Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 7276–7286

www.rsc.org/pccp

PAPER

Photolysis, OH reactivity and ozone reactivity of a proxy for isoprene-derived hydroperoxyenals (HPALDs)[†]

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Received 8th February 2012, Accepted 28th March 2012

DOI: 10.1039/c2cp40388a

The C₅-hydroperoxyenals (C₅-HPALDs) are a newly-recognized class of multi-functional hydrocarbons produced during the hydroxyl radical (OH)-initiated oxidation of isoprene. Recent theoretical calculations suggest that fast photolysis of these compounds may be an important OH source in high-isoprene, low-NO regions. We report experimental constraints for key parameters of photolysis, OH reaction and ozone reaction of these compounds as derived from a closely-related, custom-synthesized C₆-HPALD. The photolysis quantum yield is 1.0 ± 0.4 over the range 300–400 nm, assuming an absorption cross section equal to the average of those measured for several analogous enals. The yield of OH from photolysis was determined as 1.0 ± 0.8 . The OH reaction rate constant is $(5.1 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K. The ozone reaction rate constant is $(1.2 \pm 0.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K. These results are consistent with previous first-principles estimates, though the nature and fate of secondary oxidation products remains uncertain. Incorporation of C₅-HPALD chemistry with the above parameters in a 0-D box model, along with experimentally-constrained rates for C₅-HPALD production from isomerization of first-generation isoprene hydroxypetroxy radicals, is found to enhance modeled OH concentrations by 5–16% relative to the traditional isoprene oxidation mechanism for the chemical regimes of recent observational studies in rural and remote regions. This enhancement in OH will increase if C₅-HPALD photo-oxidation products also photolyze to yield additional OH or if the C₅-HPALD production rate is faster than has been observed.

1 Introduction

As the primary daytime oxidant, the hydroxyl radical (OH) defines the oxidizing capacity of the troposphere. OH-initiated degradation of volatile organic compounds (VOC) generates peroxy radicals (HO₂ and RO₂) that feed ozone production through catalytic cycling of nitrogen oxide radicals (NO_x = NO + NO₂). Reaction of OH with NO₂ to form nitric acid (HNO₃) removes radicals from this system and is the main chain-terminating step in high-NO_x regions. Oxidized VOC

can feed back into gas-phase chemistry or contribute to production of secondary organic aerosol (SOA).¹ OH levels can regulate new-particle formation in high-VOC regions² and contribute to aerosol aging,³ affecting chemistry and climate-relevant aerosol properties. Additionally, OH controls the lifetime of methane, an important climate forcer, and assumptions regarding OH concentrations and chemistry can markedly perturb model predictions of past, present and future climate.⁴

Chemical models routinely fail to reproduce observed OH concentrations in regions with large biogenic emissions, often with under-predictions by factors of 2 or more.^{5–12} Model-measurement discrepancies tend to be most severe in high-VOC regions dominated by isoprene (2-methyl-1,3-butadiene), a biogenic hydrocarbon with an annual global emission rate of ~500 Tg per year.¹³ In attempts to better understand these issues, renewed theoretical^{14–17} and experimental^{5,6,9,18,19} work on isoprene oxidation have revealed a rich chemistry previously unknown, including several mechanisms which effectively recycle HO_x (= OH + HO₂ + RO₂). One such mechanism, originally proposed by Peeters *et al.*,¹⁷ involves the isomerization and decomposition of isoprene hydroxypetroxy radicals (ISO₂) to release HO₂ and a new class of products

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[†] Electronic supplementary information (ESI) available: Details of C₆-HPALD synthesis and identification, DHB sensitivity calculations, photolysis cross section estimation, extended modeling results and ozone reactivity data. See DOI: 10.1039/c2cp40388a

known as C₅-hydroperoxyenals (C₅-HPALDs). It is further theorized that C₅-HPALDs undergo rapid photolysis (with a presumed atmospheric lifetime of 30–180 min) to produce OH and an alkoxy radical, which is then predicted to further isomerize/decompose, forming HO₂ and a peroxy-acid-aldehyde (PACALD). Photolysis of the PACALD is assumed to be even more efficient, leading to further production of OH and HO₂. Incorporation of this chemistry into numerical simulations improves model-measurement agreement for OH in some cases^{20,21} but can create additional problems, such as misrepresentation of other oxidized VOC²² and over-prediction of HO₂.¹¹

Ultimately, the impact of this mechanism on HO_x abundance depends on both the rate of C₅-HPALD production from ISO₂ isomerization and the photolysis and OH reaction rates of the C₅-HPALD products. Using isomerization rates derived from first principles, *Peeters and Müller*¹⁶ predict C₅-HPALD yields of as much as 70% from summertime isoprene oxidation. More recently, a laboratory investigation by Crounse *et al.*¹⁸ has provided experimental evidence that the C₅-HPALD production rate is 25 to 75 times slower than previously predicted. Despite the slower rate, C₅-HPALD production is still predicted to make up as much as 20% of the annual average reactive flux in high-isoprene, low-NO regions; thus, its chemistry is, in places, as significant as that of methyl vinyl ketone and methacrolein and therefore should be incorporated into chemical models.

In this work, we use a synthesized six-carbon analog to C₅-HPALDs to probe the photochemistry of this class of compounds. Specific experiments are aimed at assessing the photolysis quantum yield and OH yield, as well as the rate constants for reaction with OH and ozone (O₃). To our knowledge, this represents the first attempt to experimentally determine these parameters.

2 Methods

Four types of experiments are reported here: (1) photolysis of C₆-HPALD, either with or without an OH scavenger, (2) reaction of C₆-HPALD with OH, either with or without OH tracers, (3) reaction of C₆-HPALD with ozone and 4) reaction of isoprene-derived C₅-HPALDs with ozone. Initial conditions and key results for these experiments are summarized in the appropriate sections.

The 1000-liter Teflon-FEP reaction chamber is described in detail elsewhere.¹⁸ All experiments were performed at room temperature (296 ± 2 K) and atmospheric pressure (745 Torr, 99.3 kPa). UV lights along one wall of the chamber enclosure provide radiation with a peak emission at 340 nm as measured by a Licor spectroradiometer (LI-1800, 300–850 nm). Photolysis experiments were carried out under full illumination, giving a calculated *j*(NO₂) of 8.4 × 10^{−4} s^{−1}, approximately 1/10 that of natural sunlight. OH reaction experiments employing the photolysis of methyl nitrite (CH₃ONO) as an OH

source (R1–R2) utilized only a single shielded UV bulb, yielding ~30 times lower photon flux. Using published cross sections²³ and an assumed quantum yield of 1 with the measured photon flux gives an estimated *j*(CH₃ONO) of 0.9 × 10^{−5} s^{−1} for these experiments.

(*E*)-4-Hydroperoxyhex-2-enal (C₆-HPALD) was synthesized following established techniques.²⁴ Briefly, preparation involved oxidation of (2*E*,4*E*)-hexadien-1-ol to its corresponding aldehyde through reaction with MnO₂, followed by selective addition of a peroxide group *via* a custom-synthesized inorganic catalyst. Full details on the synthesis are provided in the Electronic Supporting Information (ESI).† NMR spectra show the purity of the condensed-phase sample to be ~80%. The main impurities were identified as the singly-saturated and doubly-saturated alcohol analogues of the C₆-HPALD (*i.e.*, replacing –OOH with –OH), which are likely side-products of the second reaction step or the result of condensed-phase decomposition. A condensed-phase UV-visible spectrum could not be obtained due to interferences from the cobalt-based catalyst, and the low vapor pressure of the C₆-HPALD precludes acquisition of gas-phase UV-Vis or IR spectra by standard techniques (*i.e.*, without a multi-pass system). C₆-HPALD samples were prepared at the University of Wisconsin, frozen in benzene and shipped to Caltech on dry ice where they were stored in the dark at −8 °C until needed. Prior to use, C₆-HPALD was separated from benzene *via* evaporation of the solvent at 5–10 °C under vacuum (~0.05 Torr), leaving behind a clear yellow oil. Gas-phase C₆-HPALD was added to the chamber by flowing zero air or nitrogen over the pure oil, providing initial mixing ratios of 1–50 ppbv (details on calibration in ESI).

Additional chemicals were purchased in high purity from Sigma-Aldrich and used without further purification. For experiments requiring an OH scavenger (HPALD photolysis and O₃ reactions), an excess of phenol (C₆H₅OH) was added by flowing zero air over the pure crystals, providing initial mixing ratios of 0.5–4 ppmv. For determination of the OH reaction rate constant *via* the relative rates technique, methacrolein (MACR) and 1,2-dihydroxybenzene (DHB) were employed as reference compounds. Gas-phase MACR standards of ~300 ppmv were prepared by evaporating a known mass of the liquid compound into a known volume of N₂ in a 75 L Teflon bag. The concentration of MACR in these standards was determined prior to each experiment using FTIR spectroscopy with tabulated cross sections, and 50 cm³ of this calibrated mixture was transferred to the chamber *via* a gas-tight ground-glass syringe. DHB was added by passing zero air over the pure crystals.

Methyl nitrite was synthesized, purified and stored in liquid nitrogen following established methods.²³ Purity was checked using FTIR spectroscopy. For use in experiments, CH₃ONO was removed from liquid nitrogen and slowly warmed, releasing ~15 Torr of the vapor into an evacuated 500 cm³ bulb. This fill was discarded, and the bulb was filled again to 5–15 Torr.

The bulb contents were then diluted by filling to atmospheric pressure with N₂ gas and pumping down to a pressure of 5–15 Torr. The contents of the bulb were then transferred to the reaction chamber.

O₃ was produced by flowing research grade O₂ through an electric discharge using a commercial ozone generator (Ozmonics V10-0). The resulting O₃ was trapped from the O₃/O₂ stream on clean, dry granular silica gel at –65 °C. The ozone/silica gel was maintained below –60 °C using a chilled isopropanol bath. For use in experiments, a small stream of N₂ was carried over the O₃/silica gel at –60 °C. The stream was used to fill a 500 mL bulb as well as an FTIR cell. The contents of the 500 mL bulb were transferred into the experiment bag, and the O₃ concentration in the IR cell was measured using known IR cross-sections.²⁵ Initial O₃ concentrations ranged from 300–3000 ppbv. O₃ addition marked the beginning of the experiment. O₃ was continuously measured using a commercial O₃ monitor (Teledyne 400E). Corrections to this measurement were made to account for the UV absorption of phenol.

For the C₅-HPALD + O₃ experiment, C₅-HPALDs were produced within the experiment bag from isoprene + OH gas-phase reaction under warm, dim conditions as described previously.¹⁸ In this case, air was not sampled from the experiment bag during the C₅-HPALD production phase. After C₅-HPALD production, the UV light was turned off, and the chamber was cooled to 296 K. Phenol and O₃ were added in the same fashion as described for the C₆-HPALD + O₃ experiment.

Dry zero air from a purge gas generator was used to fill the reaction chamber to a starting volume of 980–1000 standard liters for all experiments. After allowing ~1 h for reactants to mix, the UV lights were energized to initiate slow photochemistry. Sampling conditions provided an effective maximum runtime of 8 h. Between experiments, the reaction chamber was flushed 2–3 times with ~500 liters of zero air with all lights energized. Reactants and products were monitored with the Caltech triple quadrupole chemical ionization mass spectrometry (TQ-CIMS) instrument, utilizing CF₃O[–] as the primary reagent ion.²⁶ The chamber sampling setup was identical to that described by Crounse *et al.*¹⁸ CF₃O[–] reacts with neutral analyte molecules primarily by clustering and/or fluoride transfer, resulting in product ions at $m/z = \text{mass}_{\text{neutral}} + 85$ amu and/or $m/z = \text{mass}_{\text{neutral}} + 19$ amu, respectively. This chemistry is selective towards a wide range of oxygenates, including hydroperoxides, organic and some inorganic acids, hydroxynitrates and larger alcohols (*e.g.*, phenol and DHB). The TQ-CIMS was operated in both single MS and MS/MS modes. The latter permits separation and quantification of certain isobaric ions¹⁶ and can also help elucidate the structure of unidentified ions *via* collisional dissociation “fingerprints” specific to certain functionalities. Certain species that could not be monitored using CF₃O[–] (notably MACR) were measured using H⁺·(H₂O)_{*n*} as the reagent ion.

C₆-HPALD was monitored using the CF₃O[–] cluster ion at $m/z = 215$ amu and quantified using calculated ion-molecule collision rates.^{27†} The identity of this ion was further confirmed *via* the ¹³C isotope ratio and MS/MS spectra.[†] Phenol was monitored using the ¹³C isotope cluster ion at $m/z = 180$ amu (due to excessively high signal at the ¹²C mass) and quantified by standard addition of a gas-phase mixture, the

concentration of which was determined by FTIR spectroscopy. MACR was monitored in positive ion mode at $m/z = 71$ amu and quantified using standard additions. DHB was monitored using the fluoride transfer ion at $m/z = 129$ amu but could not be quantified by standard addition due to significant challenges associated with preparing gas-phase standards. A sensitivity for this compound was instead determined by a separate experiment involving the oxidation of phenol by OH, as described in the ESI.[†] This method has consequences for the uncertainty in the measured OH yield from C₆-HPALD photolysis, as discussed below.

Wall losses for C₆-HPALD, phenol, DHB and MACR were determined by injecting these compounds into the chamber and observing their decay in the dark several times over the course of the experiments. Average first-order wall loss coefficients (mean ± 2σ) are 7.0 ± 0.4, 1.0 ± 0.5, 5.9 ± 0.5 and 2.5 ± 0.7 × 10^{–6} s^{–1}, respectively. Measured concentration time profiles were corrected for wall loss according to

$$[X]_{\text{corr}} = [X]_{\text{meas}} e^{k_w t} \quad (1)$$

Where $[X]$ is concentration, k_w is the wall loss coefficient and t is experiment time.

Mass spectra indicate that some impurities in the C₆-HPALD sample were also introduced into the chamber. In particular, masses observed at negative m/z 197 and 199 are respectively consistent with the singly-saturated and doubly-saturated alcohol analogues of the C₆-HPALD (*i.e.*, replacing –OOH with –OH) that were also observed in NMR spectra of the condensed-phase sample. The purity of the gas-phase C₆-HPALD sample is estimated from the CIMS signals as $100 \times m_{215}/(m_{215} + m_{197} + m_{199}) = 80\%$. Tandem MS/MS spectra of these parent masses show no daughter signal at m/z 63, a strong indication that they are not peroxides. Comparison of the time profiles of these signals with those of C₆-HPALD and other reactants indicates that these compounds do not readily photolyze and thus should not impact reported OH yields or product distributions.

3 Results and discussion

3.1 Photolysis quantum yield

Fig. 1 shows a typical first-order decay profile for C₆-HPALD photolysis. Phenol comprises > 99% of the OH reactivity in these experiments, implying that the observed C₆-HPALD decay is not affected by reactions with OH. The slope of the ordinary linear least squares fit of the C₆-HPALD logarithmic decay thus provides a direct measurement of the photolysis rate constant. For the conditions of our chamber, the average photolysis rate constant from four such experiments (Table 1) is $(6.3 \pm 0.2) \times 10^{-5}$ s^{–1}. The quoted uncertainty includes contributions from the individual fits and from the wall loss correction. Note that potential systematic uncertainties in concentration measurements (*i.e.*, errors in computed calibration factors) do not affect this result, as data are normalized to starting concentrations.

Calculation of a photolysis quantum yield requires knowledge of the wavelength-dependent photon flux and C₆-HPALD absorption cross section. The former was measured as described above.

Fig. 1 Logarithmic decay of C₆-HPALD from photolysis experiment PH1.

Table 1 Summary of photolysis experiments

Exp.	[HPALD] ₀ (ppbv)	[Phenol] ₀ (ppbv)	j(HPALD) (10 ⁻⁵ s ⁻¹)	OH yield
PH1	4.39	494	6.9 ± 0.2	0.95 ± 0.05
PH2	1.61	1265	6.9 ± 0.5	1.39 ± 0.19
PH3	1.52	2517	5.4 ± 0.4	1.76 ± 0.34
PH4	3.31	3689	5.2 ± 0.3	1.05 ± 0.13
Avg			6.3 ± 0.1	0.97 ± 0.04
PH5	35.6	—	6.5 ± 0.1	—

HPALD photolysis rates are calculated as the slope of the linear least-squares fit to the logarithmic HPALD decay from the first 3 h of each experiment. OH yields are calculated from the slope of a linear least-squares fit of HPALD decay *versus* DHB growth, with the latter corrected for background OH production and a DHB yield of 80%. Errors represent the 2σ uncertainty in the fits, and averages are uncertainty-weighted (1/σ²). The last experiment was performed without phenol to examine the product distribution.

Most of the UV lamp emission occurs at 350 ± 50 nm, with a peak emission of 3.8 × 10¹³ photons cm⁻² s⁻¹.† The low vapor pressure of C₆-HPALD and the presence of low-volatility inorganic impurities prevented a direct experimental determination of the absorption cross section from gas-phase or condensed-phase UV-Visible spectroscopy. Thus, following the rationale that radiation is primarily absorbed by the O=C-C=C chromophore, we assume a cross section equal to the average of those measured for three molecules with the same chromophore (methacrolein,²⁸ acrolein²⁹ and (*E*)-2-hexenal^{30,31}).³²† Cross sections for these compounds differ by an average of 14% over our experimental wavelength range. From these values, we estimate a bulk photolysis quantum yield of 1.0 ± 0.4 over the range 300–400 nm. The uncertainty in this value includes both the uncertainty in the photolysis rate constant and a weighted-average 2σ uncertainty of 28% from the averaged cross section. This value agrees well with the unity quantum yield estimated for the isoprene-derived C₅-HPALDs.¹⁶

3.2 Photolysis products

3.2.1 OH. Production of OH from C₆-HPALD photolysis was quantified from the growth of DHB, which is

produced from the reaction of OH with phenol at a yield of 80 ± 12%.³³

Potential interferences in this experiment include loss of DHB to reaction with OH, reactions of HO₂ produced in (R3) with NO to regenerate OH, and “background OH” produced in the chamber (*e.g.*, from reactions on chamber walls). Loss of DHB to OH over the course of a typical experiment is estimated to be < 2% following a standard method.³⁴ Production of OH from reaction of HO₂ and NO cannot be calculated directly because measurements of these species are not available. HO₂NO₂, HNO₃ and HONO concentrations were below the instrument detection limit during experiments, suggesting negligibly small NO_x levels. Background OH production was determined in a separate set of experiments by filling the chamber with 1–2 ppmv phenol and observing the growth of DHB during irradiation, yielding an average background DHB production rate of 5.5 ± 2.3 pptv min⁻¹. The large uncertainty in this value stems primarily from the uncertainty in absolute DHB mixing ratios (42%).† The background OH production rate was assumed to be constant over the course of an experiment and applied as a correction to the DHB production rate. The yield of OH from C₆-HPALD photolysis, *y*_{OH}, can then be written as

$$y_{\text{OH}} = \frac{(\Delta\text{DHB} - P_{\text{bgd}}\Delta t)/y_{\text{DHB}}}{\Delta\text{HPALD}} \quad (2)$$

where *y*_{DHB} is the yield of DHB from (R3) and *P*_{bgd} is the background DHB production rate.

Fig. 2 shows the “corrected” DHB production (the numerator of eqn (2)) *versus* C₆-HPALD loss for a typical experiment. The slope of this line corresponds to the inferred OH yield. Table 1 summarizes the OH yields derived from four such experiments; the 1/σ² weighted average of these values is 0.97 ± 0.04. The total uncertainty in the average OH yield should include the weighted uncertainty from fitting (0.04), as well as uncertainties in the absolute mixing ratios of C₆-HPALD and phenol and in the background DHB production rate. Uncertainty in C₆-HPALD concentrations arises

Fig. 2 OH yield plot for the first 3 h of photolysis experiment PH1. DHB growth has been corrected for background OH and the phenol reaction yield as described in the text.

primarily from the use of calculated ion-molecule collision rates to derive the CIMS sensitivity for this compound and is estimated to be $\pm 50\%$.[†] The uncertainty in DHB concentrations is estimated as 42%, including a 15% contribution from the uncertainty in the DHB yield.[†] Because y_{DHB} appears in the denominator of eqn (2), however, a cancellation of errors effectively decreases the uncertainty in both ΔDHB and P_{bgd} (which also relies on DHB concentrations) to 27%. Combining these uncertainties gives a final estimate for the yield of OH from C₆-HPALD photolysis of 1.0 ± 0.8 .

3.2.2 Other products. To gain further insight on the mechanism of photolysis, a separate experiment was conducted where C₆-HPALD was photolyzed in the absence of phenol to allow identification of products. The expected reaction pathways are shown in Scheme 1. After scission of the O–OH bond, the resulting alkoxy radical should either rapidly decompose in the presence of oxygen to create fumaraldehyde (*trans*-2-buten-1,4-dial) and ethyl peroxy radical (upper channel) or react with O₂ to make HO₂ and a C₆ dicarbonyl (lower channel). Scission of the C₃–C₄ carbon bond to generate propanal and a vinyl radical is an alternative pathway, but this channel is energetically less favorable and therefore likely minor.³⁵ In a low-NO environment, the ethyl peroxy radical will react with HO₂ to form ethyl hydrogen peroxide. Self-reaction or reaction with other RO₂ is also a possibility, though kinetic modeling of this experiment, constrained by the observed H₂O₂ production rate, suggests this channel should comprise less than 2% of the total ethyl peroxy radical loss. The growth of a signal at negative m/z 147, observed during this experiment, may correspond to the cluster ion of ethyl hydrogen peroxide ($62 + 85$). Using the calibrated sensitivity to methyl hydrogen peroxide²⁶ to convert this signal to a concentration gives an estimated yield of 9%. Neither fumaraldehyde nor the C₆-dicarbonyl were observed in positive or negative ion mode, though without an authentic standard it is unknown if the CIMS is sensitive to these compounds. With the present dataset, we cannot provide a firm conclusion regarding the nature or fate of C₆-HPALD photolysis products.

Without an OH scavenger, OH generated during photolysis might react with C₆-HPALD, leading to an observed product distribution that includes both photolysis and OH-reaction products; however, several lines of evidence suggest this is not the case. First, the loss rate of C₆-HPALD in this experiment is comparable to that in the OH scavenging experiments (Table 1), implying that reaction with OH is not a major sink for C₆-HPALD. Secondly, none of the major products observed in the OH reaction experiments (see below) were observed in the

Scheme 1 Predicted mechanism for C₆-HPALD photolysis and subsequent degradation under low-NO conditions. The alkoxy radical should rapidly decompose in the presence of O₂ to make either fumaraldehyde and ethyl peroxy radical (upper channel) or a C₆ dicarbonyl and HO₂ (lower channel).

photolysis experiment, though this may be attributed to drastically different NO_x concentrations between these two experiments. The fate of OH in this experiment remains unclear, but the fact that the C₆-HPALD loss rate is not noticeably faster when compared to experiments that include an OH scavenger suggests the presence of unidentified OH sinks. The magnitude of this sink would need to be reasonably large to compete with C₆-HPALD ($k_{\text{OH}+\text{HPALD}}[\text{HPALD}] = 40 \text{ s}^{-1}$ at start of experiment) and would need to be even larger to compete with phenol in the OH scavenging experiments ($k_{\text{OH}+\text{Phenol}}[\text{Phenol}] = 360 \text{ to } 2700 \text{ s}^{-1}$). Still, the OH yield derived above should be considered a lower limit.

3.3 OH reaction rate

To determine the rate constant for reaction of C₆-HPALD with OH, relative rates experiments were conducted using DHB and MACR as reference compounds. These compounds were chosen because their OH reaction rate constants (1.0×10^{-10} and $2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, respectively)³⁶ bracket the value of $5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ estimated by *Peeters and Müller*¹⁶ for C₅-HPALDs using structure reactivity relationships. Photolysis of CH₃ONO under “low” illumination provided the OH source. A photochemical box model calculation suggests OH concentrations of $4\text{--}6 \times 10^5 \text{ molecules cm}^{-3}$ for the first three hours, consistent with the observed reference compound decays. Based on the measured photon flux and our earlier results, the C₆-HPALD photolysis rate constant for these experiments is estimated at $0.2 \times 10^{-5} \text{ s}^{-1}$, which is less than 8% of the observed C₆-HPALD decay. C₆-HPALD profiles were corrected for this first-order loss following eqn (1) before calculation of the OH reaction rate constant using the standard formula³⁷

$$\frac{\ln(\text{HPALD}_0/\text{HPALD})}{\ln(X_0/X)} = \frac{k_{\text{HPALD}+\text{OH}}}{k_{\text{X}+\text{OH}}} \quad (3)$$

Here, the left-hand side is given by the slope of a plot of the normalized logarithmic decays for C₆-HPALD versus the reference compound X (Fig. 3). From two such experiments (Table 2), the mean rate constant is $(5.1 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. On average, the rate constant derived from

Fig. 3 Correlations of OH-initiated decays of C₆-HPALD and reference compounds (X = DHB and MACR) for the first 3 h of experiment OH1.

Table 2 Summary of OH reaction experiments

Exp.	[HPALD] ₀ (ppbv)	[DHB] ₀ (ppbv)	[MACR] ₀ (ppbv)	[CH ₃ ONO] ₀ (ppbv)	Slope vs. DHB	Slope vs. MACR	k _{OH} vs. DHB (10 ⁻¹¹ cm ³ molec ⁻¹ s ⁻¹)	k _{OH} vs. MACR (10 ⁻¹¹ cm ³ molec ⁻¹ s ⁻¹)
OH1	2.69	27.3	14.7	183	0.72 ± 0.09	1.4 ± 0.2	7.2 ± 0.9	4.1 ± 0.6
OH2	3.89	4.6	10.7	184	0.59 ± 0.07	1.1 ± 0.2	5.9 ± 0.7	3.2 ± 0.6
Avg							5.1 ± 1.8	
OH3	46.7	0	0	490	—	—	—	—

Slopes are calculated from linear least-squares fits to scatter plots of logarithmic decays of C₆-HPALD and the reference compound (DHB or MACR) from the first 3 h of each experiment. Errors represent the 2σ uncertainty in the fits. The average and its uncertainty are calculated from the mean and standard deviation of the four values. The last experiment was performed without reference compounds to examine the product distribution.

MACR is ~40% lower than that derived from DHB. The reason for this discrepancy is not clear, thus we include results from both reference compounds in our average and use the standard deviation of these values to define the uncertainty.

3.4 OH reaction products

C₆-HPALD possesses a number of potential reaction sites; likely reaction pathways are summarized in Scheme 2. These include abstraction of the aldehydic hydrogen (C₁), addition of OH to either side of the double-bond (C₂ and C₃), and abstraction of the δ-H adjacent to the peroxide group (C₄). Abstractions of hydrogen from the peroxide or ethyl groups are likely minor channels (not shown). Given the similarity between C₆-HPALD and the isoprene-derived C₅-HPALDs, we can expect the OH reaction branching for these molecules to be loosely similar, but with some key differences (discussed below). VOC products observed during OH oxidation (experiment OH3 in Table 2) can provide some information on the branching of the C₆-HPALD + OH reaction.

Owing to high levels of NO_x (~250 pptv NO and 0–40 ppbv NO₂) from the OH source, multifunctional organic nitrates are expected as products. The most abundant of these, the C₆-HPALD acyl peroxy nitrate (APN), was identified from its mass (negative *m/z* 292) and the appearance of *m/z* 62 in the tandem mass spectrum, a fingerprint for APNs corresponding to NO₃⁻. Using the same calibration factor as that applied to C₆-HPALD, the APN yield is estimated to be 27% over the first 1.5 h of oxidation (Fig. 4a). At longer times, APN + OH reactions compete with, and eventually outrun, APN production. Thermal decomposition does not influence APN concentrations here, as the high NO₂ concentrations force all acyl peroxy radicals into the APN reservoir. Therefore, the APN yield gives a direct estimate for the branching of OH reaction *via* abstraction of the aldehydic hydrogen (pathway C₁ in Scheme 2).

The second largest product signal appears at negative *m/z* 65, corresponding to the fluoride transfer mass of formic acid. Using the sensitivity estimated from ion-molecule collision rates³⁸ gives a formic acid yield of 24% (Fig. 4a). The source of formic acid is not clear, though it is possible that this compound is produced through unidentified isomerization pathways after OH addition enables rotation about the C₂–C₃ bond.

The fraction of the reactive flux proceeding through predicted isomerization pathways (C₂ and C₃ in Scheme 2) depends on the NO concentration and the rates of the competing 1,4- 1,5- and 1,6-H-shift isomerization channels.

Crounse *et al.*³⁹ report the 1,4-H-shift of the aldehydic hydrogen in the dominant RO₂ in methacrolein oxidation to be quite fast (~0.5 s⁻¹ at *T* = 296 K). Under low-NO conditions such as those observed in the Amazon (< 20 pptv),⁶ such unimolecular chemistry may dominate the lifetime of certain RO₂. Photochemical modeling suggests an NO mixing ratio of ~250 pptv during this experiment, giving a peroxy radical lifetime of ~18 s with respect to NO using the MCM-recommended generic RO₂ + NO rate constant.⁴⁰ Rates of isomerization cannot be estimated from the available data, but the CIMS should be sensitive to the products of these reactions. Expected signals at *m/z* –219, *m/z* –235 and *m/z* –247 for clusters with the isomerization products of 3-OH and 2-OH addition were not observed (shaded molecules in Scheme 2), though the appreciable molar mass and high O:C ratios (0.8 to 1) of these compounds implies that such compounds may readily partition to chamber walls. Moreover, the growth of signals at the expected CF₃O⁻ cluster or H⁺ transfer masses for propanal (*m/z* + 59), 2-hydroperoxybutanal (*m/z* –189) and 2-hydroxydipropional (*m/z* –173 and *m/z* + 89) are qualitatively consistent with the expected products of RO₂ + NO reactions (green, black and magenta symbols/boxes Scheme 2 and Fig. 4b). It is also possible that the α-hydroperoxyalkyl radical resulting from C₂ OH addition could lead to formation of an epoxide¹⁹ that would be detected at negative *m/z* 215. Tandem MS/MS at this mass shows no evidence for such a compound, though we might expect that such a molecule would readily partition to chamber walls and not build up to an observable concentration. Unfortunately, the data does not permit a conclusive statement on the branching of the remaining OH reaction channels.

3.5 O₃ reaction rate

The reaction rates of O₃ with C₆- and C₅-HPALDs were determined from their first order decay rates over a 2-hour reaction period (data available in ESI).† During these experiments, O₃ concentrations decayed from their initial level by ~20%. For determination of rate constants, we use the average O₃ concentration over this interval. Wall-loss corrections were made for both the C₆-HPALD and C₅-HPALDs prior to determining the first-order loss rate. We find the reaction rate of O₃ with C₆-HPALD at 296 K to be (1.2 ± 0.2) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ from the average of two experiments, and the reaction rate of O₃ with C₅-HPALDs to be 1.1 × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ from a single experiment (Table 3).

Scheme 2 Predicted mechanism for C_6 -HPALD reaction with OH and subsequent degradation under high- NO_x conditions. Colored boxes correspond to product profiles shown in Fig. 4. Shaded boxes correspond to products that were not observed. Expected m/z signals in the CIMS spectra are also given.

For an atmospheric O_3 concentration of 40 ppbv, boundary layer O_3 lifetimes for isoprene-derived C_5 -HPALDs are calculated to be approximately 10 days. Given the fast photolysis and OH reaction rates, it is clear that C_5 -HPALD reaction with O_3 will not be an important loss process in the atmosphere.

3.6 Comparison between C_6 -HPALD and C_5 -HPALDs

Overall, our results for the C_6 -HPALD agree with first-principles estimates for the fate of isoprene-derived C_5 -HPALDs.¹⁶ The measured photolysis quantum yield of 1.0 ± 0.4 implies very efficient photolysis, as predicted. This number is directly dependent on the assumed absorption cross-section, and more work is needed to quantify the latter parameter directly. The high OH yield of 1.0 ± 0.8 is consistent with the expected photolysis mechanism, though the uncertainty in this value precludes a definitive conclusion. It seems unlikely that the OH yield is much less than unity, given the low quantum yield (< 0.05) for molecules featuring the same $O=C-C=C$ chromophore but without the peroxide functionality (e.g., MVK, MACR, acrolein and *trans*-2-hexenal).⁴¹ A quantum yield greater than 1 could indicate secondary OH production from decomposition of the alkoxy co-product. Though we expect the initial photolysis step to be the same for both C_5 - and C_6 -HPALDs, the subsequent

Fig. 4 (a) Formation of formic acid and the C_6 -HPALD acyl peroxy nitrate (APN292) over the first 1.5 h of the OH oxidation experiment OH3. The inset shows the time-evolution of these species over the entire experiment. (b) Growth of product ions observed during the same experiment. Signals are arbitrarily normalized to appear on the same scale. Colors correspond to predicted products as highlighted in Scheme 2: propanal ($m/z +59$), 2-hydroperoxybutanal ($m/z -189$), and 2-hydroxydipropenal ($m/z -173$ and $m/z +89$).

Table 3 Summary of O_3 reaction experiments

Exp.	[HPALD] ₀ (ppbv)	[O ₃] _{avg} (ppbv)	[Phenol] ₀ (ppbv)	Slope (10 ⁻⁵ s ⁻¹)	k _{O3} (10 ⁻¹⁸ cm ³ molec ⁻¹ s ⁻¹)
OZ1	5.10	348	2200	1.16 ± 0.05	1.4 ± 0.2
OZ2	4.16	830	1750	2.12 ± 0.07	1.1 ± 0.2
Avg					1.2 ± 0.2
OZ3	2.49	2495	1340	6.7 ± 0.1	1.1 ± 0.2

Slopes are calculated from linear least-squares fits to scatter plots of logarithmic decays of HPALD for the first 2 h of each experiment. Errors in the slopes represent the 1σ uncertainty in the fits. Ozone concentrations are given as the average over the 2-hour experiment. Errors in the rates constants include contributions from wall loss corrections for HPALDs and a 10% uncertainty from using the average O_3 concentration. The average rate constant is uncertainty-weighted ($1/\sigma^2$). Experiments OZ1 and OZ2 used C_6 -HPALD, while experiment OZ3 was performed with photochemically-generated C_5 -HPALDs.

chemistry is necessarily different. In particular, the (*E*) configuration of the C₆-HPALD prevents the unimolecular hydrogen shifts that, in the case of the (*Z*)-C₅-HPALD photolysis co-products, are predicted to lead to formation of peroxy-acid-enals (PACALDs).¹⁶ The latter are predicted to also photolyze rapidly to yield additional OH radicals; however, unlike the C₅-HPALDs, they have yet to be observed.

The measured OH reaction rate constant of $(5.1 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is also very close to the value of $5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ estimated from structure-reactivity relationships for the C₅-HPALDs.¹⁶ Combining the C₆-HPALD APN yield of 0.27 with this value gives an estimated rate constant of $1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for abstraction of the aldehydic H, in fair agreement with the value of $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CH₃CHO.³⁶ Note that the products for this channel may be different for the C₅-HPALDs; in particular, fast 1,6-H shifts may prevent formation of a C₅-HPALD APN under atmospherically-relevant NO₂ concentrations. We cannot make a quantitative comparison for the other OH reaction channels at this time. It is expected that OH addition should be somewhat slower for the C₆-HPALD since addition to either site would result in a secondary alkyl radical (as opposed to a secondary and a tertiary radical),⁴² while H-abstraction from the C₄-carbon should be roughly 2 to 3 times faster for C₆-HPALD compared to C₅-HPALD because of the secondary carbon.⁴³

It is not possible to assess the degree of HO_x recycling from reactions of OH with C₆-HPALD from the available data. As with the C₅-HPALDs,^{16,17} our proposed mechanism (Scheme 2) indicates that these reactions should be effectively HO_x-neutral. Future experiments could shed light on this component of the mechanism.

4. Atmospheric implications

The impact of C₅-HPALDs on atmospheric oxidation ultimately depends on both their production rate and their subsequent photochemistry. Global models^{20,22} have demonstrated dramatic increases in OH—by factors of 3 or more in some regions—upon incorporating the ISO₂ isomerization and C₅-HPALD chemistry as originally proposed.^{21,22} This mechanism also affects the distribution of oxidized VOC, leading Archibald *et al.*²² to suggest that calculated isomerization rates should be reduced by an order of magnitude. In a recent experimental study, Crounse *et al.*¹⁸ observed a C₅-HPALD production rate that is 25 to 75 times slower than the original quantum mechanical prediction.¹⁶

A simple 0-D box model calculation can illustrate the impact of the revised isomerization/HPALD mechanism on OH as a function of isoprene and NO concentrations. Calculations were performed using a modified version of the UW-CAFE model¹⁰ updated with Master Chemical Mechanism (MCM) v3.2 chemistry.^{40,44} The model was initialized with fixed meteorology (*T* = 298 K, *P* = 760 Torr, RH = 30%, SZA = 7°) and a “dilution rate” of 0.3 h^{−1} with background concentrations of 0 for all secondary species. Initial chemical concentrations, held fixed throughout each model run, were 50 ppbv O₃, 100 ppbv CO, 0–1 ppbv NO and 0–5 ppbv isoprene. Model integration time of 3 h was sufficient for

OH to reach steady state. Simulations included two scenarios: a base case using default MCM v3.2 chemistry, and a test case using the experimentally-constrained isomerization/HPALD chemistry. The latter includes the C₅-HPALD formation rate recommended by Crounse *et al.*,¹⁸ the 1,5-H isomerization rate calculated by da Silva *et al.*¹⁴ (consistent with auxiliary results in Crounse *et al.*¹⁸), a C₅-HPALD photolysis quantum yield of 1 (implemented by scaling the MACR photolysis rate), and a conservative C₅-HPALD photolysis OH yield of 1. Reactions of C₅-HPALD with OH were given a rate constant of $5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and were assumed to consume C₅-HPALD but not OH, implying 100% OH recycling through this pathway. This mechanism is conservative by design; thus, we do not include oxidized VOC from C₅-HPALD photolysis and OH reaction (*e.g.*, PACALDs), as the nature of these products is still uncertain. This carries consequences for the impact on OH, as discussed further below.

As expected, the fractional increase in modeled OH is greatest at low NO and high isoprene, where ISO₂ concentrations are relatively high and the lifetime of ISO₂ is relatively long (Fig. 5). A sensitivity test shows that about one third of this increase is due to the “prompt” effects of isomerization (reduced peroxide formation and increased HO₂ production), while the remaining two thirds results from C₅-HPALD photolysis. Within the range of observations (white circles in Fig. 5), modeled OH is enhanced by 5–16% relative to the standard isoprene mechanism. Most recent observational studies in rural and remote biogenically-influenced terrestrial regions require a factor of 2 to 10 increase in OH to reconcile models and measurements (Table 4).

Assumptions regarding the rate of ISO₂ isomerization and the fate of C₅-HPALD oxidation products have a direct impact on the modeled OH enhancement. Thus, we have performed several additional model runs, the detailed results of which are available in the ESI† and summarized here. First, increasing the 1,6- and 1,5-H shift isomerization rates to their theoretical predictions^{16,17} increases the above-quoted range of OH enhancement to 40–210%. This change also causes the OH enhancement to exhibit a non-monotonic dependence on NO for higher isoprene mixing ratios, reflecting the impact of additional HO₂ radicals from isomerization. Next, we revert to the experimentally-constrained isomerization rates but expand the C₅-HPALD mechanism to include 1) production of HO₂ and PACALDs from photolysis, and 2) photolysis of PACALDs to make 2 OH radicals, with a rate constant equal to twice that of the C₅-HPALDs.¹⁶ The resulting OH enhancement over the range of observations is 9–35%. Together, the above two results suggest that isomerization is the limiting step in our experimentally-constrained mechanism. Using both the theoretical isomerization rates and extended C₅-HPALD chemistry yields much larger OH enhancements, in the range of 200–475%. The full theoretical mechanism has been shown to dramatically reduce model-measurement discrepancies in OH concentrations for at least one case.²¹ On the other hand, recent work has also called into question the accuracy of OH concentrations observed *via* laser-induced fluorescence in biogenic-dominated regions.⁴⁸

As noted and accounted for in earlier theoretical work^{16,20} and recently highlighted,²¹ the influence of C₅-HPALD

Fig. 5 Simulated fractional change in OH concentrations resulting from the isomerization of isoprene peroxy radicals and the subsequent photolysis and OH oxidation of C₅-HPALDs. 0-D box model calculations use the observed rate of C₅-HPALD production from ISO₂ isomerization¹⁸ and a photolysis OH yield of 1. Circles and corresponding letters denote chemical regimes for observational studies (Table 4). Circle sizes correspond to the ratio of measured to modelled OH. The inset shows the fractional increase in OH concentrations as a function of total RO₂ lifetime at three different isoprene concentrations. Increasing RO₂ lifetimes scale with decreasing NO concentrations.

Table 4 Summary of OH model-measurement comparisons in rural and remote regions

Campaign	Isoprene (ppbv)	NO (pptv)	OH mea/mod	Symbol
AEROBIC 1997 ⁴⁵	1.4*	86*	3 [#]	A
PROPHET 1998 ⁸	2*	50*	2.66 [@]	B
INTEX-A 2004 ^{7,20}	0.9 [^]	114 [^]	2.5 [#]	C
GABRIEL 2005 ^{6,20}	2.0 ± 0.8 [^]	20 ± 20 [^]	5.3 [@]	D
PRiDe 2006 ³	1.5*	170*	2.6 [#]	E
AMMA 2006 ^{46,47}	0.3 ± 0.3 [^]	59 ± 30 [^]	0.40 [@]	F
BEARPEX 2007 (hot) ¹⁰	1.6 ± 0.7*	26 ± 12*	6 [#]	G
BEARPEX 2007 (cool) ¹⁰	0.2 ± 0.1*	135 ± 42*	0.95 [#]	H
OP3 2008 (flight) ¹¹	0.7 ± 1.6 [^]	53 ± 109 [^]	4.5 [@]	I
OP3 2008 (ground) ¹²	2.4 ± 1.0*	40 ± 10*	10 [#]	J

Isoprene and NO mixing ratios are midday averages (*) or campaign averages in “high isoprene” regions such as the forested boundary layer (^). NO mixing ratios for BEARPEX-2007 are calculated from a 1-D canopy model constrained by NO₂ observations. Standard deviations are provided when available. Ratios of measured/modelled OH are from either single averaged points (#) or a scatter plot of all data (@). The “symbol” corresponds to the location of the data point in Fig. 5 and 6.

chemistry on the radical budget depends on the relative rates of C₅-HPALD photolysis (which generates OH) and OH reaction (which removes C₅-HPALDs and, possibly, also OH). Fig. 6 illustrates this competition over a range of photolysis rates and OH concentrations. C₅-HPALD photolysis rates were derived as a function of solar zenith angle by scaling the MCM v3.2 parameterization^{40,44} for MACR photolysis to a quantum yield of 1. In this case, the maximum C₅-HPALD photolysis rate is $4.3 \times 10^{-4} \text{ s}^{-1}$ for an overhead sun. Even at fairly high OH ($\sim 10^7 \text{ molec cm}^{-3}$), photolysis comprises

Fig. 6 Ratio of C₅-HPALD photolysis and OH reaction rates as a function of solar zenith angle and OH concentration. Lines represent OH isopleths spaced by $1 \times 10^6 \text{ molec cm}^{-3}$. Letters indicate approximate midday conditions for several of the observations listed in Table 4.

$\sim 40\%$ of the C₅-HPALD sink for typical tropical and mid-latitude midday sunlight conditions. A number of OH observational studies have occurred in regions where the rate of photolysis exceeds that of OH oxidation, thus we do expect inclusion of C₅-HPALD chemistry to reduce model-measurement discrepancies.

We further evaluate the impact of C₅-HPALD photochemistry using the GEOS-Chem chemical transport model⁴⁹ v8.2.1. The model is driven by the GEOS-5 assimilated meteorology from the NASA Goddard Earth Observing System. Here the resolution of the model is 4×5 with 47 vertical layers. We use the simplified isoprene photochemical mechanism presented by Paulot *et al.*⁵⁰ In the sensitivity simulation, HPALD formation is included using the experimental reaction rate derived by Crounse *et al.*,¹⁸ and we include C₅-HPALD photolysis and reaction with OH as described in this study. C₅-HPALD photolysis is assumed to yield one OH and one HO₂ while the reaction with OH is assumed to be OH neutral. Deposition and transport of C₅-HPALD are not treated. Consistent with the results of UW-CAFE model, we find that boundary layer OH increases by up to 20% under very high isoprene/NO ratios (Fig. 7). The geographical distribution of modeled OH enhancement differs from that of the fraction of ISO₂ that isomerizes (compare with Fig. 3 of Crounse *et al.*³⁹), as the former depends also on isoprene emission rates, C₅-HPALD photolysis rates and OH concentrations.

Irrespective of the current debate surrounding isomerization rates, this new chemistry is clearly significant and should be included in isoprene oxidation mechanisms. Future studies should particularly focus on quantifying the nature and fate of HPALD oxidation products (*e.g.*, HO₂ and PACALDs), as these may also impact HO_x budgets. Moreover, isomerization mechanisms such as those discussed in this work inherently increase the O:C ratio while retaining the carbon backbone; thus, we expect C₅-HPALDs and their oxidation products to exhibit low vapor pressures. For example, the maximum amount of C₆-HPALD that could be evaporated into the

Fig. 7 GEOS-Chem simulated fractional change in boundary-layer OH concentrations resulting from the isomerization of isoprene peroxy radicals and the subsequent photolysis and OH oxidation of C₅-HPALDs. An OH yield of 1 from C₅-HPALDs photolysis is assumed. Results are averaged over one year. See text for model details.

reaction chamber (46.7 ppbv) suggests a vapor pressure on the order of 10⁻⁵ Torr for this compound. Given that isomerization can account for as much as 20% of the carbon flux in low-NO regimes,¹⁸ future work should also address the potential contribution of these oxidation products to organic aerosol growth.

Acknowledgements

This work was supported by the NOAA Climate and Global Change Postdoctoral Fellowship Program, administered by the University Corporation for Atmospheric Research. The authors thank NASA (NNX08AD29G), NSF (ATM-0934408 and ATM-0852406) and the Harvard University Center for the Environment for funding in support of this research. The authors also thank H. G. Kjaergaard for computation of ion-molecule collision rate parameters, M. Galloway for assistance with shipping logistics, and two anonymous reviewers for critical feedback on the manuscript.

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