

Supplementary Materials

Rate coefficients for the reaction of ozone with 2- and 3-carene

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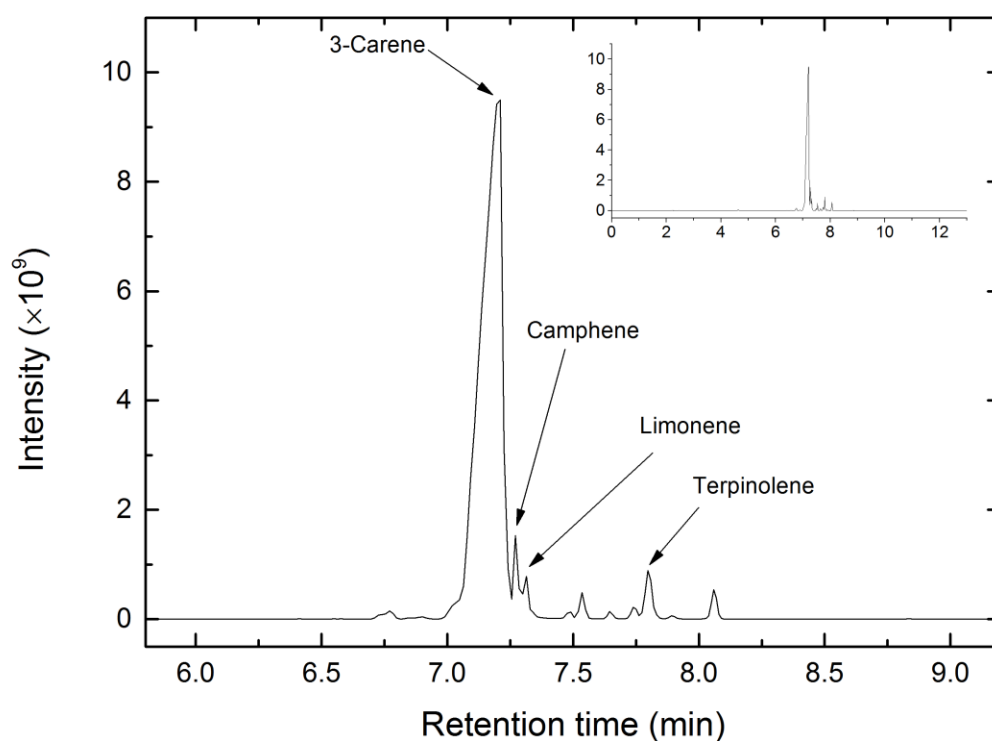
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1 1. Materials

2 The purities of the chemicals were as follows: synthetic air, O₂ and N₂, UHP certified
3 to >99.9995% (Alphagaz); 2-carene (Sigma-Aldrich, ≥97); 3-carene (Sigma-Aldrich, ≥98.5%);
4 cyclohexene (Fluka, ≥99.5); 2-butanol (Fluka, ≥99.5).

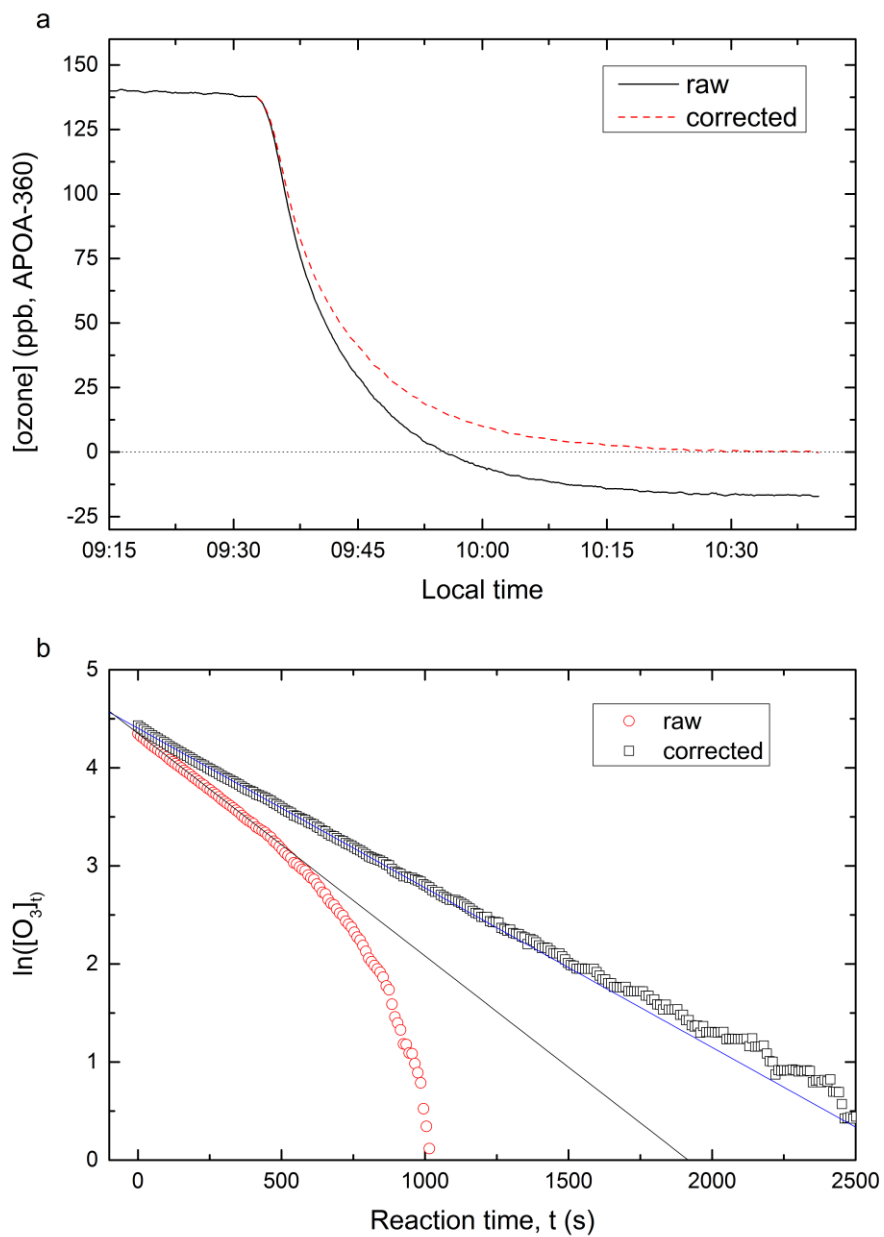
5 The purity of 3-carene was 95% determined by GC-MS, as shown in Fig. S1. The 3-carene
6 sample also consists of impurity of camphene (2%), limonene (1%) and terpinolene (2%).



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8 Supplementary Figure 1: Chromatogram spectrum for 3-carene sample.

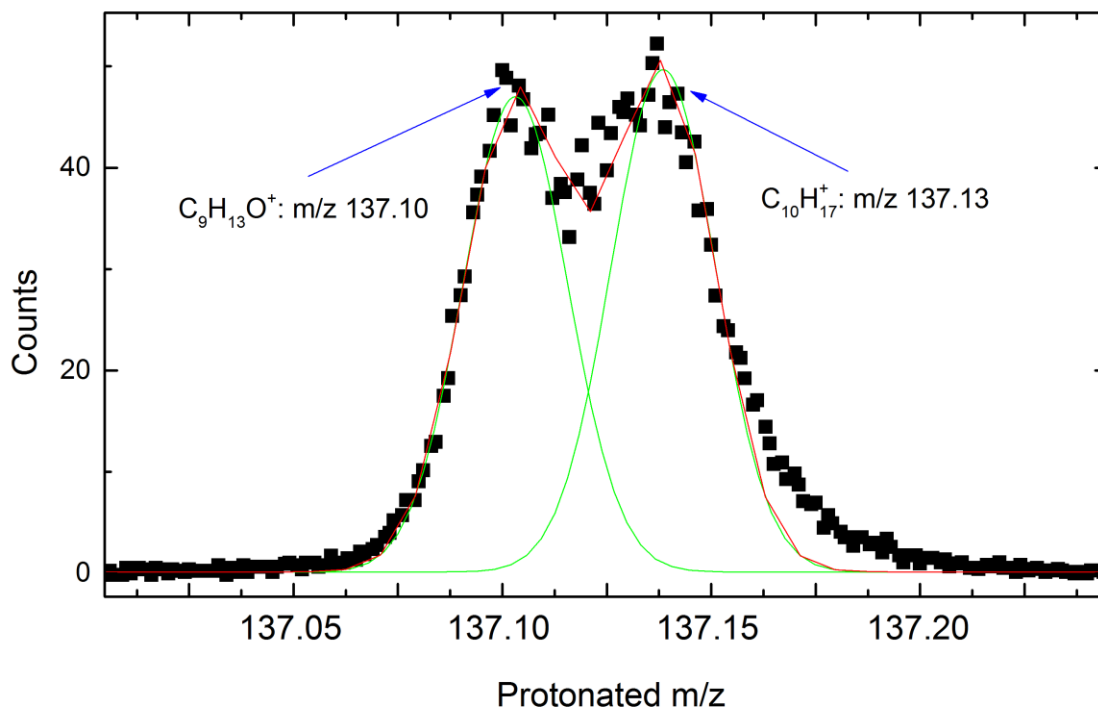
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10 2. Ozone concentration measurement by UV-absorption monitor (HORIBA APOA-360).

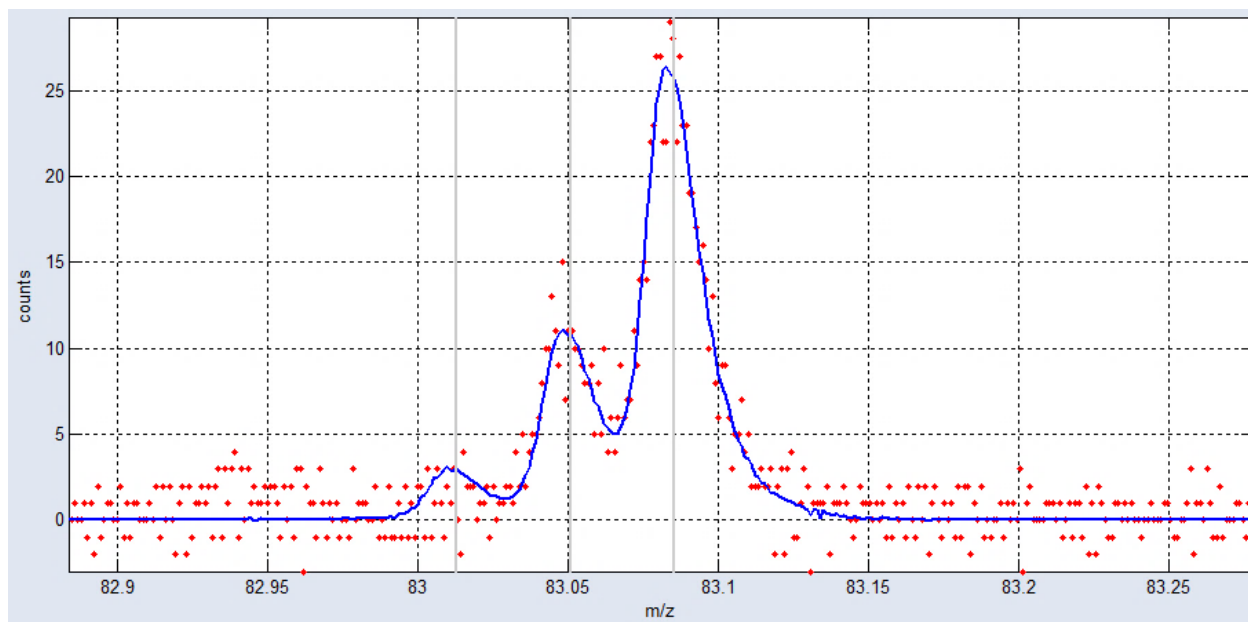


11
12 **Supplementary Figure 2:** Example for (a) concentration profile and (b) decay rate of ozone
13 before and after correction in the presence of excess 3-carene in SC.
14

15 3. Identification of VOCs in PTR-TOF spectra.



16
17 **Supplementary Figure 3:** Example of PTR-TOF mass spectra of Exp. 2CAR-3T using TMB as
18 an OH scavenger.



19
20 **Supplementary Figure 4:** Example of PTR-TOF mass spectra for isobaric peaks: m/z 83.05
21 ($C_5H_7O^+$) and m/z 83.09 ($C_6H_{11}^+$) during measurements of relative rates.

22 **Supplementary Table 1:** Initial experimental conditions performed in HELIOS.

Experiment ^(a)	Temperature K	carene ppbv	ozone ^(b) ppbv	c-hexane ^(c) ppbv	TMB ppbv	2-butanol ppbv	Injection sequences
<u>2-carene</u>							
2CAR-1C	298 ± 1	11.3	104	1700			2car; c-hexane; O ₃ ^(c)
2CAR-2C	300 ± 1	22.7	254	3990			2car; c-hexane; O ₃ ^(c)
2CAR-3T	305 ± 1	19.1	190		288		TMB; O ₃ ; 2car
2CAR-4B	293 ± 1	23.9	255			2640	2-butanol; 2car; O ₃
2CAR-5BR ^(d)	293 ± 1	6.7	410			4290	2-butanol; 2car; O ₃
<u>3-carene</u>							
3CAR-1C	299 ± 1	29.2	298	6820			c-hexane; O ₃ ; 3car ^(c)
3CAR-2C	295 ± 1	19.1	179	4490			c-hexane; 3car; O ₃ ^(c)
3CAR-3C	295 ± 1	11.3	96	2240			c-hexane; 3car; O ₃ ^(c)
3CAR-4B	294 ± 1	9.6	347			1320	2-butanol; 3car; O ₃
3CAR-5B	295 ± 1	7.7	213			1150	2-butanol; O ₃ ; 3car
3CAR-6BR ^(d)	296 ± 1	9.7	347			3960	2-butanol; 3car; O ₃
3CAR-7BR ^(d)	296 ± 1	29.1	-- ^(e)			6630	2-butanol; 3car; O ₃

23 ^(a) C = cyclohexane as a scavenger; B = 2-butanol as a scavenger; BR= cyclohexene as a reference in the presence of excess 2-butanol
 24 as a scavenger; T = 1,3,5-trimethylbenzene as a scavenger.

25 ^(b) [O₃] was monitored by APOA-360 UV-absorption monitor, which is in agreement with FTIR within 5% uncertainty.

26 ^(c) c-hexane = cyclohexane.

27 ^(d) In the presence of 29.6 ppbv cyclohexene as a reference.

28 ^(e) O₃ was injected into HELIOS in several additions.

