1	Supporting Information for:
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3	Aqueous Reactions of Organic Triplet Excited States with Atmospheric
4	Alkenes
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13	This supporting information contains: 19 Pages, 8 Tables, and 9 Figures
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17 Table S1. Reference probes and triplicate measurements of rate constants for alkenes in a solution at pH

18 5.5. Errors (in parentheses) for each replicate measurement represent ± 1 standard error, determined by 19 propagating errors in the slope of the relative rate plot and in the reference compound rate constant. Errors

щ		Abbreviation Reference		$k_{\text{ALK}+3\text{BP}^*} (10^8 \text{ M}^{-1} \text{ s}^{-1})$			
#	Alkene Name (ALK)	Addreviation	Probe	Replicate	Replicate	Replicate	Average
				1	2	3	(SD)
1	5-Hexen-1-ol	5HxO	3MBO	3.1 (0.4)	1.9 (0.3)	2.2 (0.3)	2.4 (0.6)
2	Allyl alcohol	AlO	BDO	2.8 (0.3)	2.5 (0.2)	2.8 (0.3)	2.7 (0.2)
3	3-Hexene-1,6-diol	HDO	3MBO	2.5 (0.4)	3.7 (0.5)	3.2 (0.4)	3.1 (0.7)
4	2,3-Butadien-1-ol	BDO	3MBO	3.3 (0.5)	3.8 (0.5)	3.6 (0.5)	3.6 (0.3)
5	3-Buten-1-ol	3B1O	cHxO	4.2 (0.4)	3.2 (0.3)	3.6 (0.4)	3.7 (0.5)
6	1-Penten-3-ol	PE3O	3B2O	3.9 (1.1)	4.2 (1.2)	4.7 (1.3)	4.3 (0.4)
7	3-Buten-2-ol	3B2O	cHxO	5.7 (0.5)	5.6 (0.5)	3.3 (0.5)	4.9 (1.3)
8	2-Buten-1-ol	2B1O	4M3PO	5.6 (0.2)	4.1 (0.3)	5.9 (0.5)	5.2 (1.0)
9	5-Hexenyl acetate	5HxAc	3MBO	4.7 (0.7)	5.0 (0.7)	7.9 (1.1)	5.9 (1.8)
10	trans-3-hexen-1-ol	tHxO	3MBO	13 (2)	14 (2)	14 (2)	14 (1)
11	1-Chloro-3-methyl-2-butene	CMB	BDO ^a	17 (1)	-	-	17 (1) ^b
12	3-Methyl-2-buten-1-ol	3MBO	cHxO	21 (2)	20 (2)	16(1)	19 (3)
13	2-Methyl-2-penten-1-ol	2M2PO	3MBO	29 (4)	28 (4)	28 (4)	28 (1)
14	4-Methyl-3-penten-1-ol	4M3PO	3MBO	42 (6)	39 (5)	40 (5)	40 (2)
15	cis-3-hexen-1-ol	cHxO	PhOH	62 (11) ^c	70 (13)	59 (11)	64 (6)
16	cis-3-hexenyl acetate	cHxAc	cHxO	66 (7)	71 (6)	59 (5)	65 (6)
17	Methyl jasmonate	MeJA	cHxO	80 (7)	69 (6)	75 (7)	75 (5)

20 on the average values represent $\pm 1 \sigma$ determined from the average of the replicate values.

^a Measurement of the rate constant for CMB was done in a solution containing a minimal amount of acetonitrile to dissolve the compound.

^b Error represents ± 1 SE, based on the SE of the relative rate slope and reference rate constant $k_{\text{BDO+3BP}*}$ given in the table.

21 22 23 24 25 ^c Phenol (PhOH) was used as the reference probe using the reference rate constant of 3.9 (\pm 0.7) \times 10⁹ M⁻¹ s⁻¹,

26 27 measured in this study, using 2,4,6,-trimethylphenol (TMP) as a reference compound $(k_{\text{TMP+3BP*}} = 5.1 (\pm 0.9) \times 10^9$ M^{-1} s⁻¹; Canonica et al. (2000)).

ALK Abbreviation (#)	HOMO	SOMO	HOMO+1 (eV)	SOMO+1 (eV)
HDO (3)	*38 8*	3593 8	0.39	0.45
BDO (4)	** *		0.41	0.45
PE 30 (6)	**	***	0.41	0.49
3B2O (7)			0.40	0.49
3MBO (12)	**		0.38	9 0.48
сНхО (15)	***	202	0.39	0.46

29 30 **Table S2.** Highest- and singly-occupied molecular orbitals (HOMOs, SOMOs) of representative alkenes showing removing of an electron from the π system.[†]

31 32 33

⁺HOMOs and SOMOs were computed from single point calculations at MP2/CBSB3 (Frisch et al., 2016). HOMO+1 and SOMO+1 values in eV are shown relative to HOMO and SOMO, respectively.

ALK Abbreviation (#)	НОМО	SOMO	HOMO+1 (eV)	SOMO+1 (eV)
3B1O (5)			0.40	0.45
НхАс (16)			0.39	0.44
MeJA (17)			0.37	0.19

34 **Table S3.** HOMOs and SOMOs of alkenes showing removing of an electron from the oxygen.[†]

⁺HOMOs and SOMOs were computed from single point calculations at MP2/CBSB3 (B3LYP/CBSB7 was used for ALKs 16 and 17). HOMO+1 and SOMO+1 values in eV are shown relative to HOMO and SOMO, respectively.

- **Table S4.** Oxidation potentials (in units of V) of various isomers of isoprene- and limonene-derived
- OVOCs, calculated using the CBS-QB3 compound method. The lowest energy isomer for each OVOC
 is highlighted using a blue box. Compounds not shown here (18, 20 and 22) have no relevant isomers.

δ4 ISOPOOH (19)	δISONO2 (21)	LMNALD (23)	2,50H-LMNALD (24)	4,70H-LMNALD (25)
ноон		2.22		HO HO
HO			2.06 2.24 $\downarrow \qquad \qquad$	2.17 0 HO 2.17 HO 2.17
2.28	2.45	2.28	2.12 2.26 $\downarrow \qquad \downarrow \qquad$	
			<u>ен</u> 0 0 0 0 0 0 0 0 0 0 0 0 0	H, O, W, H H, O, W, H 2.41
				но,

ovoc				Gas-phase	rate constants (cm ³ mlc ⁻¹ s ⁻¹)				
#	Name	k _{ovoc+oH}	Reference	k _{ovoc+o3}	Reference	$j_{ m Photolysis} \ ({ m s}^{-1})$	Reference		
18	β4-ISOPOOH	1.2E-10	St. Clair et al. (2015)	1.3E-17	Khamaganov and Hites (2001)				
19	δ4-ISOPOOH	1.2E-10	St. Clair et al. (2015)	1.3E-17	Khamaganov and Hites (2001)				
20	β-ISONO2	5.4E-11	Lee et al. (2014)	5.0E-19	Lee et al. (2014)				
21	δ-ISONO2	1.1E-10	Lee et al. (2014)	2.8E-17	Lee et al. (2014)				
22	HPALD2	5.1E-11	Wolfe et al. (2012)	1.2E-18	Wolfe et al. (2012)	6.3E-05	Wolfe et al. (2012)		
23	LMNALD	1.6E-10	Gill and Hites (2002)	2.1E-16	Khamaganov and Hites (2001)				
24	2,50H-LMNALD	1.6E-10	Gill and Hites (2002)	2.1E-16	Khamaganov and Hites (2001)				
25	4,70H-LMNALD	1.6E-10	Gill and Hites (2002)	2.1E-16	Khamaganov and Hites (2001)				
26	HPALD1	5.1E-11	Wolfe et al. (2012)	1.2E-18	Wolfe et al. (2012)	6.3E-05	Wolfe et al. (2012)		
	OVOC	Aqueous-phase rate constants (L mol ⁻¹ s ⁻¹)							
#	Name	k _{ovoc+oH}	Reference	k _{ovoc+03}	Reference	$k'_{ m Hydrolysis} (s^{-1})$	Reference		
18	β4-ISOPOOH	2.5E+09	Rivera-Rios et al. (2018)	4.7E+04	Schöne and Herrmann (2014) ^a				
19	δ4-ISOPOOH	2.5E+09	Rivera-Rios et al. (2018)	4.7E+04	Schöne and Herrmann (2014) ^a				
20	β-ISONO2	5.0E+09	Herrmann et al. (2015) ^b	4.7E+04	Schöne and Herrmann (2014) ^a	1.6E-05	Jacobs et al. (2014)		
21	δ-ISONO2	5.0E+09	Herrmann et al. (2015) ^b	4.7E+04	Schöne and Herrmann (2014) ^a	6.8E-03	Jacobs et al. (2014)		
22	HPALD2	9.0E+09	Schöne et al. (2014) ^c	2.3E+04	Schöne and Herrmann (2014) ^c				
23	LMNALD	1.0E+10	Witkowski et al. (2018) ^d	4.0E+04	Witkowski et al. (2018) ^d				
24	2,50H-LMNALD	1.0E+10	Witkowski et al. (2018)	4.0E+04	Witkowski et al. (2018) ^d				
25	4,70H-LMNALD	1.0E+10	Witkowski et al. (2018) ^d	4.0E+04	Witkowski et al. (2018) ^d				
20		$0.0E \pm 0.0$	Schöne et al. $(2014)^{\circ}$	23E+04	Schöne and Herrmann (2014) ^c				

Table S5. Measured or estimated rate constants for reactions of OVOCs with oxidants, photolysis, and hydrolysis.

^a Average of rate constants for methacrolein and methyl vinyl ketone used as a proxy.

 ^b Estimate based on the rate constants for similar unsaturated compounds with [•]OH in the indicated reference.
 ^c Rate constant for methacrolein used as a proxy.
 ^d Rate constants for neutral dicarbonyl derivatives of limonic and limononic acids, used a proxies.

				Pseudo-first-order rate constant for loss due to oxidants in the gas- phase (s^{-1})		Pseu	ıdo-first-ord in	er rate constan the aqueous-p	t for loss due t bhase (s^{-1})	o oxidants	
#	OVOC Name	$K_{\rm H}^{a}$ (M atm ⁻¹)	Xaq ^b	k' _{OH,g} °	$k'_{\rm O3,g}{}^{\rm d}$	$j_{ m hv}{}^{ m e}$	$k'_{ m OH,aq}{}^{ m f}$	$k'_{ m O3,aq}{}^{ m g}$	k' _{3BP*,aq} ^h (High Triplet Reactivity)	k' _{3C*,aq} ⁱ (Typical Triplet Reactivity)	k' _{Hyd} ^j
18	β4-ISOPOOH	1.5E+06	0.97	1.2E-04	9.6E-06		5.0E-06	1.6E-05	4.0E-06	1.4E-07	
19	δ4-ΙΣΟΡΟΟΗ	1.2E+06	0.97	1.2E-04	9.6E-06		5.0E-06	1.6E-05	6.8E-05	2.4E-06	
20	β-ISONO2	5.1E+04	0.55	5.4E-05	3.7E-07		1.0E-05	1.6E-05	2.1E-05	7.3E-07	1.6E-05
21	δ-ISONO2	4.3E+04	0.51	1.1E-04	2.1E-05		1.0E-05	1.6E-05	4.6E-05	1.6E-06	6.8E-03
22	HPALD2	1.2E+05	0.75	5.1E-05	8.9E-07	6.3E-05	1.8E-05	7.6E-06	2.0E-05	7.0E-07	
23	LMNALD	4.5E+03	0.10	1.6E-04	1.6E-04		2.0E-05	1.3E-05	8.3E-05	2.9E-06	
24	2,50H-LMNALD	8.0E+05	0.95	1.6E-04	1.6E-04		2.0E-05	1.3E-05	7.3E-05	2.6E-06	
25	4,70H-LMNALD	8.0E+05	0.95	1.6E-04	1.6E-04		2.0E-05	1.3E-05	4.4E-05	1.6E-06	
26	HPALD1	1.2E+05	0.75	5.1E-05	8.9E-07	6.3E-05	1.8E-05	7.6E-06	- ^k	- ^k	

45 **Table S6.** Loss rate constants for OVOCs due to different pathways.

^a Henry's law constants calculated using EPISuite version 4.1 (US EPA. Estimation Programs Interface Suite[™] for Microsoft® Windows v 4.1, 2016).

⁴⁸ ^b Fraction of OVOC in the aqueous phase, calculated as $\chi_{aq} = 1/(1+1/(K_H \times L \times R \times T))$, where K_H is the Henry's law constant of the OVOC, *L* is the assumed liquid water content (1 × 10⁻⁶ L-aq/L-g), *R* is the universal gas constant (0.082 L atm K⁻¹ mol⁻¹), and *T* = 298 K.

50 ^{c,d,f,g,h,i} Pseudo-first-order rate constant for loss of OVOC due to oxidation by the given oxidant in the gas or aqueous phase, calculated by

51 multiplying the bimolecular reaction rate constant (Table S6) with the corresponding steady-state concentration of the oxidant: $[^{\circ}OH(g)] = 1 \times 10^{6}$

52 molecules cm⁻³, $[O_3(g)] = 30$ ppbv = 7.4 × 10¹¹ molecules cm⁻³, $[^{\bullet}OH(aq)] = 2 \times 10^{-15}$ M (estimate in typical fog drops, includes gas-to-aqueous 53 partitioning, Kaur and Anastasio (2017)).

54 $[O_3(aq)] = 3.3 \times 10^{-10} \text{ M}$ (based on 30 ppbv $O_3(g)$ and $K_H = 1.1 \times 10^{-2} \text{ M}$ atm⁻¹; Seinfeld and Pandis (2012), and $[{}^{3}C^{*}(aq)] = 5 \times 10^{-14} \text{ M}$ (average concentration measured in Davis fog, Kaur and Anastasio (2017)).

⁵⁶ ^h Pseudo-first-order rate constant for loss of OVOC due to oxidation by highly reactive triplets such as ³BP*. This was calculated using the

57 predicted second-order rate constants $k_{OVOC+3BP*}$ (Table 1, main text) and [³C*(aq)] given in the footnote above.

ⁱ Pseudo-first-order rate constant for loss of OVOC due to oxidation by triplets of typical reactivity as measured in fog and particles in Davis, CA

59 (Kaur and Anastasio, 2017; Kaur and Anastasio, 2018). To estimate these rate constants we multiplied the predicted second-order rate constants

60 with ³BP* ($k_{OVOC+3BP*}$) by a factor of 0.04, which is the ratio of the average of the rate constants of reaction of MeJA with ³3MAP* and ³DMB*

61 $(2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}, \text{ Table S8})$ divided by the rate constant for MeJA with ³BP* $(7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}, \text{ Tables S1 and S8})$.

62 ^{e, j} First-order rate constants for gas-phase photolysis and aqueous hydrolysis of the OVOC, respectively (also given in Table S5).

k The value of $k_{ALK+3BP*}$ for HPALD1 could not be determined due to challenges with calculating its oxidation potential. Because the CB3-QB3

64 method scales at N^7 (where N is the number of atoms), the larger compound required more computational power than available.

Hi	gh Triplet Reactivity Scenario	Тс	otal		Frac	ction of OV	OC lost due	to each path	nway ^c	
#	OVOC Name	$k'_{ m OVOC}$ a (s ⁻¹)	τ^{b} (h)	•OH(g)	O ₃ (g)	hv(g)	•OH(aq)	O ₃ (aq)	³ BP*(aq)	Hyd(aq)
18	β4-ISOPOOH	2.7E-05	10	13%	1.0%	0%	18%	54%	14%	0%
19	δ4-ISOPOOH	9.0E-05	3.1	3.9%	0.32%	0%	5.4%	17%	74%	0%
20	β-ISONO2	5.9E-05	4.7	41%	0.28%	0%	9.4%	15%	19%	15%
21	δ-ISONO2	3.6E-03	0.078	1.5%	0.29%	0%	0.14%	0.22%	0.66%	97%
22	HPALD2	6.3E-05	4.4	20%	0.35%	25%	21%	9.1%	24%	0%
23	LMNALD	3.0E-04	0.93	49%	47%	0%	0.67%	0.44%	2.8%	0%
24	2,50H-LMNALD	1.2E-04	2.4	6.9%	6.7%	0%	16%	11%	59%	0%
25	4,70H-LMNALD	8.9E-05	3.1	9.0%	8.8%	0%	21%	14%	47%	0%
26	HPALD1	4.8E-05	5.8	27%	0.46%	33%	28%	12%	- ^d	0%
Typical Triplet Reactivity Scenario				Fraction of OVOC lost due to each pathway ^c						
Тур	ical Triplet Reactivity Scenario	Тс	otal		Frac	ction of OV	OC lost due	to each path	nway ^c	
Тур #	ical Triplet Reactivity Scenario OVOC Name	$\frac{\text{To}}{\substack{k'_{\text{OVOC}}\\(\text{s}^{-1})}}$	τ (h)	•OH(g)	Frac O ₃ (g)	tion of OV hv(g)	OC lost due •OH(aq)	to each path $O_3(aq)$	³ C*(aq)	Hyd(aq)
Typ # 18	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH		τ (h) 12	•OH(g) 15%	Frac O ₃ (g) 1.2%	etion of OV hv(g) 0%	OC lost due •OH(aq) 20%	to each path $O_3(aq)$ 63%	³ C*(aq)	Hyd(aq) 0%
Typ # 18 19	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH		τ (h) 12 11	•OH(g) 15% 14%	Frac O ₃ (g) 1.2% 1.1%	tion of OV hv(g) 0%	OC lost due •OH(aq) 20% 19%	to each path O ₃ (aq) 63% 58%	away ^c ³ C*(aq) 0.58% 9.0%	Hyd(aq) 0% 0%
Typ # 18 19 20	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2		τ (h) 12 11 5.8	•OH(g) 15% 14% 51%	Frac O ₃ (g) 1.2% 1.1% 0.43%	of OV hv(g) 0% 0% 0%	OC lost due OH(aq) 20% 19% 12%	to each path O ₃ (aq) 63% 58% 18%	³ C*(aq) 0.58% 9.0% 0.84%	Hyd(aq) 0% 0% 18%
Typ # 18 19 20 21	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2 δ-ISONO2	$\begin{array}{c} & \text{Tc} \\ k'_{\text{OVOC}} \\ (s^{-1}) \\ \hline 2.4\text{E-05} \\ \hline 2.6\text{E-05} \\ \hline 4.8\text{E-05} \\ \hline 3.5\text{E-03} \end{array}$	τ (h) 12 11 5.8 0.079	•OH(g) 15% 14% 51% 1.5%	Frac O ₃ (g) 1.2% 1.1% 0.43% 0.29%	of OV hv(g) 0% 0% 0% 0%	 OC lost due OH(aq) 20% 19% 12% 0.14% 	to each path O ₃ (aq) 63% 58% 18% 0.22%	³ C*(aq) 0.58% 9.0% 0.84% 0.02%	Hyd(aq) 0% 0% 18% 98%
Typ # 18 19 20 21 22	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2 δ-ISONO2 HPALD2	$\begin{array}{c} & \text{Tc} \\ k'_{\text{OVOC}} \\ (s^{-1}) \\ \hline 2.4\text{E-05} \\ \hline 2.6\text{E-05} \\ \hline 4.8\text{E-05} \\ \hline 3.5\text{E-03} \\ \hline 4.8\text{E-05} \end{array}$	τ (h) 12 11 5.8 0.079 5.7	*OH(g) 15% 14% 51% 1.5% 26%	Frac O ₃ (g) 1.2% 1.1% 0.43% 0.29% 0.46%	of OV hv(g) 0% 0% 0% 0% 33%	OC lost due •OH(aq) 20% 19% 12% 0.14% 28%	to each path O ₃ (aq) 63% 58% 18% 0.22% 12%	³ C*(aq) 0.58% 9.0% 0.84% 0.02% 1.1%	Hyd(aq) 0% 0% 18% 98% 0%
Typ # 18 19 20 21 22 23	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2 δ-ISONO2 HPALD2 LMNALD	$\begin{array}{c} & \text{Tc} \\ k'_{\text{OVOC}} \\ (s^{-1}) \\ \hline 2.4\text{E-05} \\ \hline 2.6\text{E-05} \\ \hline 4.8\text{E-05} \\ \hline 3.5\text{E-03} \\ \hline 4.8\text{E-05} \\ \hline 2.9\text{E-04} \end{array}$	τ (h) 12 11 5.8 0.079 5.7 1.0	*OH(g) 15% 14% 51% 1.5% 26% 50%	Frac O ₃ (g) 1.2% 1.1% 0.43% 0.29% 0.46% 49%	bv(g) 0% 0% 0% 0% 0% 0% 0% 0% 0%	OC lost due •OH(aq) 20% 19% 12% 0.14% 28% 0.69%	to each path O ₃ (aq) 63% 58% 18% 0.22% 12% 0.45%	ansatz ansatz<	Hyd(aq) 0% 0% 18% 98% 0% 0%
Typ # 18 19 20 21 22 23 24	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2 δ-ISONO2 HPALD2 LMNALD 2,5OH-LMNALD	$\begin{array}{c} & \text{Tc} \\ k'_{\text{OVOC}} \\ (s^{-1}) \\ \hline 2.4E-05 \\ \hline 2.6E-05 \\ \hline 4.8E-05 \\ \hline 3.5E-03 \\ \hline 4.8E-05 \\ \hline 2.9E-04 \\ \hline 5.0E-05 \\ \end{array}$	τ (h) 12 11 5.8 0.079 5.7 1.0 5.6	*OH(g) 15% 14% 51% 1.5% 26% 50% 16%	Frac O ₃ (g) 1.2% 1.1% 0.43% 0.29% 0.46% 49% 16%	bv(g) 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0%	OC lost due •OH(aq) 20% 19% 12% 0.14% 28% 0.69% 38%	to each path O ₃ (aq) 63% 58% 18% 0.22% 12% 0.45% 25%	"way c" ³ C*(aq) 0.58% 9.0% 0.84% 0.02% 1.1% 0.10% 4.9%	Hyd(aq) 0% 0% 18% 98% 0% 0% 0%
Typ # 18 19 20 21 22 23 24 25	ical Triplet Reactivity Scenario OVOC Name β4-ISOPOOH δ4-ISOPOOH β-ISONO2 δ-ISONO2 HPALD2 LMNALD 2,5OH-LMNALD 4,7OH-LMNALD	$\begin{array}{c} & \text{Tc} \\ k'_{\text{OVOC}} \\ (s^{-1}) \\ \hline 2.4E-05 \\ \hline 2.6E-05 \\ \hline 4.8E-05 \\ \hline 3.5E-03 \\ \hline 4.8E-05 \\ \hline 2.9E-04 \\ \hline 5.0E-05 \\ \hline 4.9E-05 \\ \hline \end{array}$	τ π 12 11 5.8 0.079 5.7 1.0 5.6 5.7	*OH(g) 15% 14% 51% 1.5% 26% 50% 16% 16%	Frac O ₃ (g) 1.2% 1.1% 0.43% 0.29% 0.46% 49% 16% 16%	bv(g) 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0%	OC lost due •OH(aq) 20% 19% 12% 0.14% 28% 0.69% 38% 39%	to each path O ₃ (aq) 63% 58% 18% 0.22% 12% 0.45% 25% 26%	"way c ³ C*(aq) 0.58% 9.0% 0.84% 0.02% 1.1% 0.10% 4.9% 3.0%	Hyd(aq) 0% 0% 18% 98% 0% 0% 0% 0% 0%

65 Table S7. OVOC lifetimes and fractions lost due to various pathways.

^a Total pseudo-first order rate constant for loss of OVOC, calculated as $k'_{OVOC} = \Sigma(\chi_{aq} \times k'_{Ox,aq} + (1 - \chi_{aq}) \times k'_{Ox,gas})$. All pseudo-first-order rate 66

constants ($k'_{Ox,aq}$, $k'_{Ox,gas}$, j_{hv} , k'_{Hyd}) are given in Table S6. ^b Total lifetime of OVOC, calculated as $1/k'_{OVOC}$. 67

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^c Fraction of OVOC lost due to each pathway, calculated as $(\chi_{aq} \times k'_{OX,aq})/k'_{OVOC}$ for aqueous pathways and $((1-\chi_{aq}) \times k'_{OX,gas})/k'_{OVOC}$ for gas-phase 69 70 processes.

^d We were unable to compute the oxidation potential for HAPLD1 (see footnote k in Table S6), and thus could not estimate its rate constant with 71

72 triplets.

73 **Table S8.** Second-order rate constants for reaction of some alkenes with model triplet excited states.

ALK		${k_{ m ALK+3C^*} \over 10^8 { m M}^{-1} { m s}^{-1}}$	Average $(k_{MeJA+33MAP*}, k_{MeJA+3DMB*})/$	
	³ 3MAP*	³ DMB*	³ BP*	$k_{\rm MeJA+3BP*}$
cHxO (15)	$1.1 (\pm 0.2)^{a}$	$0.24 (\pm 0.10)^{a}$	64 (± 6) ^b	0.010
cHxAc (16)	$7.9 (\pm 2.0)^{a}$	$15 (\pm 4)^{a}$	65 (± 6) ^b	0.18
MeJA (17)	$1.2 (\pm 0.3)^{a}$	4.1 (± 1.6) ^a	75 (± 5) ^b	0.035 ^d

^a Rate constants from Richards-Henderson et al. (2014). Listed uncertainties are ± 1 standard errors.

^b Rate constants measured in this work (also shown in Table S1). Listed uncertainties here are ± 1 standard deviation, n = 3.

 $^{\circ}$ The ratio of the average bimolecular rate constants for reaction of MeJA with model triplets ³3MAP* and

78 ³DMB* to the rate constant for MeJA with ³BP*.

^d This is the rate constant ratio for MeJA as well as the median value of the rate constant ratio (see footnote *a*)

80 for the three alkenes.



84 **Figure S1.** Figure from Kaur and Anastasio (2017) shown here for reference. Red line:

85 Measured transmittance of the combination of our two illumination system filters. Blue line:

86 Davis midday, winter solstice actinic flux from the TUV model (Madronich et al., 2002). Input

87 parameters for the TUV model were: solar zenith angle: 62°, measurement altitude: 0 km, surface

albedo: 0.1, aerosol optical depth: 0.235, cloud optical depth: 0.00.

89

83



Figure S2. Illustration of the relative rate technique used for measuring rate constants (Finlayson-Pitts and Pitts Jr, 1999; Richards-Henderson et al., 2014). Top panel: Aqueous loss of the alkene (4M3PO) and reference compound (3MBO) in the presence of the BP triplet under solar simulated light (298 K, pH 5.5 (\pm 0.2)). Bottom panel: Plot of change in concentration of reference compound against alkene. The slope represents the ratio (\pm 1 SE) of the bimolecular rate constants with the BP triplet.





100 **Figure S3.** Measured bimolecular rate constants of 17 alkenes with triplet benzophenone. Green

101 bars represent biogenic volatile organic compounds known to be emitted from plants; grey bars

102 represent other C_3 - C_6 alkenes. Error bars represent ±1 standard deviation (n = 3) except for

103 compound 11, where n = 1 and the error is ± 1 SE (see Table S1 for details). Experimental

104 conditions: 298 K, pH 5.5 \pm 0.2, 1.0 mM phosphate buffer).



106 **Figure S4.** Bond dissociation enthalpies (in italics) and bond dissociation free energies (in parentheses) in kcal mol⁻¹ for various

107 hydrogens in each alkene. For each compound the hydrogen most likely to be abstracted, i.e., with the lowest bond dissociation

108 energy, is shown in green.



110 Figure S5. Correlation plots for measured rate constants and various computed bond dissociation

111 energies. (a) Log $k_{ALK+3BP*}$ versus the lowest bond dissociation enthalpy of the allylic hydrogen

112 in each alkene (i.e., the green values in Fig. S4). (b) Log $k_{ALK+3BP^*}$ versus the lowest bond

113 dissociation free energy of the allylic hydrogen. (c) Log $k_{ALK+3BP*}$ versus the bond dissociation

- enthalpy of the hydrogen attached to the carbon adjacent to the -OH or $-OCH_3$ group. (d) Log
- 115 $k_{ALK+3BP^*}$ versus the bond dissociation free energy of the hydrogen attached to the carbon
- 116 adjacent to the –OH or –OCH₃ group. (e): $\log k_{ALK+3BP*}$ versus bond dissociation free energy of
- 117 the O-H or OH_2C -H bond. Bond dissociation energies are shown in Fig. S4.



Figure S6. Log $k_{ALK+3BP*}$ versus lowest transition state free energy barrier. The alkenes are broken down into two groups: $k_{ALK+3BP*} < 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (slow, red) and $k_{ALK+3BP*} \ge 5 \times 10^8 \text{ M}^{-1}$ $^1 \text{ s}^{-1}$ (fast, green). The slopes ($\pm 1 \text{ SE}$) of these lines are $-0.077 (\pm 0.041)$ and $-0.15 (\pm 0.06)$ mol kcal⁻¹, respectively. Transition state energy barrier values are given in Table 1 of the main text. The orange line (plotted on the secondary y-axis) shows the trend in *k* values expected from transition state theory ($k_{ALK+3BP*} = A \times \exp(-\Delta G^{\ddagger}/RT)$).



Figure S7. Lowest transition state energy barriers for two alkenes: **7**, 3B2O, in the top panel and

16, cHxAc, in the bottom panel. Both show the hydrogen most likely to be abstracted duringoxidation; in both cases this is an allylic H.



131



133 concentration of cHxO. Since these experiments were performed on different days, the values are

134 normalized to the photon flux of the illumination system on the day of the experiment by

135 dividing by j_{2NB} (details in Kaur and Anastasio (2017)). The average (±1 σ) value is 4.3 ± 0.5

136 \min^{-1}/s^{-1} , giving a relative standard deviation of 12 %.



137

138 Figure S9. Lowest energy isomers of isoprene- and limonene-derived OVOCs, determined with

139 gas-phase calculations using the CBS-QB3 compound method.

140 **References**

141	Canonica, S., Hellrung, B., and Wirz, J.: Oxidation of phenols by triplet aromatic ketones in
142	aqueous solution, Journal of Physical Chemistry A, 104, 1226-1232, 2000.
143	Finlayson-Pitts, B. J., and Pitts Jr, J. N.: Chemistry of the Upper and Lower Atmosphere:
144	Theory, Experiments, and Applications, Academic press, 1999.
145	Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., Scalmani, G.,
146	Barone, V., Petersson, G., Nakatsuji, H., Li, X., Caricato, M., Marenich, A., Bloino, J.,
147	Janesko, B., Gomperts, R., Mennucci, B., Hratchian, H., Ortiz, J., Izmaylov, A.,
148	Sonnenberg, J., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng,
149	B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N.,
150	Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida,
151	M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., J. A.
152	Montgomery, J., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin,
153	K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K.,
154	Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M.,
155	Adamo, C., CammI, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., JB,
156	F., and DJ, F.: Gaussian 09, Revision D.01; Gaussian: Wallingford, CT, USA, 2016,
157	Gill, K. J., and Hites, R. A.: Rate constants for the gas-phase reactions of the hydroxyl radical
158	with isoprene, α -and β -pinene, and limonene as a function of temperature, The Journal of
159	Physical Chemistry A, 106, 2538-2544, 2002.
160	Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.:
161	Tropospheric aqueous-phase chemistry: Kinetics, mechanisms, and its coupling to a
162	changing gas phase, Chemical Reviews, 115, 4259-4334, 2015.
163	Jacobs, M. I., Burke, W., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived
164	hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis,
165	Atmospheric Chemistry and Physics, 14, 8933-8946, 2014.
166	Kaur, R., and Anastasio, C.: Light absorption and the photoformation of hydroxyl radical and
167	singlet oxygen in fog waters, Atmospheric Environment, 164, 387-397, 2017.
168	Kaur, R., and Anastasio, C.: First Measurements of Organic Triplet Excited States in
169	Atmospheric Waters, Environmental science & technology, 52, 5218-5226, 2018.
170	Khamaganov, V. G., and Hites, R. A.: Rate Constants for the Gas-Phase Reactions of Ozone
171	with Isoprene, α -and β -Pinene, and Limonene as a Function of Temperature, The Journal
172	of Physical Chemistry A, 105, 815-822, 2001.
173	Lee, L., Teng, A. P., Wennberg, P. O., Crounse, J. D., and Cohen, R. C.: On Rates and
174	Mechanisms of OH and O_3 Reactions with Isoprene-Derived Hydroxy Nitrates, The
175	Journal of Physical Chemistry A, 118, 1622-1637, 2014.
176	Madronich, S., Flocke, S., Zeng, J., Petropavlovskikh, I., and Lee-Taylor, J.: Tropospheric
177	Ultraviolet-Visible Model (TUV) version 4.1, National Center for Atmospheric Research,
1/8	PO Box, 3000, 2002.
1/9	Richards-Henderson, N. K., Pham, A. T., Kirk, B. B., and Anastasio, C.: Secondary organic
180	aerosol from aqueous reactions of green leaf volatiles with organic triplet excited states
181	and singlet molecular oxygen, Environmental Science and Technology, 49, 268-276,
182	2014. Diver Dies L.C. Zhee D. Lee A.K.V. Akhett L.D.D. Cremer L.D. Cremer 11. C
103	KIVEIA-KIOS, J. C., ZHAO, K., LEE, A. K. Y., ADDAIL, J. P. D., Crounse, J. D., Compernolle, S., Wannhara, D. O. and Kautaah, F. N. In Programtian, 2019
184	wennberg, P. O., and Keutsch, F. N.: In Preparation, 2018.

- Schöne, L., and Herrmann, H.: Kinetic measurements of the reactivity of hydrogen peroxide and
 ozone towards small atmospherically relevant aldehydes, ketones and organic acids in
 aqueous solutions, Atmospheric Chemistry and Physics, 14, 4503, 2014.
- Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K. J.,
 Szmigielski, R., and Herrmann, H.: Atmospheric aqueous phase radical chemistry of the
 isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and
 acrylic acid–kinetics and product studies, Physical Chemistry Chemical Physics, 16,
 6257-6272, 2014.
- Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: From air pollution to
 climate change, John Wiley & Sons, 2012.
- St. Clair, J. M., Rivera-Rios, J. C., Crounse, J. D., Knap, H. C., Bates, K. H., Teng, A. P.,
 Jørgensen, S., Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and
 Products of the Reaction of the First-Generation Isoprene Hydroxy Hydroperoxide
 (ISOPOOH) with OH, The Journal of Physical Chemistry A, 120, 1441-1451, 2015.
- US EPA. Estimation Programs Interface Suite[™] for Microsoft® Windows v 4.1: Estimation
 Programs Interface Suite[™] for Microsoft® Windows, v 4.1. United States Environmental
 Protection Agency, Washington, DC, USA., 2016.
- Witkowski, B., Al-sharafi, M., and Gierczak, T.: Kinetics of Limonene Secondary Organic
 Aerosol Oxidation in the Aqueous Phase, Environmental science & technology, 52,
 11583-11590, 2018.
- Wolfe, G. M., Crounse, J. D., Parrish, J. D., Clair, J. M. S., Beaver, M. R., Paulot, F., Yoon, T.
 P., Wennberg, P. O., and Keutsch, F. N.: Photolysis, OH Reactivity and Ozone Reactivity
 of a Proxy for Isoprene-Derived Hydroperoxyenals (HPALDs), Physical Chemistry
 Chemical Physics, 14, 7276-7286, 2012.