOPOOH. This will decrease OH concentrations, thereby lowering oxidative capacity. However, the net effect on the oxidative capacity also has to reflect the fact that OH is recycled during the oxidation of ISOPOOH: oxidation of ISOPOOH is OH neutral as OH is reformed via production of isoprene epoxydiols (IEPOX) [*Paulot et al.*, 2009]. The reaction to form MVK and MACR is $HO_x$ neutral, as OH is consumed and $HO_2$ is formed, but according to current mechanisms, $HO_2$ is not recycled efficiently to OH at low NO concentrations. Figure 4 shows the difference in OH recycling efficiency of the urban and pristine products at low NO concentrations based on the Master Chemical Mechanism version 3.2 (MCM v3.2) but also using the OH recycling of MACR recently described by *Crounse et al.* [2012] shown in red. The overall effect of the difference in reactivity between ISOPOOH and MVK/MACR on $HO_x$ is highly dependent on conditions. However, this effect is important to consider because oxidative capacity is directly related to the rate of oxidative processing, which in turn influences the rate of particle nucleation, the rate of SOA formation, and, outside of low-$NO_x$ regimes, ozone production.

The large difference in gas-phase chemical reactivity between the pristine and urban reaction products has implications for our understanding of the reactive carbon budget, the rate at which reactive carbon is being processed, and the role of VOC oxidation in radical cycling. There have been extensive efforts investigating sources of reactive carbon that are currently eluding measurements, often referred to as "missing reactivity." Evidence for these missing VOCs comes from the considerations of the overall reactive carbon budget [*Goldstein and Galbally*, 2007] as well as the measurements of the total sink strength of the OH radical (OH reactivity) [*Di Carlo et al.*, 2004]. In regions with high biogenic emissions, the measured OH reactivity is often much higher than the reactivity calculated from the sum of the measured or modeled compounds [*Edwards et al.*, 2013]. The missing OH reactivity corresponds to the missing VOC emissions or missing reaction products. The average rate constant for the reaction of OH with ISOPOOH isomers is 3.75 times that of the reaction of OH with MVK and MACR based on the MCM v3.2 [*Jenkin et al.*, 1997, 2003; *Saunders et al.*, 2003], see supporting information. This affects the rate of carbon processing, as shown later, but it is also worth considering the effect of the interference on missing reactivity.

Mistaking ISOPOOH for MVK/MACR causes an underestimation of the *true* OH reactivity. This is due to the fact that the OH loss rate is much higher for ISOPOOH than for MVK/MACR. However, the reaction of OH with ISOPOOH recycles OH rapidly with high yield [*Paulot et al.*, 2009], which makes it OH neutral. Despite the fast reaction rate constant of ISOPOOH, an OH-neutral reaction will not be reflected in the *measured* OH reactivity since it does not deplete OH. Therefore, care has to be taken when comparing the modeled and measured OH reactivity if the modeled OH reactivity includes the loss of OH to reaction with ISOPOOH.
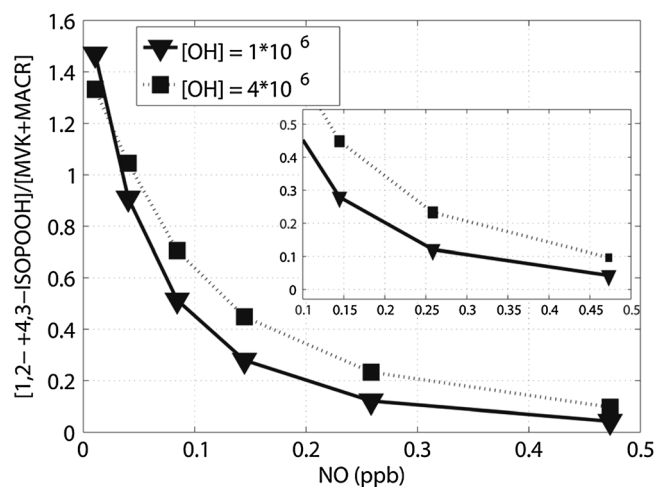
**Figure 5.** Ratio of the sum of 1,2- and 4,3-ISOPOOHs to the sum of MVK + MACR as a function of OH (dashed versus solid lines, molecules*cm$^{-3}$), NO (x axis) using a steady state model of isoprene (3 ppb) oxidation at a solar zenith angle of zero based on the MCM v3.2 taking into account the reaction of RO$_2$ with NO, HO$_2$, and RO$_2$ as well as isomerization. MVK + MACR at low NO arises from RO$_2$ + RO$_2$ reactions under the conditions of the model run.

The fact that the *measured* OH reactivity does not reflect ISOPOOH suggests that if ISOPOOH is mistaken for MVK/MACR, the *calculated* OH reactivity will be overestimated.

The interference also affects estimates of the amount of reactive carbon being oxidized. For a given production rate of isoprene-RO$_2$, as determined by isoprene emissions and oxidative capacity, the steady state concentration of ISOPOOH will be 3.75 times lower than that of MVK/MACR, due to the shorter lifetime of ISOPOOH with respect to OH. The net carbon flow through first-generation oxidation products under this scenario remains identical. Alternatively, if ISOPOOH and MVK/MACR mixing ratios are the same, a steady state scenario implies a much higher carbon processing rate for ISOPOOH than for MVK/MACR.

Hence, if the carbon processing rate through these products is estimated on the basis of an observation that assumes MVK/MACR, but actually corresponds to ISOPOOH, the total rate will differ by a factor of 3.75.

Globally, the reaction of RO$_2$ is expected to be dominated by the reaction with HO$_2$ [*Crounse et al.*, 2011]. Although the fate of this reaction depends on the details of the specific RO$_2$, large concentrations of organic hydroperoxides will be formed. The work presented here demonstrates that the observational artifact, which projects these pristine products causally onto their urban counterparts, has introduced an observational bias as urban product concentrations have likely been overestimated while pristine products have been underrepresented. This effect is compounded by the fact that very few observations of hydroperoxides, in particular, the globally important isoprene-derived hydroxy hydroperoxides, have been published. In combination, this has resulted in a bias in our view of tropospheric chemistry even in regions with a moderate impact from urban NO$_x$ emission. Figure 5 shows the ratio of ISOPOOH/(MVK + MACR) as a function of NO, HO$_2$, and OH, using a modified version of the MCM v3.2 that includes isomerization reactions as recent results suggest [*Crounse et al.*, 2011]. This shows that even at approximately 500 parts per trillion of NO, as much as 5–10% MVK/MACR signal may correspond to ISOPOOH, whereas under pristine conditions, the signal may be dominated by ISOPOOH. The magnitude of the interference also depends on the conversion efficiency, which we have shown is high, but may depend on instrumental details and the identity of the hydroperoxide. Conditions globally will mostly be in an intermediate regime where the reactions of RO$_2$ with both HO$_2$ and NO are important. Under these conditions, RO$_2$ formed from pristine products can react with "urban" NO and RO$_2$ formed from urban products with HO$_2$. This implies that mechanistic studies of the mixed regime chemistry, e.g., the products and radical propagation from the reactions of urban products under pristine conditions (and vice versa), need to be pursued.

Overall, our work calls for studies of instrument characterization with other highly functionalized compounds, e.g., multifunctional isoprene epoxydiols and organic nitrates that could also decompose to form artifacts. Furthermore, careful reevaluation of conclusions drawn using previous observations is required, and our work calls for renewed efforts in the measurement of urban products. Reactive carbon and oxidative capacity together determine the rate of secondary pollutant production and the lifetime of greenhouse gases. The instrumental bias described here suggests that the role of pristine versus urban products should be revisited. This will improve our understanding of the fate of reactive carbon, change the view of surface-atmosphere exchange of VOC oxidation products, and may shed light on current questions of how oxidative capacity is maintained in low-NO$_x$ environments or conditions.

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