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Primary Formation of Highly Oxidized Multifunctional Products in the OH-Initiated Oxidation of Isoprene. A Combined Theoretical and Experimental Study

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TOC Graphic

15 **Abstract** It is generally assumed that isoprene-derived secondary organic aerosol (SOA) precursors
16 are mainly formed from the secondary reactions of intermediate products with OH radical in gas
17 phase and multiphase oxidation in particle. In this paper, we predicted theoretically a mechanism for
18 the primary formation of highly oxygenated molecules (HOM) in the gas phase through successive
19 intramolecular H-shift and O₂-addition in the specific Z- δ isomer of hydroxyl-peroxy radicals
20 (ISOPO₂) and alkoxy radicals (ISOPO). The position of O₂ addition is different from that in forming
21 hydroperoxy aldehydes (HPALDs). The prediction was further supported experimentally by
22 successfully identifying a few highly oxidized peroxy radicals and closed-shell products such as
23 C₅H₉O_{7,9}, C₅H₁₀O_{6,7,8}, and C₄H₈O₅, *etc*, in a flow reactor by chemical ionization mass spectrometry
24 at air pressure. These HOM products could serve as important precursors to isoprene-derived SOA.
25 Further modeling studies on the effect of NO concentration suggested that HOM formation could
26 account for up to ~11% of the branching ratio (~9% from 4-OH channel and ~2% from 1-OH
27 channel) in the reaction of isoprene with OH when lifetimes of peroxy radicals due to bimolecular
28 reactions are ~100 s which is typical in the forest regions.

29 **Keywords:** Isoprene; OH-initiated Oxidation; Intramolecular Hydrogen Shift; Highly Oxidized
30 Multifunctional Product; Mass Spectrometry

31 Introduction

32 Isoprene, a biogenic volatile organic compound (VOC) primarily emitted by deciduous plants
33 and as the largest source of nonmethane hydrocarbons with the global emission exceeding 500 Tg C
34 yr^{-1} , plays a pivotal role in atmospheric chemistry due to its high reactivity.¹ Even a small amount of
35 aerosol derived from isoprene would have a significant influence in a global scale. In the atmosphere,
36 isoprene reacts rapidly with the OH radicals, followed by O_2 addition to generate hydroxyperoxy
37 radical intermediates (ISOPO_2 , including six dominant isomers). In the atmosphere, the ISOPO_2
38 radicals would react with NO, forming methacrolein, methyl vinyl ketone, formaldehyde, and
39 hydroxynitrates. In the low- NO_x regions, ISOPO_2 would react mainly with HO_2 , forming
40 hydroxyhydroperoxide (ISOPOOH) which can be further oxidized by the OH radicals to form
41 isoprene epoxydiols (IEPOX),^{2,3} and recently identified low-volatility multifunctional compounds
42 through the non-IEPOX pathways.⁴⁻⁷ All these products can contribute to organic aerosols to
43 different degrees. Recently, 1,6 H-shift in Z- δ - ISOPO_2 , being suggested from theoretical predictions
44 and confirmed by experimental studies, has emerged as an essential process related to OH
45 regeneration in pristine forest environments through photolysis of hydroperoxy aldehydes (HPALDs)
46 and other products (Scheme 1).⁸⁻¹³

47 The isoprene-derived SOA, especially under low- NO_x conditions, has received intensive
48 attentions over a decade. It is generally accepted that the products formed in the secondary reactions
49 of intermediate products, such as IEPOX, lead to a subsequent formation of SOA in the presence of
50 acidic aerosols. However, recent studies^{12,13} showed that the primary processes and products from the
51 1,6 H-shift in Z- δ - ISOPO_2 radical might also be pivotal in the isoprene oxidation and SOA formation.

Theoretical calculation predicted that the rate of 1,6 H-shift in Z- δ -ISOPO₂ from 4-OH system can be as fast as 5.72 s⁻¹ at 298 K (Scheme 1),¹² which was further confirmed by Teng et al.¹³ who obtained a closely agreed value of 3.7 $\pm$ 1.0 s⁻¹ by fitting the measured yields of HPALD (a typical product of 1,6 H-shift in Z- δ -ISOPO₂) to a kinetics model. Meanwhile, Teng et al.¹³ also found that the distribution of ISOPO₂ isomers depends on their bimolecular lifetimes, and suggested that approximately half of ISOPO₂ in the 4-OH channel would react through this unimolecular pathway at 25°C at bimolecular lifetimes of 100 s.

Scheme 1. Reaction scheme of OH-initiated oxidation of isoprene (4-OH system)

The mechanism after the H-shift remains highly uncertain and the products, have not hitherto been fully identified. Experimentally, a large fraction of oxidation products remained unidentified, e.g., at least 30% in the study by Teng et al., while theoretically, only part of the reaction pathways have been examined. For example of the 4-ZH radical (Scheme 1), oxygen can add to both C₂ and C₄ positions of the allylic groups. HPALD, a product receiving extensive attention, is formed from the C₄-addition followed by elimination of HO₂, while the fate after the C₂-addition is unclear.

In this paper, we investigated the reactions after the O₂-additions to C₂-position of 4-ZH. We

68 expect relatively fast H-shifts in the peroxy radicals formed as the 1,6 H-shift in Z- δ -ISOPO₂. The
69 primary formation of highly oxygenated molecules (HOMs) through alternate intramolecular H-shift
70 and O₂-addition has been observed in the peroxy radicals formed in the atmospheric oxidation of
71 many other VOC.^{14–19} The fate of the alkoxy radicals (ISOPO), formed in the bimolecular reaction of
72 ISOPO₂ with NO, which can undergo a similar H-shift and subsequent autoxidation chemistry, was
73 also examined. Our theoretical calculations suggested the primary formation of highly oxygenated
74 peroxy radicals and HOMs from the unimolecular processes of Z- δ -ISOPO₂ and Z- δ -ISOPO radicals.
75 The predictions were confirmed experimentally by detection of the corresponding radicals and
76 closed-shell products in a gas-phase flow reactor by chemical ionization–atmospheric pressure
77 interface–time-of-flight (CI-API-TOF) mass spectrometry. Formation yield of HOMs and the effect
78 of NO were also modeled. Here we define the products containing 5 or more O-atoms as HOMs.

79 **Methods**

80 **Theoretical Methods** All the structures of reactants, products, and transition states were
81 optimized using the DFT-M06-2X/6-311++G(2df,2p) method.²⁰ For these structures, accurate
82 electronic energies were calculated by using the complete-basis-set model chemistry (CBS-QB3)²¹
83 and the explicitly correlated CCSD(T)-F12a (F12) method with cc-pVDZ-F12 basis set,^{22,23} all using
84 the restricted open-shell wavefunctions for the radical species. The values of T_1 diagnostics in the
85 CCSD calculations were used to check the multireference characteristics of the wavefunction and to
86 determine the reliability of the results. All these calculations were performed by using the Gaussian
87 09 suite of programs²⁴ except for the F12 ones, which were carried out using the Molpro 2015
88 package.²⁵

89 The rates of the unimolecular reactions were calculated using the unimolecular rate theory
90 coupled with the energy-grained master equation for collisional energy transfer (RRKM-ME),²⁶ and
91 the rate coefficients of bimolecular reactions were determined using the traditional transition state
92 theory. The RRKM-ME calculations were carried out by using the Mesmer program.²⁷ We used a
93 single exponential-down model to simulate the collision energy transfer ($\langle \Delta E \rangle_{\text{down}} = 200 \text{ cm}^{-1}$), and
94 used the method of Gilbert and Smith²⁸ to estimate the collision parameters. The asymmetry Eckart
95 model was used to calculate the tunneling correction factors.²⁹

96 **Experimental Methods** The reactions were conducted in a gas flow tube reactor with a length
97 of 205 cm and an inner diameter of 4.7 cm as described in previous study.¹⁶ Residence time of the
98 gas in the tube can be varied by adjusting the flow rate and was set as 10.7 s in this work with a total
99 volumetric flow rate of 20 lpm. The experiments were performed at room temperature ($293 \pm 3 \text{ K}$)
100 and atmospheric pressure. The OH radicals were generated by ozonolysis of tetramethylethylene
101 (TME).³⁰ The highly oxygenated peroxy radicals and closed-shell products were detected using a
102 CI-APi-TOF^{31,32} mass spectrometer with nitrate (NO_3^-) as the reagent ion. Typical concentrations of
103 O_3 , TME, and isoprene, in molecules cm^{-3} , are $(1.5 \text{ or } 4.6) \times 10^{12}$, 1.6×10^{12} , and 2.28×10^{13} ,
104 respectively, resulting in upper limits for the formation rate of $\sim 10^9 \text{ molecule cm}^{-3} \text{ s}^{-1}$ and
105 concentration of $\sim 10^6 \text{ molecules cm}^{-3}$ for the OH radicals. A set of experiments were also carried out
106 by using photolysis of H_2O_2 to generate OH radical and using the same mass spectrometer but using
107 a reduce pressure ion-molecule reaction (IMR) region with iodide (I^-) as the reagent ions.³³

108 Results and Discussion

109 **Primary Formation of HOMs from 4-ZH-OO Radicals** Due to the presence of allylic group

in 4-ZH, two peroxy radicals 4-ZH-2OO and 4-ZH-4OO would be formed from the O₂ additions. The latter is relatively more stable by ~15 kJ/mol in energy. Peeters et al. obtained similar results for the two peroxy radicals in the 1-OH channel.¹² The fate of 4-ZH-4OO is quite clear, i.e., to eliminate an HO₂ radical with an energy barrier of 49.3 kJ/mol only, forming a hydrogen-bonded complex and then decomposing to products HPALD and HO₂. The present study focused on the fate of 4-ZH-2OO.

Figure 1. Schematic potential energy profiles for the subsequent reactions in 4-ZH at the ROCBS-QB3 level (ΔE_{0K} , in kJ mol⁻¹).

Figure 1 depicts the potential energy surface of possible reactions starting from O₂ addition to the C₂ position in the 4-OH channel, and the values of reaction energies and barrier heights are listed in Table 1. Structures of important transition states are shown in Figure S1. The addition is

122 exothermic by -67.3 kJ/mol (ΔE_{0K}). In the newly formed peroxy radical 4-ZH-2OO, a second
 123 intramolecular H-shift would take place rapidly by transferring H atom from $-OH$ to $-OO$ group
 124 with an energy barrier of only 48.1 kJ/mol and an effective rate of $\sim 10^2$ s $^{-1}$, forming radical
 125 4-ZH-2OOH'. This H-shift would be fast enough to diminish possible bimolecular reactions of
 126 4-ZH-2OO with NO and/or HO $_2$ in the atmosphere. Radical 4-ZH-2OOH' then recombines instantly
 127 with O $_2$, forming a highly oxidized species 4-ZH-2OOH'-3OO (C $_5$ H $_9$ O $_7$), which contains two $-OOH$
 128 groups, one $-CHO$, and one $-OO$ group. Note that the intramolecular isomerization of 4-ZH-2OOH'
 129 to an epoxide product (as the formation of IEPOX from ISOPOOH 2) is unavailable due to a high
 130 energy barrier of ~ 100 kJ/mol. From the rate coefficients for O $_2$ additions to C $_4$ - and C $_2$ -positions of
 131 4-ZH from transition state theory calculations here, we predicted the formation of HPALD and
 132 4-ZH-2OOH'-3OO with branching ratios of 51% and 49%, respectively (77% and 23% in the 1-OH
 133 system).

134 As for other peroxy radicals, the bimolecular reaction of 4-ZH-2OOH'-3OO with HO $_2$ radical
 135 might form products as 4-ZH-2OOH'-3OOH (C $_5$ H $_{10}$ O $_7$), 4-ZH-2OOH'-3OH (C $_5$ H $_{10}$ O $_6$),
 136 4-ZH-2OOH'-3=O (C $_5$ H $_8$ O $_6$), and radical 4-ZH-2OOH'-3O (C $_5$ H $_9$ O $_6$), though the branching ratios
 137 could not be determined here. The radical 4-ZH-2OOH'-3O would decompose rapidly to glyoxal
 138 (HCOCOH), CH $_3$ C(O)CH $_2$ OOH, and OH radical. Besides the bimolecular reactions, two competing
 139 intramolecular H-shifts are also available in 4-ZH-2OOH'-3OO by shifting an H-atom from $-C_1H_2$
 140 group through a six-membered-ring transition state and from $-C_4HO$ group through a
 141 five-membered-ring transition state. Effective unimolecular rates were estimated as $k_{(-CH_2)} = 0.92$ s $^{-1}$
 142 and $k_{(-CHO)} = 0.86$ s $^{-1}$ at 298 K when using the barrier heights at ROCBS-QB3 level. Note that we

used the multi-conformer transition state theory to calculate the unimolecular rates.³⁴ Nine conformers were identified for 4-ZH-2OOH'-3OO with respect to the internal rotations of C₁-C₂ bond and C₃-C₄ bond, while only four of them could undergo H-shift from the -C₁H₂ group and all of them from the -CHO group.

Table 1. Reaction energies and barrier heights (ΔE_{0K} and $\Delta E_{0K}^\ddagger$, in kJ/mol) at ROCBS-QB3 level

	ΔE_{0K}	$\Delta E_{0K}^\ddagger$
4-ZH + O ₂ → 4-ZH-2OO	-67.26	
4-ZH-2OO → 4-ZH-2OOH'	-3.39	48.08
4-ZH-2OOH' + O ₂ → 4-ZH-2OOH'-3OO	-75.65	
4-ZH-2OOH'-3OO → 4-ZH-Q(O)		86.68 ^a
4-ZH-Q(O) → 4-ZH-PC ₄ + OH + CO		35.75
4-ZH-2OOH'-3OO → 4-ZH-PO + OH		83.61 ^a
4-ZH + O ₂ → 4-ZH-4OO	-82.26	
4-ZH-4OO → HPALD + HO ₂		49.28
4-Z'H + O ₂ → 4-Z'H-2OO	-75.31	
4-Z'H-2OO → 4-Z'H-2OOH'	-23.37	41.07
4-Z'H-2OOH' + O ₂ → 4-Z'H-2OOH'-3OO	-82.21	
4-Z'H-2OOH'-3OO → 4-Z'H-Q(O)		89.19 ^a
4-Z'H-Q(O) → 4-Z'H-PC ₄ + OH + CO		88.70 ^a
4-Z'H + O ₂ → 4-Z'H-4OO	-76.60	
4-Z'H-4OO → HC ₅ + HO ₂		39.66
1-ZH + O ₂ → 1-ZH-3OO	-56.43	
1-ZH-3OO → 1-ZH-3OOH'	-35.82	36.88
1-ZH-3OOH' + O ₂ → 1-ZH-3OOH'-2OO	-75.84	
1-ZH + O ₂ → 1-ZH-1OO	-70.83	
1-ZH-1OO → HPALD		39.81
1-Z'H + O ₂ → 1-Z'H-3OO	-66.65	
1-Z'H-3OO → 1-Z'H-3OOH'	-39.96	35.17
1-Z'H-3OOH' + O ₂ → 1-Z'H-3OOH'-2OO	-70.02	
1-Z'H + O ₂ → 1-Z'H-1OO	-87.83	
1-Z'H-1OO → HC ₅ + HO ₂		51.27

a. selected one of the conformers

The H-shift from -C₁H₂ in 4-ZH-2OOH'-3OO is followed by rapid elimination of OH radical,

150 forming the closed shell product 4-ZH-PO ($C_5H_8O_6$), while the H-shift from $-C_4HO$ group forms
151 radical 4-ZH-Q(O), which could either recombine with O_2 to form acylperoxy radical 4-ZH-Q(O)O₂
152 ($C_5H_9O_9$) or decompose to the closed shell compound 4-ZH-PC4 ($C_4H_8O_5$) accompanied by CO and
153 OH (Figure 1). The decomposition of 4-ZH-Q(O), with an energy barrier of 35.8 kJ/mol
154 (ROCBS-QB3) and a rate of $6.6 \times 10^6 \text{ s}^{-1}$ at 298 K, is comparable to while being slower than the
155 recombination with an effective rate of $3.0 \times 10^7 \text{ s}^{-1}$ in the atmosphere (assuming a rate coefficient of
156 $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).³⁵

157 In summary, the alternate H-shift and O_2 addition processes after 4-ZH-2OO might lead to the
158 formation of radical 4-ZH-2OOH'-3OO ($C_5H_9O_7$), which could transform unimolecularly to radical
159 4-ZH-Q(O)O₂ ($C_5H_9O_9$), and closed-shell species 4-ZH-PO ($C_5H_8O_6$) and 4-HO-PC4 ($C_4H_8O_5$).
160 Other HOM compounds might also be formed from the reactions of peroxy radicals with HO₂. Such
161 a reaction scheme would also exist in the 1-OH channel even though the H-shift reaction in
162 (1-OH-)Z- δ -ISOPO₂ would be much slower. Note that the products from 1-OH channel are similar to
163 those from 4-OH channel except for the position of the methyl group. According to Teng et al., at
164 298 K, when the bimolecular removal rate is 0.01 s^{-1} for ISOPO₂, only ~8% of ISOPO₂ in the 1-OH
165 channel undergoes the intramolecular H-shift reaction (compared to 50% in the 4-OH system), thus
166 the yield of HOM compounds formed from subsequent reactions is also low.

167 These highly oxygenated multifunctional products would have low volatility, readily partition
168 into the particle phase, and likely undergo heterogeneous reactions therein. Taking 4-ZH-PO as an
169 example (Scheme 2), in the acidic conditions, the $-OOH$ group might be reduced to $-OH$,³⁶ while the
170 carbonyl group could hydrolyze to a diol product, forming eventually a hexahydric alcohol $C_5H_{12}O_6$.

171 Liu et al.⁵ detected a species with the same molecular weight by using FIGAERO HR-ToF-CIMS in
172 the absence of NO, and found it accounted for 30-50% of total SOA. Liu et al. assigned this species
173 as ISOP(OOH)₂ (containing two –OH and two –OOH groups), and suggested its formation from the
174 secondary gas-phase reaction of the primary product ISOPOOH with OH radicals in presence of high
175 HO₂ concentration. However, D'Ambro et al.(Ref) found reduced production of ISOP(OOH)₂ at low
176 HO₂, due to the competition from the unimolecular isomerization of intermediate peroxy radical.

177 Under low-NO_x conditions, 4-ZH-2OOH'-3OO reacts mainly with HO₂, forming closed shell
178 hydroperoxide. This multifunctional compound might be easily taken up by the particles and then be
179 converted to pentahydric alcohol C₅H₁₂O₅ (Scheme 2). The mechanism involves the reduction of the
180 hydroperoxide group in 4-ZH-PO. The reduction of hydroperoxide to alcohol was initially suggested
181 by Claeys et al.³⁷ as a mechanism of 2-methyltetrol formation. This might provide an alternative
182 mechanism for the formation of polyols in particle phase from the primary gas-phase products, in
183 addition to the IEPOX mechanism from the secondary gas-phase reactions by Paulot et al.² The
184 mechanisms by Paulot et al., Surratt et al.,³ and Claeys et al.³⁷ were both based on the secondary
185 reactions of intermediate products ISOPOOHs or methyl butenediols with OH radical in the gas
186 phase. Similarly, 4-ZH-2OOH'-3OO reacts with NO, forming organic nitrate and then transforming
187 to product C₅H₁₁O₇N and C₅H₁₂O₅ in the particle phase, which were also observed in previous
188 studies.^{5, 38} Further studies on the multiphase chemistry of these primary products are desired.

Scheme 2. The possible reactions in particle phase in acidic conditions

Primary Formation of HOMs from Z- δ -ISOPO

In addition to bimolecular reaction with HO_2 or the unimolecular intramolecular H-shift, as for other peroxy radicals, Z- δ -ISOPO $_2$ could also react with atmospheric NO to generate the alkoxy radical ISOPO. Previous studies have shown that ISOPO can undergo a 1,5-hydrogen shift extremely rapidly, e.g., $\sim 10^8 \text{ s}^{-1}$ at 298 K.³⁹

The product 4-Z'H has a conjugated allyl structure similar to that of 4-ZH. Addition of O_2 to the C_4 -position, followed by elimination of HO_2 , forms a hydroxyl aldehyde compound (HC_5).³⁹ The reaction is similar to the HPALD formation in Z- δ -ISOPO $_2$. Note the fate of Z- δ -ISOPO is much different from that in MCM 3.3.1, in which 4-OH-Z- δ -ISOPO has three channels as H-migration (30%), reaction with O_2 (52%), and isomerization to 3-methylfuran (18%).(Ref) So is the fate of 1-OH- Z- δ -ISOPO.

Scheme 3. Subsequent reaction mechanisms of Z- δ -ISOPO₂

However, O₂ can also add to the C₂-position, giving 4-Z'H-2OO. The adduct 4-Z'H-2OO is more stable than the adduct 4-Z'H-4OO, being different to the peroxy radicals from 4-ZH. The ensuing reaction steps of 4-Z'H-2OO are similar to those of 4-ZH-2OO. Scheme 3 summarizes the possible reaction routes of 4-ZH-2OO and 4-Z'H-2OO in the presence of NO, and the reaction energies and barrier heights are given in Table 1. The unimolecular H-shift in 4-Z'H-2OO to 4-Z'H-2OOH' would be virtually the sole fate of 4-Z'H-2OO with an energy barrier of only 41.1 kJ/mol. Additions of O₂ to C₂ and C₄ of 4-Z'H ultimately lead to the formation of products 4-Z'H-2OOH'-3OO and HC₅, respectively, with branching ratios of ~92% and ~8% (~55% and ~45% in the 1-OH system) from transition state theory calculations. A value of 45 ± 10% of HC₅ in both 4-OH and 1-OH channels

213 was reported in a previous study by Teng et al.,¹³ who obtained the ratios from the ratio of [HC₅] to
 214 [δ -ISOPN] (nitrate) under high-NO conditions. The ratio depends highly on yield of δ -ISOPN in the
 215 reaction of δ -ISOPOO and NO.

216 Two different H-shifts are possible in 4-Z'H-2OOH'-3OO from either the -CHO group through
 217 a five-membered-ring transition state or the -CH₂ group, of which the former is followed by the
 218 addition of oxygen to form acyl peroxy radicals or by decomposition to CO, OH, and a closed-shell
 219 compound (C₄H₈O₄, 4-Z'H-PC₄). Formation of 4-Z'H-PC₄ and 1-Z'H-PC₄ from these pathways was
 220 also suggested in MCM 3.3.1 as MACROOH and HMVKBOOH,(Ref) however, we expect higher
 221 yields for them because we predict almost complete transformation from Z- δ -ISOPO to 1-/4-Z'H.
 222 Under the conditions of forming ISOPO by reacting with NO, 4-Z'H-2OOH'-3OO would also be
 223 converted to the alkoxy radical 4-Z'H-2OOH'-3O which would then decompose to hydroxyacetone,
 224 glyoxal and an OH radical. Generally, 4-ZH and 4-Z'H should react similarly in the atmosphere, and
 225 their corresponding products differ by one O-atom.

226 It is worth noting that the alkoxy radical E- δ -ISOPO, once formed, will isomerize to
 227 Z- δ -ISOPO extremely rapidly at a rate of 10^8 – 10^9 s⁻¹.⁴⁰ This would increase the fraction of 4-Z'H
 228 and lead to increased yields for HOM.

230 **Experimental Identification of the Highly Oxygenated Radicals and Products The**

231 formation of HOMs in the reaction of isoprene with OH radical was confirmed here experimentally
 232 by using a CI-API-TOF. Figure 2 shows the mass spectra recorded by using NO_3^- as the ionizing
 233 reagent, showing clearly signals from highly oxygenated peroxy radicals and closed-shell products.
 234 The short residence time in the flow reactor (i.e. 10.7 s) suggested that these radicals and compounds
 235 are formed primarily without involving the secondary gas-phase reactions between intermediate
 236 products and OH radical even though our method of generating OH radical was accompanied by the
 237 subsequent formation of HO_2 radical. Under our experimental conditions, HO_2 could accumulate to
 238 $\sim 1.4 \times 10^{10} \text{ molecules cm}^{-3}$ ($\sim 0.5 \text{ ppb}$) at the exit of the reactor if assuming the HO_2 yield from the
 239 reaction of TME with O_3 is 0.18.⁴¹ This leads to the bimolecular reaction rates from 0 at the entrance
 240 to 0.28 s^{-1} at the exit of the reactor between peroxy radicals and HO_2 (assuming the rate coefficient
 241 of $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).³⁵ Note the signal levels for different species do not reflect the
 242 concentrations of the species because the ionizing reagent NO_3^- used here is likely more sensitive to
 243 products with more $-\text{OOH}$ groups.^{16,17,42}

244
 245 **Figure 2.** Mass spectra recorded from the reaction of OH radicals with isoprene. Signals of radicals
 246 and closed shell species are marked as blue and red, respectively. Products are detected as adduct
 247 with nitrate. $\text{C}_4\text{H}_6\text{O}_6$ marked as grey is from the reaction of isoprene with O_3 .

248 The signals at nominal mass-to-charge ratios 211, 243, and 275 Th could correspond to the
 249 peroxy radicals from 4-ZH as 4-ZH-2OO ($C_5H_9O_5$), 4-ZH-2OOH'-3OO ($C_5H_9O_7$), and 4-ZH-Q(O)O₂
 250 ($C_5H_9O_9$) with NO_3^- , while the mass-to-charge ratios 227 and 259 Th to the peroxy radicals as
 251 4-Z'H-2OOH'-3OO ($C_5H_9O_6$) and 4-Z'H-Q(O)O₂ ($C_5H_9O_8$) from 4-Z'H (Scheme 3). Slow
 252 unimolecular and bimolecular reactions under the experimental conditions lead to the accumulation
 253 of these radicals in the flow and their detections by CI-APi-TOF. Other radicals are depleted rapidly
 254 either by recombination with O₂ or by unimolecular decompositions, e.g., 4-ZH-2OOH' recombines
 255 rapidly with O₂ to 4-ZH-2OOH'-3OO, and 4-ZH-Q(O) decomposes rapidly at a rate of $6.6 \times 10^6 \text{ s}^{-1}$
 256 at 298 K.

257 Within 10.7 s of residence time in the flow tube, these peroxy radicals can react with HO₂
 258 through three possible product channels as ROOH + O₂, ROH + O₃, and R-HO + OH + HO₂.³⁵ The
 259 signals at 212, 228, 244, 260, and 276 Th might arise from the products ROOH and/or ROH as
 260 $C_5H_{10}O_x$ ($x = 5-9$), while the signals at 226, 242, 258, and 274 Th might arise from the carbonyl
 261 products R-HO as $C_5H_8O_x$ ($x = 6-9$). In addition, $C_5H_8O_6$ and $C_4H_8O_5$ could also be formed after the
 262 unimolecular H-shifts in 4-ZH-2OOH'-3OO and 4-Z'H-2OOH'-3OO. $C_5H_8O_6$ might correspond to
 263 the 4-ZH-PO in Scheme 3, and $C_4H_8O_5$ to 4-ZH-PC4. Note that the presence of O₃ in the system
 264 would initiate the isoprene ozonolysis and lead to the formation of C₄ compounds, such as $C_4H_6O_6$
 265 (Figure 2).

Figure 3. Time series of the identified HOMs with different O₃ concentrations (zero before 17:45, 1.5×10^{12} molecules cm⁻³ between 17:45 and 18:30, and 4.6×10^{12} molecules cm⁻³ after 18:30). The solid and dashed lines denote closed shell products and peroxy radicals, respectively.

Figure 3 shows the signal levels of the main species detected at two different O₃ concentrations (tripled at 18:30 with other conditions unchanged). High OH concentrations from higher O₃ boost the concentration of original ISOPO₂. However, HO₂ also increases, leading to faster reactions between ISOPO₂ and HO₂ therefore reducing the proportion of the unimolecular H-shift in Z-δ-ISOPO₂. In addition, high HO₂ concentrations effectively increase the formation of closed-shell products, as shown in Figure 3. The increases of RO₂ radicals are much less pronounced than the closed-shell species. Based on our proposed mechanisms, C₅H₉O₈ is formed via the 4-Z'H route, while C₅H₉O₉ and C₅H₉O₇ via the 4-ZH route. Increasing O₃ concentration means the increase of OH and HO₂, and higher HO₂ favors the 4-Z'H route, namely, a distinctive increase of C₅H₉O₈. Moderate increase of C₅H₉O₇ (4-ZH-2OOH'-3OO) is due to a compromise between the increased formation with more OH and the decreased fraction of 4-ZH (higher HO₂ favors the 4-Z'H channel). Also 4-ZH-2OOH'-3OO would react faster with HO₂, reducing the fraction of the unimolecular process to 4-ZH-Q(O)O₂ (C₅H₉O₉). The overall effect of HO₂/RO₂ on the formation of HOM species requires further detailed modeling analysis.

In the same flow tube reactor, we also studied the reaction of isoprene with OH using I⁻ as the

chemical ionization reagent ion in the presence of NO (concentration monitored by a NO_x-analyzer). OH radicals were generated by photolyzing H₂O₂ with a UV light centered at ~350 nm, which also photolyzes NO₂ to NO. Figure S2 shows the formation of C₅H₈O_{2,3}, C₅H₈-OH-OOH (C₅H₁₀O₃) and C₅H₈-OH-ONO (C₅H₈NO₃) at different H₂O₂ and NO₂ concentrations, and Figure S3 the mass spectrum. No HOM formation was detected in these experiments, due probably to the high HO₂ concentration which suppresses the intramolecular H-shifts in peroxy radicals. However, in presence of NO (100 ppt to 1 ppb), the signal of C₄H₈O₄ was clearly captured and the signal intensity increased with increasing NO concentration. This product may correspond to the 4-Z'H-PC₄ in Scheme 3 and/or to the similar compound in 1-OH channel, which also illustrates the possibility of the HOM formation through alkoxy radicals ISOPO.

Modeling Study on Effects of NO Previous studies^{12,13} have shown that the fraction of Z-δ-ISOPO₂ depends on the bimolecular reaction rates of ISOPO₂ radicals, i.e., the concentration of NO/HO₂ in the environment. The slower the bimolecular reactions, the higher the fraction of Z-δ-ISOPO₂. At low levels of NO and HO₂, formation of HPALD and HOMs from Z-δ-ISOPO₂ would be increasingly important. These conditions would also favor HOM formation from other channels. On the other hand, with the increase of NO, both Z-δ-ISOPO₂ and E-δ-ISOPO₂ are increasingly converted to alkoxy radical Z-δ-ISOPO, which could also lead to formations of HOMs. A modeling study on the effect of NO is required to predict the total yield of HOMs.

Scheme 4. Main reaction routes of isoprene with OH radical to form HOM

Scheme 4 shows the reaction scheme. We applied that the ratios of OH additions at the C₄ and C₁ positions of isoprene are 37% and 63%, respectively, and the reaction of ISOPO₂ with NO results in 87% of alkoxy radical ISOPO and 13% of organic nitrates.^{12,43} In our modeling studies here, products containing 5 or more O-atoms were defined as HOMs, including the nitrates. Table 2 lists the kinetic parameters used in the model, and the results are shown in Figures S4 and S5. A total rate coefficient of $2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was assumed for O₂ additions to 1-/4-OH isomer.⁴⁴ The total rate coefficients were disseminated to the four forward channels (k_1 to k_4) according to their rate coefficients obtained from transition state theory calculations based on potential energy surfaces at RHF-UCCSD(T)-F12/cc-pVTZ-F12a level, while the reverse rates of decompositions back to *cis*-/ *trans*-OH + O₂ were obtained from the calculated equilibrium constants. Corrections for multiple configurations of peroxy radicals and quantum tunneling effect were included in these kinetics calculations. As shown in Table 2, large discrepancies were found on the back-decomposition rates k_3 and k_4 compared to previous work for the 4-OH channel.¹³ In addition, our rate coefficients for intramolecular H-shifts in 4-OH and 1-OH systems were determined as 0.51 s^{-1} and 0.02 s^{-1} , also being lower than the values of $3.7 \pm 1.0 \text{ s}^{-1}$ and $0.36 \pm 0.14 \text{ s}^{-1}$ reported by Teng et al. Nevertheless,

our modeling study showed that the branching ratios of the two H-shifts in Z- δ -ISOPO₂ in 4-OH and 1-OH systems were 44% and 9%, respectively, at the bimolecular reaction rate of 0.01 s⁻¹, being consistent with the experimental results of ~50% and ~7% by Teng et al.¹³

Figure 4 shows the branching ratios of specific products (or reaction channels) as a function of the bimolecular reaction rate with NO. The fractions of intramolecular H-shift in Z- δ -ISOPO₂ and Z- δ -ISOPO are denoted as ZH and Z'H. Clearly, ZH decreases rapidly with the increase of bimolecular rate, e.g., from 0.22 at $k = 0.01$ s⁻¹ to 0.05 only at $k = 0.1$ s⁻¹; while Z'H remains low and increases slowly with the increase of k . The yield of methacrolein (MACR) from β -ISOPO agrees well with previous experimental results,⁴⁵⁻⁴⁶ as shown in Figure 4, while the methyl vinyl ketone (MVK) yield might be slightly overestimated and is sensitive to the NO conditions. Yield of HPALD decreases rapidly from 0.42 to 0.13 and to 0.03 when k increases from 0.001 s⁻¹ to 0.01 s⁻¹ and to 0.1 s⁻¹. The yield of 0.13 at $k = 0.01$ s⁻¹ agrees with the yield of 0.25 with an uncertainty factor of 2 by Teng et al.¹³ The yield of HC₅, arising from E/Z-ISOPO, rises with increasing k to 0.14 at $k = 200$ s⁻¹.

Table 2. Forward and reverse rate constants for O₂ additions used in the model

	4-OH + O ₂			1-OH + O ₂		
	Forward	reverse	Teng et al.	Forward	reverse	Teng et al.
k1	1.87×10^{-13}	0.55	3.7	1.33×10^{-13}	17.1	16
k2	1.15×10^{-12}	0.14	0.08	1.94×10^{-13}	0.42	1.4
k3	5.60×10^{-13}	0.07	1.12	1.34×10^{-12}	2.9	2
k4	1.20×10^{-13}	0.46	10	3.27×10^{-13}	12.1	22

The relation between NO concentration and the yields of HOMs and other compounds is very complex. In the 4-OH channel, the process from 4-ZH to 4-ZH-2OOH'-3OO is virtually not affected by NO because the H-shift in 4-ZH-2OO, which is the bottleneck in the path, is orders of magnitude faster than its possible reaction with NO. Our modeling calculations obtained the branching ratios of

338 4-ZH-2OOH'-3OO + 4-Z'H-2OOH'-3OO as 8.8% at $k = 0.01 \text{ s}^{-1}$ and decreased to 3% at $k = 0.1 \text{ s}^{-1}$
 339 (1.4% and 1.5% in the 1-OH channel). Part of the 4-ZH-2OOH'-3OO and 4-Z'H-2OOH'-3OO
 340 radicals would react with NO and then decompose to low-MW products. Adding the primary
 341 formation of HOMs in both 4-OH and 1-OH channels, the formation yield of total HOMs were
 342 obtained as (10.7–11.2)% at $k = 0.01 \text{ s}^{-1}$ and reduced rapidly to (2.8–4.0)% at $k = 0.1 \text{ s}^{-1}$. See Figure
 343 S4 for yields through different reaction paths. The values to the lower end were obtained by reducing
 344 the unimolecular rates in 4-ZH-2OOH'-3OO and 4-Z'H-2OOH'-3OO by 10 folds.

345 **Figure 4.** Branching ratios of ZH and Z'H, lower and upper limit of HOMs, and yields of four
 346 classical products, as functions of the traditional sink rate with NO (the rate of 1 s^{-1} at 298 K is
 347 equivalent to a bimolecular removal by NO of $\sim 5 \text{ ppb}$)
 348

349 **Implications in the Atmosphere**

350 It is generally considered that the SOA precursors from
 351 isoprene are formed from the second or multiple generation reactions with OH radical in the gas
 352 phase, and that the primary oxidation products play minor roles due to their high volatility. In this
 353 work, we proposed the primary formation of HOM via autooxidation process in Z- δ -ISOPO₂ in the
 oxidation of isoprene. These highly oxygenated species might be important precursors for

354 isoprene-derived SOA. We have detected the formation of highly oxygenated peroxy radicals and
355 HOMs in flow tube where the bimolecular rate could reach as high as $\sim 0.28 \text{ s}^{-1}$. According to our
356 modeling results here, this high bimolecular rate would partially suppress the HOM formation.
357 Moreover, the nitrate-CIMS used in our experiment may not be sensitive to the species containing
358 six oxygen atoms,⁴² such as $\text{C}_5\text{H}_8\text{O}_6$ and $\text{C}_5\text{H}_9\text{O}_6$ which could account for a large fraction of HOM
359 species. Thus, the formation of HOMs in the pristine atmosphere, where the bimolecular rate is ~ 0.01
360 s^{-1} , is expected to be more substantial than our laboratory observations here. This might be the
361 reasons in a previous study in which production of extremely low volatility organic compounds
362 (ELVOC) with only marginal quantities was reported in isoprene oxidation.⁴⁷ Slow bimolecular
363 reactions in the pristine atmosphere would also result in high yields of HPALD.

364 Under typical atmospheric conditions in forest regions, where lifetimes of peroxy radicals are
365 $\sim 100 \text{ s}$ (equivalent to NO of $\sim 50 \text{ pptv}$), the branching ratios of HOMs could be as high as $\sim 11\%$ of
366 the isoprene consumed, therefore contributing substantially to the formation of isoprene-derived
367 SOA. Photolysis of the hydroperoxide groups in HOMs might also contribute to regeneration of OH
368 radical in the pristine atmosphere, in addition to the OH production by HPALD photolysis.¹⁰

369 ASSOCIATED CONTENT

370 **Supporting Information.** Figures S1-S4.

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375 Notes

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