

1 **Aqueous Reactions of Organic Triplet Excited States with Atmospheric**

2 **Alkenes**

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11

12 **Abstract**

13 Triplet excited states of organic matter are formed when colored organic matter (i.e., brown
14 carbon) absorbs light. While these “triplets” can be important photooxidants in atmospheric
15 drops and particles (e.g., they rapidly oxidize phenols), very little is known about their reactivity
16 toward many classes of organic compounds in the atmosphere. Here we measure the bimolecular
17 rate constants of the triplet excited state of benzophenone (³BP*), a model species, with 17
18 water-soluble C₃ – C₆ alkenes that have either been found in the atmosphere or are reasonable
19 surrogates for identified species. Measured rate constants ($k_{\text{ALK}+3\text{BP}^*}$) vary by a factor of 30 and
20 are in the range of $(0.24 - 7.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Biogenic alkenes found in the atmosphere – e.g.,
21 cis-3-hexen-1-ol, cis-3-hexenyl acetate, and methyl jasmonate – react rapidly, with rate constants
22 above $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Rate constants depend on alkene characteristics such as the location of the
23 double bond, stereochemistry, and alkyl substitution on the double bond. There is a reasonable
24 correlation between $k_{\text{ALK}+3\text{BP}^*}$ and the calculated one-electron oxidation potential (OP) of the
25 alkenes ($R^2 = 0.58$); in contrast, rate constants are not correlated with bond dissociation
26 enthalpies, bond dissociation free energies, or computed energy barriers for hydrogen
27 abstraction. Using the OP relationship, we estimate aqueous rate constants for a number of

28 unsaturated isoprene and limonene oxidation products with $^3\text{BP}^*$: values are in the range of
29 $(0.080\text{--}1.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, with generally faster values for limonene products. Rate constants
30 with less reactive triplets, which are probably more environmentally relevant, are likely roughly
31 25 times slower. Using our predicted rate constants, along with values for other reactions from
32 the literature, we conclude that triplets are probably minor oxidants for isoprene and limonene-
33 related compounds in cloudy or foggy atmospheres, except in cases where the triplets are very
34 reactive.

35

36 **1 Introduction**

37 Photochemical processes in atmospheric aqueous phases (e.g., cloud and fog drops and
38 aqueous particles) are important sources and sinks of secondary organic species (Blando and
39 Turpin, 2000; Lim et al., 2010; Kroll and Seinfeld, 2008; Volkamer et al., 2009; Gelencsér and
40 Varga, 2005), which represent a large fraction of aerosol mass (Zhang et al., 2007; Hallquist et
41 al., 2009). Many of these reactions involve photooxidants, including hydroxyl radical ($\bullet\text{OH}$),
42 which is widely considered to be the dominant aqueous oxidant (Herrmann et al., 2010;
43 Herrmann et al., 2015). But there are numerous other aqueous photooxidants, such as singlet
44 molecular oxygen, hydroperoxyl radical/superoxide radical anion, hydrogen peroxide, and triplet
45 excited states of organic matter ($^3\text{C}^*$ or triplets) (Lee et al., 2011; Anastasio and McGregor,
46 2001; Kaur and Anastasio, 2017; Anastasio et al., 1996; Anastasio et al., 1994; Zepp et al., 1977;
47 Wilkinson et al., 1995; Kaur and Anastasio, 2018). Formed from the photoexcitation of colored
48 organic matter (i.e., brown carbon), triplets are important oxidants in surface waters for several
49 classes of organic compounds, including phenols, anilines, amines, phenylurea herbicides, and
50 heterocyclic sulfur-containing compounds (Canonica et al., 1995; Canonica and Hoigné, 1995;
51 Arnold, 2014; Canonica et al., 2006a; Bahnmüller et al., 2014; Boreen et al., 2005); however,
52 very little is known about atmospheric triplets.

53 Recent studies have shown that aqueous triplets can be the dominant oxidants for phenols
54 emitted during biomass combustion (Smith et al., 2014), with phenol lifetimes on the order of a
55 few hours in fog drops (Kaur and Anastasio, 2018) and aqueous particle extracts (Kaur et al.,
56 2018). There is also evidence that triplets can oxidize some unsaturated aliphatic compounds.
57 Richards-Henderson et. al. (Richards-Henderson et al., 2014b) measured rate constants for five
58 unsaturated biogenic volatile organic compounds (BVOCs) with the model triplets 3,4-
59 dimethoxybenzaldehyde and 3'-methoxyacetophenone, and found that rate constants ranged
60 between 10^7 and $10^9 \text{ M}^{-1} \text{ s}^{-1}$. Other laboratory studies have shown that triplet states of
61 photosensitizers such as imidazole-2-carboxaldehyde and 4-benzoylbenzoic acid can oxidize
62 gaseous aliphatic BVOCs, e.g., isoprene and limonene, and model aliphatic compounds, e.g., 1-
63 octanol, at the air-water interface to form low-volatility products that increase particle mass (Fu
64 et al., 2015; Rossignol et al., 2014; Li et al., 2016; Laskin et al., 2015). However, the
65 atmospheric importance of these types of processes are unclear (Tsui et al., 2017). Additionally,
66 we recently reported that natural triplets in illuminated fog waters and particle extracts are
67 significant oxidants for methyl jasmonate, an unsaturated aliphatic BVOC, accounting for 30–80
68 % of its aqueous loss during illumination (Kaur et al., 2018; Kaur and Anastasio, 2018).

69 Abundant BVOCs such as isoprene and limonene are rapidly oxidized in the gas phase to
70 form unsaturated C_3 – C_6 oxygenated volatile organic compounds (OVOCs) that include isoprene
71 hydroxyhydroperoxides, isoprene hydroxynitrates, and isoprene and limonene aldehydes (Surratt
72 et al., 2006; Paulot et al., 2009b; Crounse et al., 2011; Ng et al., 2008; Walser et al., 2008; Paulot
73 et al., 2009a). Several of these first-generation products have high Henry's law constants, above
74 10^4 M atm^{-1} (Marais et al., 2016) and partition significantly into cloud and fog drops and, to a
75 smaller extent, into aerosol liquid water. There, they can undergo further oxidation by aqueous
76 photooxidants, including $\bullet\text{OH}$ and ozone (Wolfe et al., 2012; St. Clair et al., 2015; Khamaganov
77 and Hites, 2001; Schöne and Herrmann, 2014; Lee et al., 2014) and possibly triplets. Our past

78 measurements have shown that steady-state concentrations of $^3\text{C}^*$ are orders of magnitude higher
79 than $^{\bullet}\text{OH}$ in fog waters and aqueous particles (Kaur et al., 2018; Kaur and Anastasio, 2018) and
80 thus they might contribute significantly to the loss of OVOCs derived from isoprene and other
81 precursors. However, testing this hypothesis requires rate constants for the reactions of triplets
82 with alkenes, which are scarce.

83 To address this gap, we studied the reactions of 17 $\text{C}_3 - \text{C}_6$ unsaturated compounds with
84 the triplet state of the model compound benzophenone (Fig. 1). While our 17 unsaturated
85 compounds include alcohols, esters, and chlorinated compounds, for simplicity we refer to them
86 all as “alkenes”. The tested alkenes include BVOCs emitted into the atmosphere as well as
87 surrogates for some of the small unsaturated gas-phase products formed as secondary OVOCs.
88 The goals of this study are to: 1) measure rate constants for reactions of the alkenes with the
89 triplet excited state of benzophenone, 2) explore quantitative structure-activity relationships
90 (QSARs) between the measured rate constants and calculated alkene properties (e.g., the one-
91 electron oxidation potential) and 3) use a suitable QSAR to estimate rate constants for triplets
92 with some unsaturated isoprene and limonene oxidation products to predict whether or not
93 triplets are significant oxidants for these species in cloud and fog drops.

94

95 **2 Methods**

96 **2.1 Chemicals**

97 All chemicals were purchased from Sigma-Aldrich with purities of 95 % and above, and
98 were used as received: the compound numbers, compound names, and abbreviated names are
99 listed in Table 1. All chemical solutions were prepared using purified water (Milli-Q water) from
100 a Milli-Q Plus system (Millipore; $\geq 18.2 \text{ M}\Omega \text{ cm}$) with an upstream Barnstead activated carbon

101 cartridge. To mimic fog drop acidity (Kaur and Anastasio, 2017), the pH of each reaction
102 solution was adjusted to 5.5 (\pm 0.2) using a 1.0 mM phosphate buffer.

103 **2.2 Kinetic Experiments**

104 Bimolecular rate constants of the alkenes with the triplet state of benzophenone ($^3\text{BP}^*$)
105 were measured using a relative rate technique, as described in in the literature (Richards-
106 Henderson et al., 2014a; Finlayson-Pitts and Pitts Jr, 1999). The technique involves illuminating
107 a solution containing the triplet precursor (BP), a reference compound with a known second-
108 order rate constant with $^3\text{BP}^*$, and one test alkene for which the rate constant is unknown. The
109 reference compound for each alkene was chosen so that the triplet-induced loss rates for test
110 alkene and reference compound were similar. Buffered, air-saturated solutions containing 50 μM
111 each of the reference and test compounds and 100 μM of BP were prepared and then 10 mL of
112 this solution was illuminated in a stirred 2-cm, air-tight quartz cuvette (Spectrocell) at 25 $^\circ\text{C}$.
113 Samples were illuminated with a 1000 W Xenon arc lamp filtered with an AM 1.0 air mass filter
114 (AM1D-3L, Sciencetech) and 295 nm long-pass filter (20CGA-295, Thorlabs) to mimic
115 tropospheric solar light (Fig. S1 of the Supplemental Information). At various intervals, aliquots
116 of illuminated sample were removed and analyzed for the concentration of reference compound
117 and test alkene using HPLC (Shimadzu LC-10AT pump, ThermoScientific BetaBasic-18 C_{18}
118 column (250 \times 33 mm, 5 μM bead), and Shimadzu-10AT UV-Vis detector). For each alkene,
119 illumination experiments were performed in triplicate (Table S1), using total illumination times
120 typically between 60 and 150 min. Parallel dark controls were employed with every experiment
121 using an aluminum foil-wrapped cuvette containing the same solution and analyzed in the same
122 manner as the illuminated solutions. The dark cuvette was placed in a corner of the sample
123 chamber, out of the path of the light beam. As a direct photodegradation control, each alkene was
124 also illuminated (separately) in solution without benzophenone; there was no loss for any of the
125 compounds.

126 In every case, loss of test and reference compounds followed first-order kinetics. Plotting
127 the change in concentration of the test alkene against that of the reference compound yields a
128 linear plot that is represented by:

$$129 \ln \frac{[\text{Reference}]_0}{[\text{Reference}]_t} = \frac{k_{\text{Reference}+3\text{BP}^*}}{k_{\text{ALK}+3\text{BP}^*}} \ln \frac{[\text{ALK}]_0}{[\text{ALK}]_t} \quad (1)$$

130 where $[\text{Reference}]_0$, $[\text{Reference}]_t$, $[\text{ALK}]_0$, and $[\text{ALK}]_t$ are the concentrations of the reference
131 and test alkenes at times zero and t , respectively, and $k_{\text{Reference}+3\text{BP}^*}$ and $k_{\text{ALK}+3\text{BP}^*}$ are the
132 bimolecular rate constants for the reaction of the reference and test alkenes with $^3\text{BP}^*$,
133 respectively. A plot of Eq. (1) (with the y-intercept fixed at the origin) gives a slope equal to the
134 ratio of the bimolecular rate constants; dividing $k_{\text{Reference}+3\text{BP}^*}$ by the slope gives $k_{\text{ALK}+3\text{BP}^*}$. The
135 measurement technique is illustrated in Fig. S2. While $^3\text{BP}^*$ makes singlet molecular oxygen
136 ($^1\text{O}_2^*$), the latter is an insignificant oxidant of alkenes in our solutions: the concentrations of the
137 two oxidants are similar (McNeill and Canonica, 2016), but our measured rate constants of
138 alkenes with $^3\text{BP}^*$ are approximately 2500 times faster than the corresponding rate constants
139 with $^1\text{O}_2^*$ (Richards-Henderson et al., 2014a).

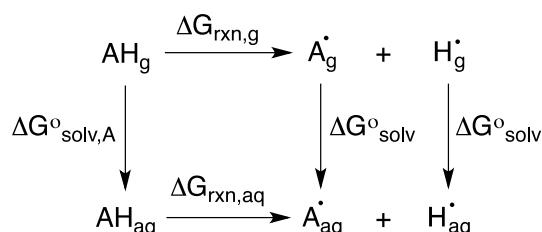
140 2.3 Calculation of Oxidation Predictor Variables

141 All calculations were completed using the Gaussian 09 software suite (Frisch et al.,
142 2009). Structures of alkenes were optimized using uB3LYP/6-31+G(d,p) (Becke, 1992, 1993;
143 Lee et al., 1988; Stephens et al., 1994; Tirado-Rives and Jorgensen, 2008) for reaction coordinate
144 calculations and the CBS-QB3 (Montgomery Jr et al., 1999) method for predicting bond
145 dissociation enthalpies (BDEs), bond dissociation free energies (BDFEs), and oxidation
146 potentials (OPs). This method has a mean absolute deviation of approximately 1 kcal mol^{-1}
147 which corresponds to 0.04 V in E_{ox} (i.e., OP). Transition state structures (TSSs) were optimized
148 in the triplet state using uB3LYP/6-31+G(d,p) (Becke, 1992, 1993; Lee et al., 1988; Stephens et
149 al., 1994; Tirado-Rives and Jorgensen, 2008). TSSs were confirmed by the presence of an

150 imaginary frequency and minima (reactants and products) were confirmed by the absence of
 151 imaginary frequencies. Free energy (ΔG) and enthalpy (ΔH) differences were determined by
 152 comparing TSS energies relative to their reactant energies. For solvent phase calculations, the
 153 solvent model density (SMD) (Marenich et al., 2009) continuum model was used with water as
 154 the solvent. To calculate BDEs, the neutral (AH) and radical species (A^\bullet) (resulting from H atom
 155 abstraction) of each alkene and the H radical (H^\bullet) were optimized in the gas phase. Using the
 156 computed enthalpies (H) and Eq. (2), the predicted BDEs of each alkene were determined.

$$157 \quad BDE = H_{A^\bullet} + H_{H^\bullet} - H_{AH} \quad (2)$$

158 To determine the predicted BDFEs, the neutral (AH_g , AH_{aq}) and radical species (A^\bullet_g ,
 159 A^\bullet_{aq}) of each alkene and the H radical (H^\bullet_g , H^\bullet_{aq}) were optimized in the gas and solvent phases
 160 and their differences taken to give $\Delta G^\circ_{solv,AH}$, $\Delta G^\circ_{solv,A^\bullet}$, and $\Delta G^\circ_{solv,H^\bullet}$, respectively. Based on
 161 the thermodynamic cycle shown (Scheme 1), these values were used in Eqs. (3) and (4) to
 162 calculate the BDFEs of C–H and O–H bonds.



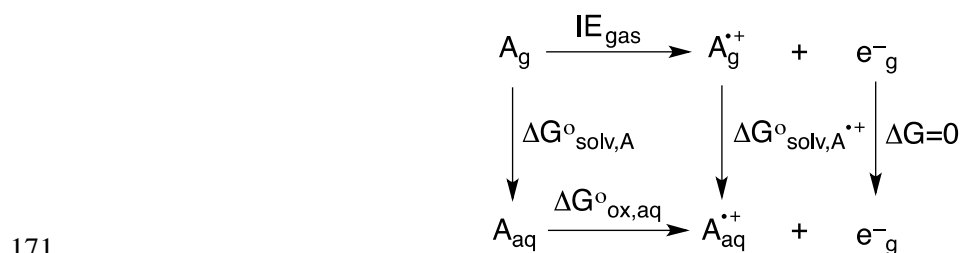
164 **Scheme 1.** Thermodynamic cycle used to calculate bond dissociation free energies.

$$165 \quad \Delta\Delta G_{solv} = \Delta G^\circ_{solv,A^\bullet} + \Delta G^\circ_{solv,H^\bullet} - \Delta G^\circ_{solv,AH} \quad (3)$$

$$166 \quad \Delta G^\circ_{ox} = \Delta G_g + \Delta\Delta G_{solv} \quad (4)$$

167 To predict OPs, the neutral (A_g , A_{aq}) and radical cation ($A^{\bullet+}_g$, $A^{\bullet+}_{aq}$) forms of each alkene
 168 were optimized in the gas and solvent phase, their difference giving $\Delta G^\circ_{solv,A}$ and $\Delta G^\circ_{solv,A^\bullet}$.

169 Based on the thermodynamic cycle shown below (Scheme 2), these values were used in Eqs. (5–
 170 7) to calculate the OP (i.e., E_{ox}) of each alkene.



172 **Scheme 2.** Thermodynamic cycle used to calculate oxidation potentials.

173
$$\Delta\Delta G_{solv} = \Delta G^{\circ}_{solv,A^{*+}} - \Delta G^{\circ}_{solv,A} \quad (5)$$

174
$$\Delta G^{\circ}_{ox} = IE_{gas} + \Delta\Delta G_{solv} \quad (6)$$

175
$$E_{ox} = -\left(\frac{-\Delta G^{\circ}_{ox}}{nF} + SHE\right) \quad (7)$$

176 where n is the number of electrons, F is Faraday's constant (96485.3365 C/mol), and SHE is the
 177 potential of the standard hydrogen electrode (4.28 V).

178 Subsequent MP2/CBSB3 (Petersson et al., 1988; Petersson and Al-Laham, 1991;
 179 Petersson et al., 1991; Mayer et al., 1998) single point calculations were used to compute the
 180 highest occupied molecular orbitals (HOMOs) and singly occupied molecular orbitals (SOMOs).
 181 Structural drawings were produced using CYLView (Legault, 2009).

182

183 3 Results and discussion

184 3.1 Alkene-triplet bimolecular rate constants ($k_{ALK+3BP^*}$)

185 Fig. 1 shows the chemical structures for all 17 alkenes and the triplet precursor,
 186 benzophenone. The alkenes have molecular weights ranging between 58 and 220 g mol⁻¹ and
 187 include 13 alcohols, three esters and one chlorinated compound. The model triplet precursor
 188 benzophenone (BP) has been previously employed in surface water studies, and its triplet state

189 rapidly reacts with aromatics such as substituted phenols and phenyl urea herbicides with rate
190 constants faster than $10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Canonica et al., 2000; Canonica et al., 2006b).

191 The bimolecular rate constants for the alkenes with the excited triplet state of BP
192 ($k_{\text{ALK}+3\text{BP}^*}$) vary by a factor of 30, spanning the range of $(0.24\text{--}7.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Values are
193 shown in Tables 1 and S1, and in Fig. S3, where the alkenes are numbered in ascending order of
194 their reactivity towards $^3\text{BP}^*$. Based on their rate constants, the alkenes appear to be broadly split
195 into two groups – the slower alkenes (**1–9**), whose rate constants lie below $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and
196 span a range of only a factor of 2.5, and the faster alkenes (**10–17**) which vary by a factor of 5.
197 Notably, three of the four BVOCs identified in emissions to the atmosphere – 3MBO (**12**), cHxO
198 (**15**), cHxAc (**16**) and MeJA (**17**) – react rapidly with $^3\text{BP}^*$, with rate constants greater than $1 \times$
199 $10^9 \text{ M}^{-1} \text{ s}^{-1}$.

200 Three alkene characteristics appear to increase reactivity: internal (rather than terminal)
201 double bonds; methyl substitution on the double bond; and alkene stereochemistry. To more
202 specifically examine the impact of these variables, we compare the rate constants for three sets of
203 alkenes (Fig. 2). The lowest free energy and enthalpy barriers for the abstraction of a hydrogen
204 atom are also shown in Fig. 2 (and in Table 1); while overall these computed barriers are not
205 well-correlated with rate constants (discussed below), lower barriers generally correspond to
206 higher rate constants for the sets of alkenes in Fig. 2. The first two sets of compounds in Fig. 2
207 indicate that internal alkenes react faster with $^3\text{BP}^*$ than do terminal isomers: cHxAc (**16**), an
208 internal hexenyl acetate, has a reaction rate constant 11 times faster than its terminal isomer
209 5HxAc (**9**). The corresponding alcohols also exhibit the same trend: the internal alkenes cHxO
210 (**15**) and tHxO (**10**) react 27 and 5.8 times faster, respectively, than the terminal isomer 5HxO
211 (**1**). This dependence of reactivity on double bond location has implications for isoprene
212 hydroxyhydroperoxides (ISOPOOH) and hydroxynitrates (ISONO₂), which have both terminal
213 (β -) and non-terminal (δ -) isomers formed from gas-phase oxidation (Marais et al., 2016; Paulot

214 et al., 2009b; Paulot et al., 2009a). Based on our results we expect that the δ -isomers react more
215 quickly with organic triplets than the β -isomers.

216 Alkene stereochemistry also affects the triplet-alkene reaction rate constant. The data in
217 the middle of Fig. 2 shows that cis-HxO (**15**) reacts nearly five times more quickly with $^3\text{BP}^*$
218 than does trans-HxO (**10**), consistent with the lower predicted energy barrier for hydrogen atom
219 abstraction from the cis isomer. Finally, addition of electron-donating substituents (methyl
220 groups) on an unsaturated carbon atom also increases the rate constant. This is evident from
221 comparing 2B1O (**8**) and its methyl-substituted analog 3MBO (**12**): $k_{\text{ALK}+^3\text{BP}^*}$ is 3.7 times faster
222 with the methyl group (Fig. 2). Mechanistically, triplet-induced oxidation can proceed via either
223 hydrogen atom transfer or a proton-coupled-electron transfer (Canonica et al., 1995; Warren et
224 al., 2010; Erickson et al., 2015) and the presence of an electron-donating substituent on the
225 double bond likely selectively stabilizes the intermediates (e.g., radical or radical cation) formed
226 from these two processes, as well as the transition state structures for their formation.

227 **3.2 Relationship between k and one-electron oxidation potential**

228 Our next goal was to develop a quantitative structure-activity relationship (QSAR) so that
229 we can predict rate constants for alkene-triplet reactions. To use as predictor variables in the
230 QSARs we computed several properties of the alkenes: bond dissociation enthalpy and free
231 energy for various hydrogen atoms (Fig. S4), free energy and enthalpy barriers for hydrogen
232 atom abstraction (Table 1), and one-electron oxidation potentials (Table 1). Apart from the
233 oxidation potential, none of the other properties correlate well with the measured rate constants
234 (Figs. S5 and S6). While there is no correlation between the rate constants and predicted energy
235 barriers, alkenes with lower predicted free energy barriers (ΔG^\ddagger) are predicted to be fast-reacting,
236 with rate constants above $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. S6). As shown in Fig. S6, computed barriers
237 predict a much larger variation in rate than observed experimentally, suggesting that the breaking
238 of the C–H or O–H bond does not occur in the rate-determining step for all alkenes.

239 Of all the properties examined, the one-electron oxidation potential (OP) of the alkenes
240 best correlates with the (log of) measured rate constants, with rate constants generally increasing
241 as the alkenes are more easily oxidized, i.e., at lower OP values ($R^2 = 0.58$) (Fig. 3). Measured
242 rate constants for 13 of the 16 alkenes lie within (or very near to) the 95 % confidence interval
243 (blue lines) of the regression fit, but there are three notable outliers: hexen-1,3-diol (**3**, HDO),
244 cis-3-hexen-1-ol (**15**, cHxO) and cis-3-hexenylacetate (**16**, cHxAc). The measured HDO rate
245 constant is 3.3 times lower than that predicted by the regression line, while measured rate
246 constants for cHxO and cHxAc are 3.9 and 4.9 times higher, respectively, than predicted.

247 To try to assess why these compounds differ from the others, we calculated the highest
248 occupied molecular orbital (HOMO) of the alkene and the singly occupied molecular orbital
249 (SOMO) of the alkene radical cation (i.e., after oxidation) (Fig. 4). Depending on the system,
250 oxidation is predicted to occur by removing an electron either from the π system of the C–C
251 double bond or from a lone pair on the O atom. This is illustrated in Fig. 4, which shows the
252 HOMO and SOMO structures for HDO (**3**), where the electron is removed from the C–C double
253 bond, and 3B1O (**5**), where the electron is removed from the oxygen atom. However, the three
254 outliers in the correlation do not all fall into just one of these categories: for cHxAc (**16**) the
255 electron is most likely abstracted from the oxygen, while for HDO (**3**) and cHxO (**15**) the
256 electron is likely removed from the π system (Tables S2 and S3). This suggests that the location
257 of electron removal does not control the rate constants. We also examined if the rate of loss of
258 cHxO might be enhanced due to oligomerization, where an initially formed cHxO radical leads
259 to additional cHxO loss. Since the pseudo-first-order rate constant of oligomerization should
260 increase with initial cHxO concentration, we measured the rate constant for cHxO loss over a
261 range of initial concentrations (2–50 μM). However, as shown in Fig. S8, the rate constant for
262 cHxO loss does not depend on its concentration, suggesting that oligomerization is an
263 unimportant loss process for cHxO in our experiments. Thus, it is not clear why these three
264 compounds do not fall closer to the regression line of Fig. 3. However, except for **16**, all of the

265 alkenes fall within a factor of four of the correlation line (grey lines). Finally, even though there
266 is a good correlation between rate constant and OP in Fig. 3, it does not indicate whether these
267 reactions proceed via pure electron transfer, proton-coupled electron transfer, or hydrogen
268 transfer. As discussed earlier, since the predicted energy barriers for hydrogen abstraction do not
269 correlate with measured rate constants (Fig. S6) and appear to split into two groups, there
270 remains uncertainty about the mechanism of triplet-induced oxidation of the alkenes.

271 **3.3 Predicted triplet-OVOC bimolecular rate constants**

272 We next use the relationship in Fig. 3, along with calculated oxidation potentials, to
273 predict second-order rate constants for $^3\text{BP}^*$ with a set of unsaturated oxygenated VOCs formed
274 by the oxidation of isoprene and limonene. As shown in Fig. 5, we predict that limonene
275 products generally react faster with $^3\text{BP}^*$ than do isoprene products. For the five isoprene-
276 derived OVOCs that we considered, rate constants vary by a factor of 17, and range between
277 $(0.080\text{--}1.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1, Fig. 5). The δ -isomers of ISOPOOH and ISONO₂, which
278 contain internal double bonds, have lower computed one-electron oxidation potentials and thus
279 higher predicted rate constants compared to the terminal β -isomers. This is similar to the trend
280 observed with the other alkenes (Fig. 2). In case of isoprene hydroperoxyaldehydes, we were
281 able to determine the oxidation potential for only HPALD2 (**22**), and its predicted reaction rate
282 constant (± 1 SE) of $4.0 (\pm 0.9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is among the lowest of the isoprene-derived alkenes
283 (Fig. 5).

284 We calculated OP values and triplet rate constants for three limonene-derived OVOCs:
285 limonene aldehyde (LMNALD) and two dihydroxy-limonene aldehydes (2,5OH-LMNALD and
286 4,7OH-LMNALD). Compared to the isoprene-derived alkenes, the rate constants for all three
287 limonene products are high, and range between $(0.89\text{--}1.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. All of the limonene
288 aldehydes (as well as the isoprene products) can have several isomers whose calculated oxidation
289 potentials can vary, which affects the predicted rate constant. For example, for 4,7OH-LMNALD

290 (25) the computed oxidation potential for five of its isomers vary between 2.17 and 2.48 V
291 (Table S4), which leads to a relative standard deviation of 40 % in the predicted rate constants
292 for the various isomers. For each OVOC, the predicted rate constants in Table 1 are for the
293 lowest energy isomers whose structures are shown in Fig. S9.

294 **3.4 Role of triplets in the fate of isoprene- and limonene-derived OVOCs**

295 Next, we use our estimated rate constants, along with previously published estimated
296 values for rates of other loss processes (Table S5), to understand the importance of triplets as
297 sinks for isoprene- and limonene-derived OVOCs in a foggy/cloudy atmosphere. For our simple
298 calculations we use a liquid water content of 1×10^{-6} L-aq/L-g, a temperature of 25 °C, and
299 calculated Henry's law constants from EPISuite (US EPA. Estimation Programs Interface
300 Suite™ for Microsoft® Windows v 4.1, 2016) (Table S6). From these inputs, we estimate that
301 between 10 and 97 % of the OVOCs will be partitioned into the aqueous phase under our
302 conditions (Table S6). The OVOC sinks we consider are photolysis and reactions with hydroxyl
303 radical (\bullet OH) and ozone (O_3) in the gas phase as well as hydrolysis and reactions with \bullet OH, O_3 ,
304 and triplets in the aqueous phase (Table S5). Based on typical oxidant concentrations in both
305 phases and available rate constants with sinks, the overall pseudo-first-order rate constants for
306 initial OVOC losses are estimated to be in the range of $(0.27\text{--}3.0) \times 10^{-4} \text{ s}^{-1}$, corresponding to
307 overall lifetimes of 0.93 to 10 h (Table S7). The only exception is δ -ISONO2, which is expected
308 to undergo rapid hydrolysis to form its corresponding diol (Jacobs et al., 2014) with a lifetime of
309 just 0.078 h (280 s).

310 Fig. 6 shows the overall loss rate constants, and the contribution from each pathway, for
311 four of these OVOCs: δ 4-ISOPOOH (19), β -ISONO2 (20), HPALD2 (22) AND 4,7-OH
312 LMNALD (25). Overall, aqueous-phase processes dominate the fate of these OVOCs,
313 accounting for the bulk of their loss; but the contribution of aqueous triplets to OVOC loss
314 depends strongly on the triplet reactivity. Panel (a) of Fig. 6 shows OVOC loss when we assume

315 that the aqueous triplets are highly reactive, i.e., using rate constants estimated for ³BP* (Fig. 5).
316 Since our recent measurements (Kaur et al., 2018; Kaur and Anastasio, 2018) indicate that, on
317 average, ambient triplets are not this reactive, this scenario likely represents an upper bound for
318 the triplet contribution. In this case highly reactive triplets are the dominant sinks for δ4-
319 ISOPOOH and 4,7-OH LMNALD, accounting for 74 % and 47 % of their total losses,
320 respectively (Fig. 6a). For β-ISONO₂ and HPALD₂, triplets are not dominant but still significant,
321 accounting for 19 % and 24 % of loss, respectively, while other sinks dominate. For the OVOCs
322 where we calculated rate constants with ³BP* (Fig. 5) but that are not shown in Fig. 6, the triplet
323 contribution varies widely, from less than 1 % for δ-ISONO₂ (**21**), where hydrolysis dominates,
324 to 59 % for 2,5-OH LMNALD (**24**) (Table S7).

325 While ³BP* likely represents an upper bound of triplet reactivity in atmospheric waters,
326 our recent measurements indicate that the triplets in fog waters and particles have an average
327 reactivity that is typically similar to 3'-methoxyacetophenone (3MAP) and 3,4-
328 dimethoxybenzaldehyde (DMB) (Kaur et al., 2018; Kaur and Anastasio, 2018). A comparison of
329 our ³BP* rate constants (Table 1) with the average values for the 3MAP and DMB triplets for a
330 subset of the alkenes (Richards-Henderson et al., 2014b) indicates that the average 3MAP/DMB
331 triplet rate constants are 1–18 % of the corresponding ³BP* values. Thus to scale alkene-triplet
332 rate constants from ³BP* to the 3MAP and DMB triplets we take the median value of 4 %, which
333 is derived from the MeJA rate constants (Table S8). Fig. 6b shows the calculated fates of the
334 OVOCs in the case where we consider “typical reactivity” triplets, i.e., where we multiply the
335 ³BP* + OVOC rate constants (Fig. 5) by a factor of 0.04. Under these conditions, triplets are
336 minor oxidants (Fig. 6b), accounting for 9 % and 3 % of the loss of δ4-ISOPOOH and 4,7-
337 LMNALD, respectively, and approximately 1 % for the other two OVOCs. This suggests that
338 aqueous triplets are generally minor sinks for OVOCs derived from isoprene and limonene, in
339 contrast to the case for phenols, where triplets appear to be the major sink (Smith et al., 2014; Yu

340 et al., 2014; Kaur and Anastasio, 2018). However, there are several important uncertainties in
341 our determination that triplets are likely minor sinks for oxygenated alkenes. First, the factor we
342 used to adjust from ³BP* rate constants to triplet 3MAP/DMB rate constants (i.e., a factor of
343 0.04) is quite uncertain: values for the three BVOCs examined range from 0.01 to 0.18 (Table
344 S8). Additionally, there are very few measurements of triplets in atmospheric drops or particles
345 (Kaur et al., 2018; Kaur and Anastasio, 2018), and only from two sites, so it is possible that we
346 are underestimating the average reactivity and/or concentrations of triplets in atmospheric drops
347 and particles.

348 **4 Conclusions**

349 To explore whether triplet excited states of organic matter might be important sinks for
350 unsaturated organic compounds in atmospheric drops, we measured rate constants for 17 C₃–C₆
351 alkenes with the triplet excited state of benzophenone (³BP*). The resulting bimolecular rate
352 constants span the range of (0.24–7.5) × 10⁹ M⁻¹s⁻¹. Notably, the rate constants are high (above
353 10⁹ M⁻¹s⁻¹) for some important green leaf volatiles emitted from plants – 3MBO, cHxO, cHxAc,
354 and MeJA. Rate constants appear to be enhanced by alkene characteristics such as an internal
355 double bond, cis-stereochemistry, and alkyl substitution on the double bond.

356 To be able to predict rate constants for other alkenes, we examined QSARs between our
357 measured rate constants and a variety of calculated properties for the alkenes and ³BP*-alkene
358 transition states. Rate constants are not correlated with bond dissociation enthalpies, free
359 energies or predicted energy barriers for removal of various hydrogen atoms, but are reasonably
360 correlated with the one-electron oxidation potential of the alkenes ($R^2 = 0.58$). Based on the
361 relationship between rate constants and oxidation potential, we predict that highly reactive
362 triplets will react with first generation isoprene- and limonene- oxidation products with rate
363 constants on the order of 10⁸–10⁹ M⁻¹ s⁻¹, with higher values for the δ-isomers compared to
364 terminal β-isomer products. Using these rate constants in a simple model of OVOC chemistry in

365 a foggy/cloudy atmosphere suggests that highly reactive aqueous triplets could be significant
366 oxidants for some isoprene hydroxyhydroperoxides and limonene aldehydes. However, for our
367 current best estimate of typical reactivities, triplets are a minor sink for isoprene- and limonene-
368 derived OVOCs.

369 To more specifically quantify the contributions of triplet excited states towards the loss of
370 alkenes in particles and drops requires more insight into both the reactivities and concentrations
371 of atmospheric triplet species. In addition, assessing whether triplets might be important sinks for
372 other organic species requires more measurements of reaction rate constants with
373 atmospherically relevant organics.

374 **Competing Interests**

375 The authors declare that they have no conflict of interest.

376 **Author Contribution**

377 CA and RK conceptualized the research goals and designed the experiments. RK and JD
378 performed the laboratory work, while BH and DT planned and performed the computational
379 calculations. RK analyzed the experimental data and prepared the manuscript with contributions
380 from all co-authors, particularly BH, who wrote the sections on computational calculations and
381 prepared the corresponding figures. CA reviewed and edited the manuscript. CA and DT
382 provided oversight during the entire process.

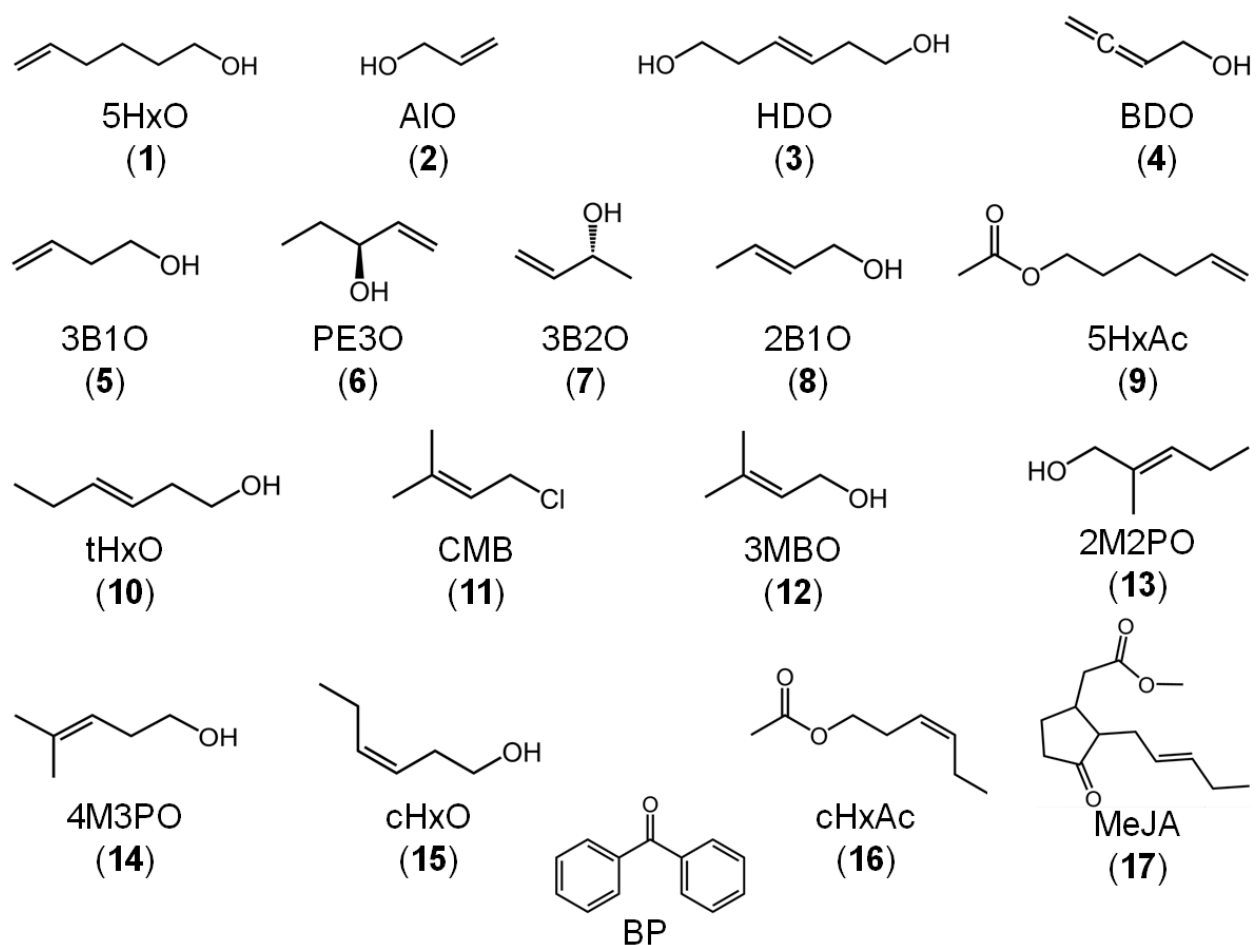
383 **Data Availability**

384 Data are available upon request.

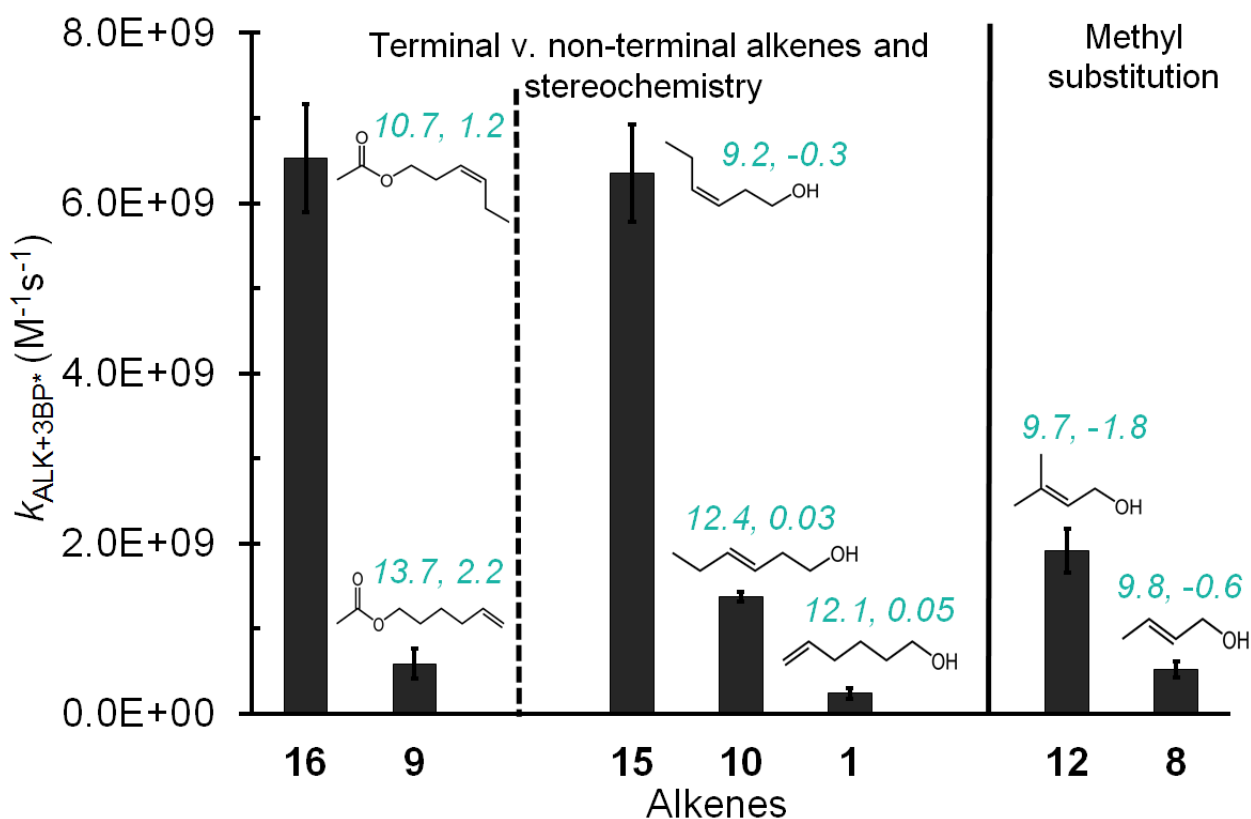
385 **Acknowledgements**

386 We thank Jacqueline R. Labins for assistance with rate constant measurements, Ted Hullar for
387 irradiance measurements, and Tran Nguyen for helpful discussions on the reactivity of isoprene

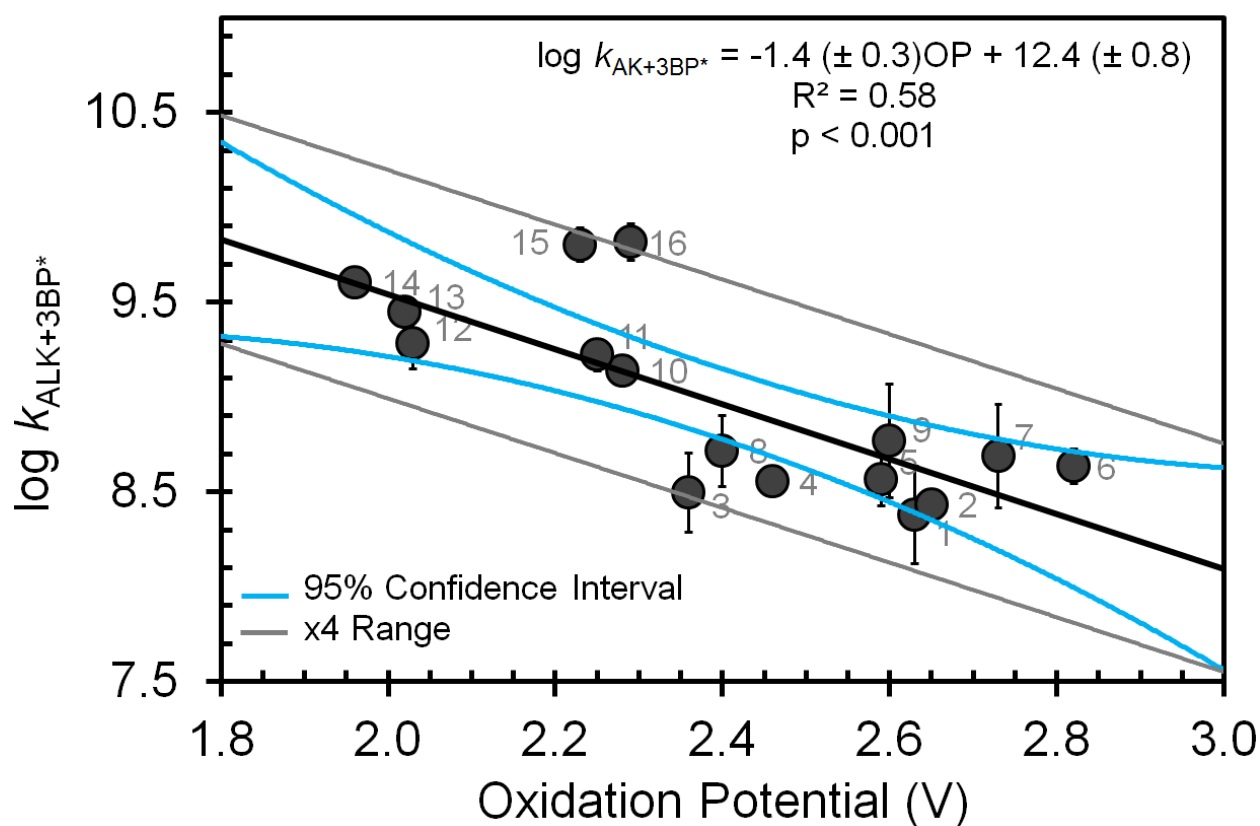
388 oxidation products. This research was funded by the National Science Foundation (Grants AGS-
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390 LAW-6403-RR), the University of California - Davis Office of Graduate Studies, a UC Guru
391 Gobind Singh Fellowship, and the Agricultural and Environmental Chemistry Graduate Group at
392 UC Davis.



393
 394 **Fig. 1** Chemical structures of the reactant species used in this study: 17 alkenes and one model
 395 triplet, benzophenone. Compound numbers are in parentheses.



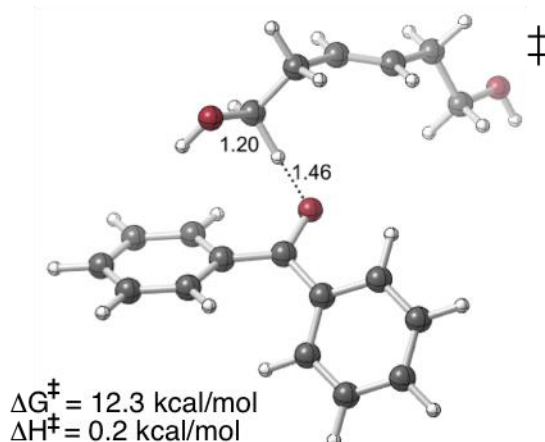
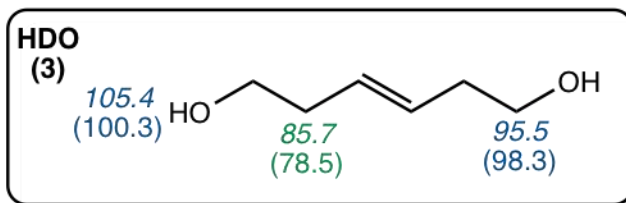
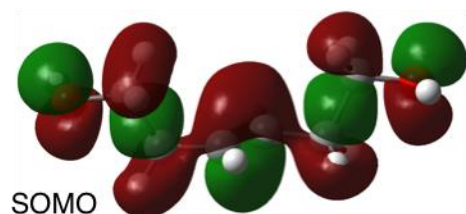
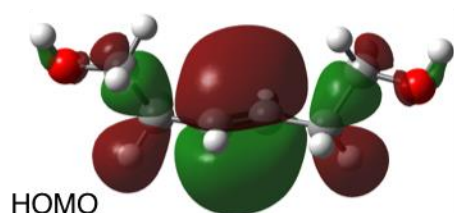
396
 397 **Fig. 2** Comparison of three sets of alkenes to illustrate how rate constants with the benzophenone
 398 triplet state vary with double bond location, stereochemistry, and methyl substitution. The teal
 399 numbers on each alkene represent the lowest free energy (ΔG^\ddagger) and enthalpy (ΔH^\ddagger) transition
 400 state barriers in kcal mol⁻¹ for H-abstraction by triplet benzophenone; these were calculated at
 401 the uB3LYP/6-31+G(d,p) level of theory. Though computed barriers (Table 1) are not correlated
 402 with the overall rates measured, they broadly match the rate trends within a given set of alkenes
 403 in this figure.



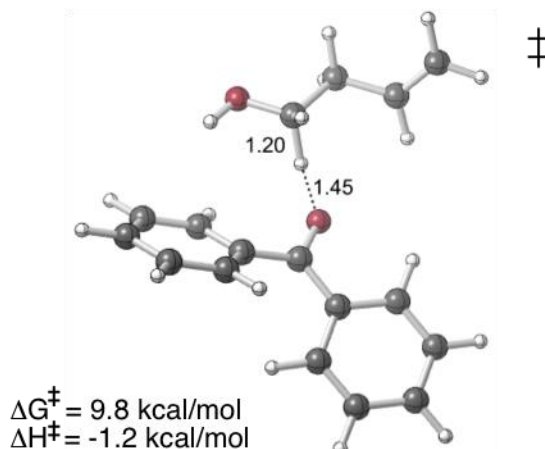
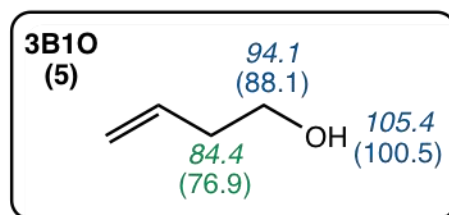
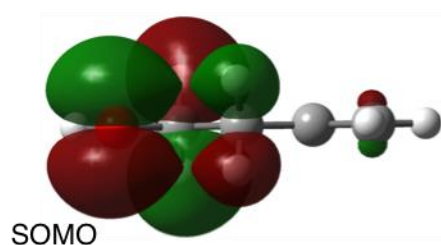
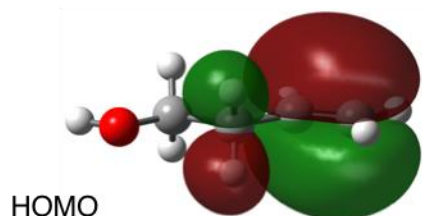
404

405 **Fig. 3** Correlation between measured bimolecular rate constants for alkenes with the triplet
 406 excited state of benzophenone ($k_{\text{ALK}+3\text{BP}^*}$) and the computed one-electron oxidation potentials of
 407 the alkenes. Numbers on each point represent the alkene numbers in Table 1. Blue lines represent
 408 95 % confidence intervals of the regression prediction. The gray lines bound the region that is
 409 within a factor of four of the regression prediction; all but one of the alkene values fall within
 410 this. Methyl jasmonate (**17**) is not included in this figure due to computational challenges in
 411 calculating its OP (see Table 1).

a) Electron removed from the π system



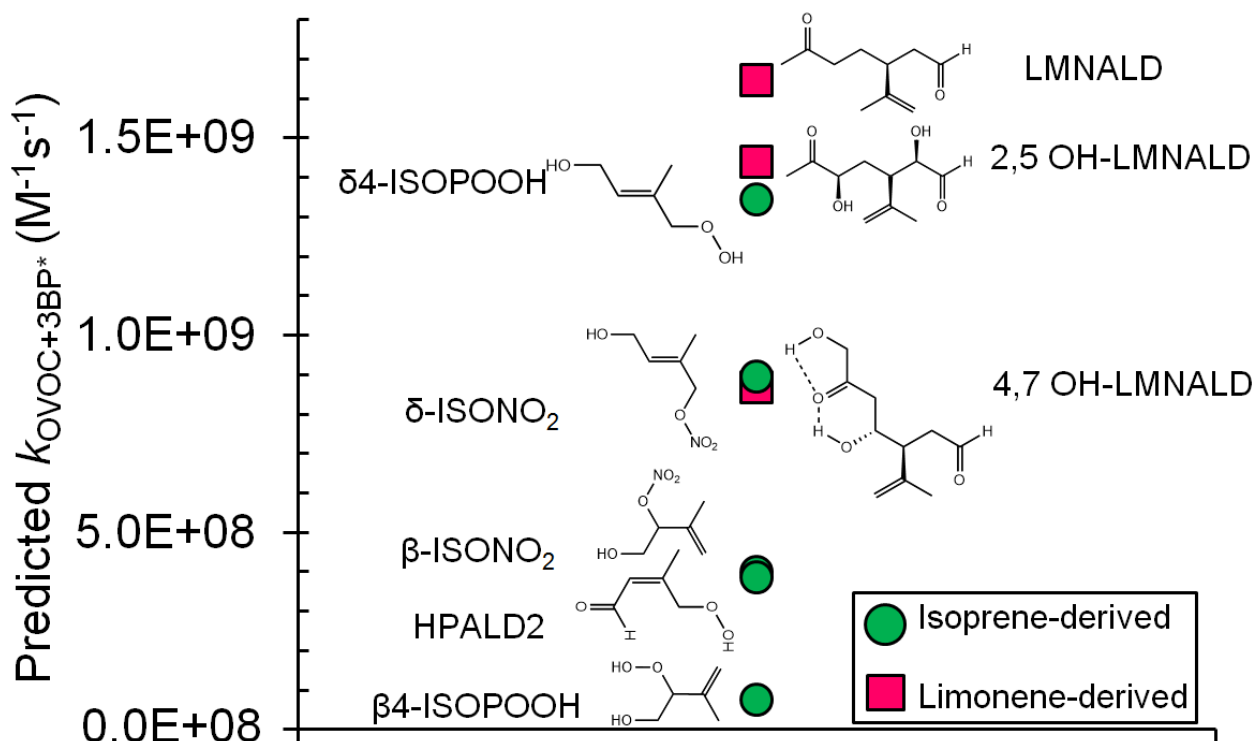
b) Electron removed from the oxygen



412

413

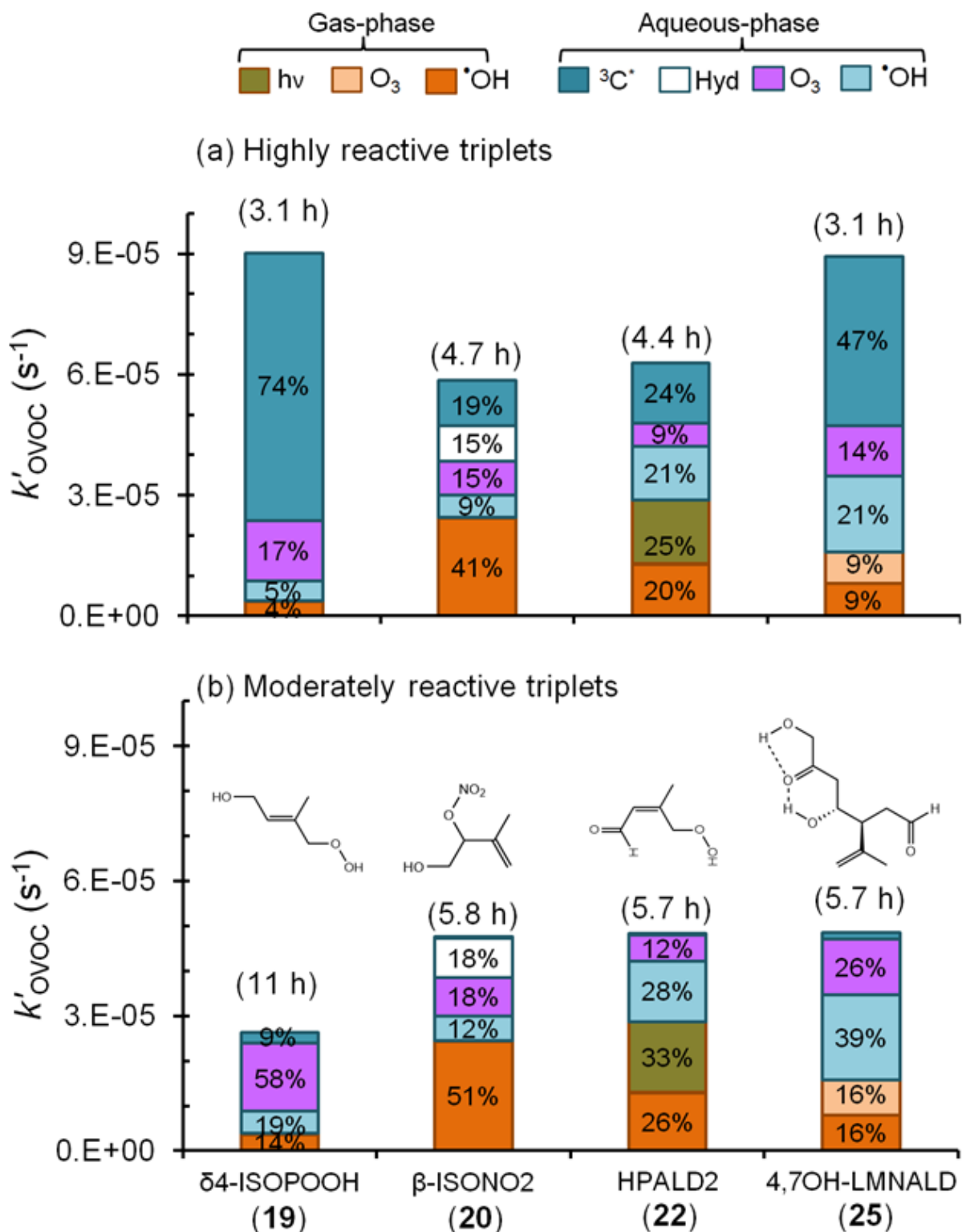
414 **Fig. 4** Diagrams of the highest occupied molecular orbitals (HOMOs) of the alkenes before
 415 oxidation, and the singly occupied molecular orbitals (SOMOs) after removal of one electron
 416 from the alkenes, and lowest energy transition state structures (‡) of alkenes **3** and **5**. Bond
 417 dissociation enthalpy (italicized) and free energy (in parentheses) for various hydrogen atoms (in
 418 kcal mol⁻¹) for each alkene are shown in the boxes. Numbers in green are the lowest values, and
 419 thus represent the most labile hydrogen in each alkene. *a*) The electron removed during H-
 420 abstraction of HDO is predicted to come from the π system, but this results in delocalization due
 421 to hyperconjugation. *b*) The electron removed from 3B10 during H-abstraction is predicted to
 422 come from the oxygen. See SI Tables S2 and S3 for HOMO/SOMO structures and Fig. S4 for
 423 the bond dissociation enthalpies and free energies for other alkenes.



424

425

426 **Fig. 5** Predicted bimolecular rate constants for a range of limonene and isoprene oxidation
 427 products (OVOCs) with the triplet state of BP. Rate constants are estimated from the QSAR with
 428 one-electron oxidation potentials (OPs) (Fig. 3). Oxidation potentials used to predict the rate
 429 constants here (and in Table 1) are for the lowest energy isomers of the OVOCs, which are the
 430 structures shown here. The structures of some of the other, higher energy, isomers are shown in
 431 Table S4.



432

433 **Fig. 6** Estimated pseudo-first-order loss rate constants and corresponding lifetimes (in
 434 parentheses) for representative isoprene- and limonene-derived oxidation products in a foggy
 435 atmosphere (Tables S5–S7). Colors and data labels indicate the percentage of OVOC lost via
 436 each gas and aqueous pathway, including direct photoreaction (hv) and hydrolysis (Hyd);
 437 pathways contributing less than 4 % are not labeled. Panel (a) is a likely upper bound for the
 438 triplet contributions to OVOC loss where we assume that all fog triplets are highly reactive, like
 439 benzophenone. Panel (b) shows the more likely contribution from triplets, assuming moderately
 440 reactive triplets that are more representative of the average measured in fog waters and aqueous
 441 particle extracts (Kaur et al., 2018; Kaur and Anastasio, 2018) (Tables S5–S7).

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639

640 **Table 1.** Measured alkene-benzophenone triplet reaction rate constants, predicted OVOC-
 641 benzophenone triplet reaction rate constants, and computed parameters for the alkenes.

#	Name	Abbreviation	OP ^a (V)	ΔG^\ddagger ^b (kcal mol ⁻¹)	ΔH^\ddagger ^c (kcal mol ⁻¹)	Measured $k_{\text{ALK}+3\text{BP}^*}$ ^d (10 ⁸ M ⁻¹ s ⁻¹)
Alkenes						
1	5-Hexen-1-ol	5HxO	2.63	12.1	0.05	2.4 (0.6)
2	2-Propen-1-ol (Allyl alcohol)	AIO	2.65	10.8	-0.04	2.7 (0.2)
3	3-Hexene-1,6-diol	HDO	2.36	12.3	0.2	3.1 (0.7)
4	2,3-Butadien-1-ol	BDO	2.46	10.5	-1.5	3.6 (0.3)
5	3-Buten-1-ol	3B1O	2.59	9.8	-1.2	3.7 (0.5)
6	1-Penten-3-ol	PE3O	2.82	11.3	-1.0	4.3 (0.4)
7	3-Buten-2-ol	3B2O	2.73	10.6	-1.0	4.9 (1.3)
8	2-Buten-1-ol	2B1O	2.40	9.8	-0.6	5.2 (1.0)
9	5-Hexenyl acetate	5HxAc	2.60	13.7	2.2	5.9 (1.8)
10	trans-3-hexen-1-ol	tHxO	2.28	12.4	0.03	14 (1)
11	1-Chloro-3-methyl-2-butene	CMB	2.25	14.1	2.7	17 (1) ^e
12	3-Methyl-2-buten-1-ol (Prenol)	3MBO	2.03	9.7	-1.8	19 (3)
13	2-Methyl-2-penten-1-ol	2M2PO	2.02	11.6	-1.4	28 (1)
14	4-Methyl-3-penten-1-ol	4M3PO	1.96	11.5	-0.4	40 (2)
15	cis-3-Hexen-1-ol	cHxO	2.23	9.2	-0.3	64 (6)
16	cis-3-Hexenyl acetate	cHxAc	2.29	10.7	1.2	65 (6)
17	Methyl jasmonate	MeJA	- ^f	- ^f	- ^f	75 (5)
						Predicted
Predictions for isoprene- and limonene-derived OVOCs						$k_{\text{OVOC}+3\text{BP}^*}$ ^g (10 ⁸ M ⁻¹ s ⁻¹)
18	β 4-Isoprene hydroxyhydroperoxide	β 4- ISOPOOH	3.13	13.2	0.3	0.80 (0.18)
19	δ 4-Isoprene hydroxyhydroperoxide	δ 4- ISOPOOH	2.28	10.5	-2.0	14 (3)
20	β -Isoprene hydroxynitrate	β -ISONO2	2.64	13.2	1.4	4.1 (0.9)
21	δ -Isoprene hydroxynitrate	δ -ISONO2	2.40	10.0	-1.9	9.2 (2.1)
22	Isoprene hydroperoxyaldehyde 2	HPALD2	2.65	10.4	-2.6	4.0 (0.9)
23	Limononaldehyde	LMNALD	2.22	9.9	-1.4	17 (4)
24	2,5-Dihydroxy limononaldehyde	2,5OH- LMNALD	2.26	10.1	-2.2	15 (3)
25	4,7-Dihydroxy limononaldehyde	4,7-OH- LMNALD	2.41	10.6	-0.8	8.9 (2.0)

642 ^a One-electron oxidation potential, calculated using the CBS-QB3 compound method.

643 ^{b,c} Lowest transition state energy barrier for H-abstraction by triplet benzophenone, calculated using
 644 uB3LYP/6-31+G(d,p).

645 ^d Measured bimolecular rate constant for alkene reacting with ³BP* with uncertainties of ± 1 standard
 646 deviation, determined from triplicate measurements (Table S1 of the supplement).

647 ^c Listed uncertainty is ± 1 standard error, $n = 1$.

648 ^f The oxidation potential and energy barriers could not be computed for MeJA (**17**). Because the CB3-
649 QB3 method scales at N^7 (where N is the number of atoms), the larger compound required more
650 computational power than available.

651 ^g Predicted bimolecular rate constant for select isoprene- and limonene-derived OVOCs reacting with
652 ³BP*, determined from the correlation between OP and $k_{\text{ALK}+3\text{BP}^*}$. Listed uncertainties are ± 1 standard
653 error propagated from the error of the slope of the quantitative structure-activity relationship between
654 oxidation potential and $k_{\text{ALK}+3\text{BP}^*}$ (Fig. 3).