The gas phase ozonolysis and secondary OH production of cashmeran, a musk compound from fragrant volatile chemical products

Ayomide A. Akande and Nadine Borduas-Dedekind*

Department of Chemistry, University of British-Columbia, Vancouver

E-mail: borduas@chem.ubc.ca

Phone: +1 604-822-4435

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1. Experimental setup

Figure S1: The schematic illustrates the experimental setup for the ozonolysis of cashmeran. During the experiments, the chamber was filled with either N_2 or particle-free air. The particle-free air was produced using an oil-less air compressor, which was then passed through a particle filter, a water separator, and a dryer unit. To generate N_2, the particle-free air was further sent into a nitro pack generator (Parker Balston, Model 76-97) to remove O_2, CO_2, hydrocarbons and particles more than 0.01 microns.
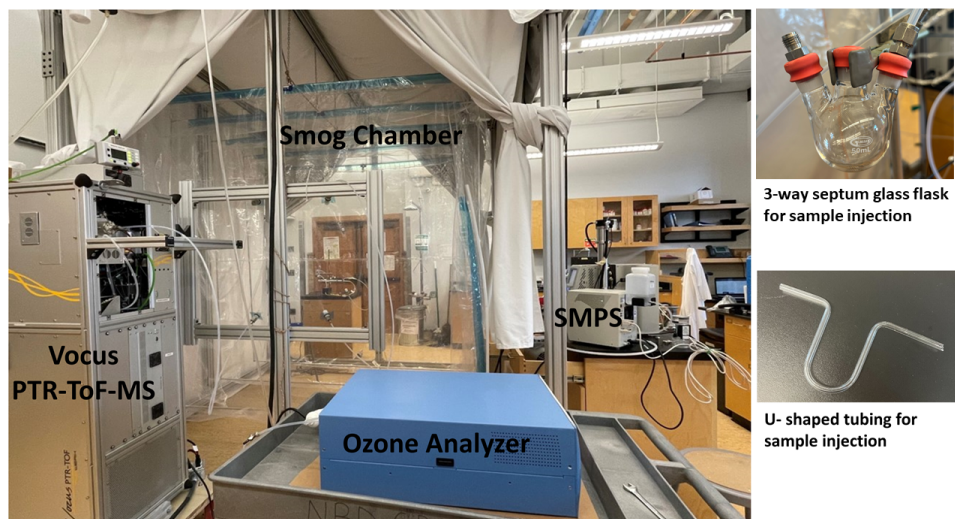
Figure S2: Images of the experimental setup for the gas-phase ozonolysis reactions. The smog chamber is at the center of the image and is operated with the curtains drawn during the experiment to avoid any possible photochemistry. The Vocus 2R, the ozone analyser and the SMPS are also labelled. The ozone generator is behind the chamber. Additionally, we included the two images depicting the sample introduction system into the chamber: the 3 neck round bottom flask and the U-shaped sample tubing.

2. GC confirmation of cashmeran in commercial fragrance
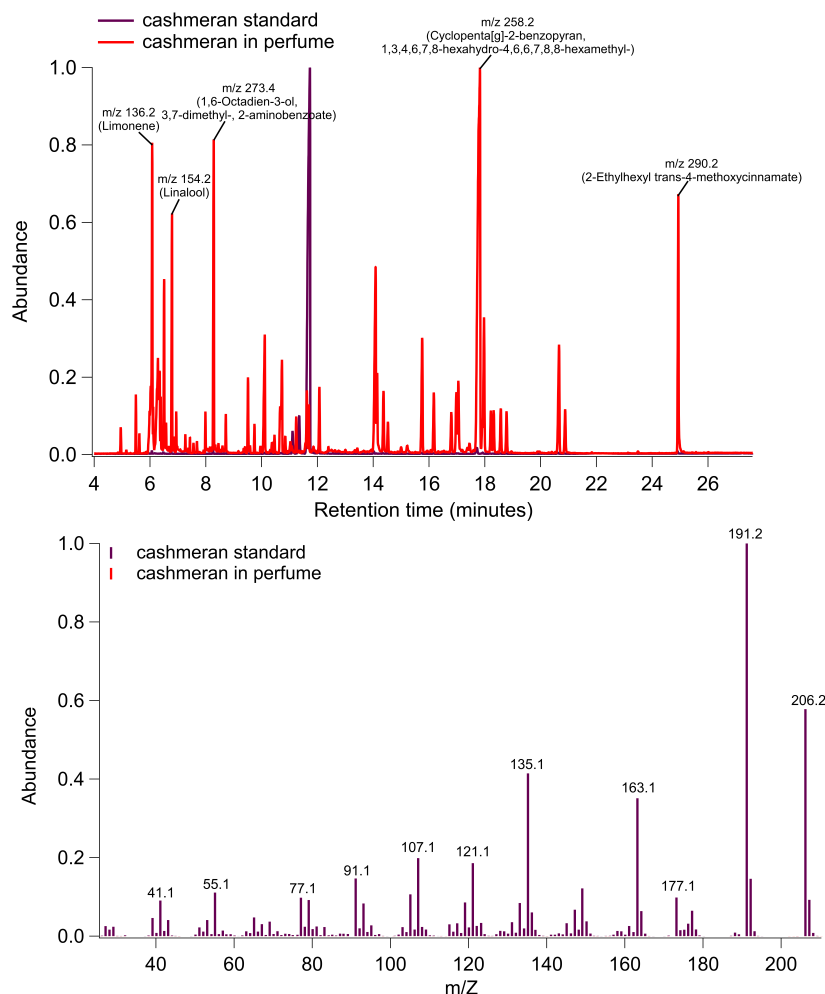
Figure S3: Top panel: The chromatogram of the compounds present in the commercial perfume measured by the GC-MS is overlaid with the chromatogram of the cashmeran standard. Cashmeran eluted at 11.6 minutes. The m/z values of other prominent peaks have also been identified, with likely compounds from library searches noted in parentheses. Bottom panel: For further confirmation of the identity of cashmeran in the perfume, a mass spectrum taken by GC-MS showed that the fragmentation pattern of the molecule $C_{14}H_{22}O$ matched precisely the fragmentation pattern of the cashmeran standard. We can therefore confirm that cashmeran is indeed present in the perfume. The peaks have been normalized to their highest intensity in both graphs.

3. Peak fitting, calibration plot and sensitivity of cashmeran
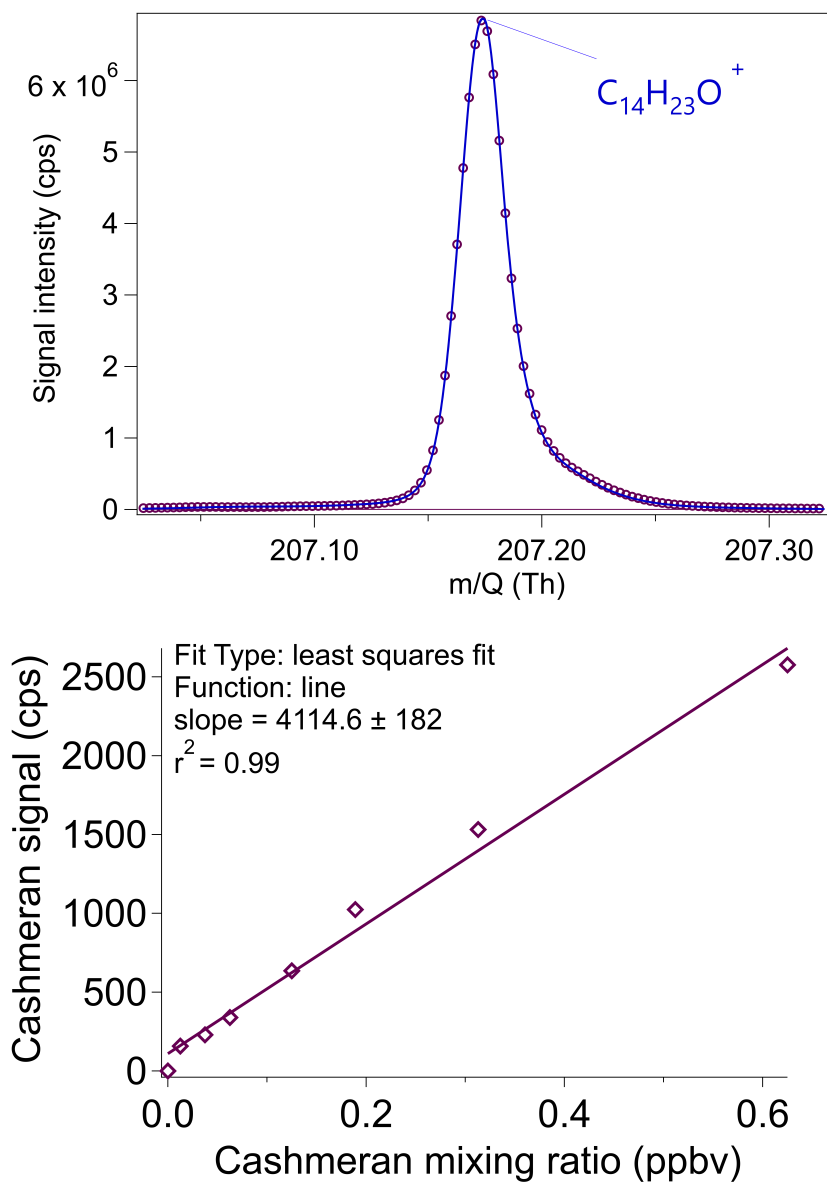
Figure S4: Top panel: $C_{14}H_{23}O^+$ was measured by the Vocus 2R as the protonated molecular ion of cashmeran at m/z 207.1743. Bottom panel: A calibration plot showing the linear response of $C_{14}H_{23}O^+$ as a function of concentration as measured by the Vocus. We determined the sensitivity of the compound to be 4115 cps/ppb.

4. Stability of cashmeran in chamber and negligible wall loss
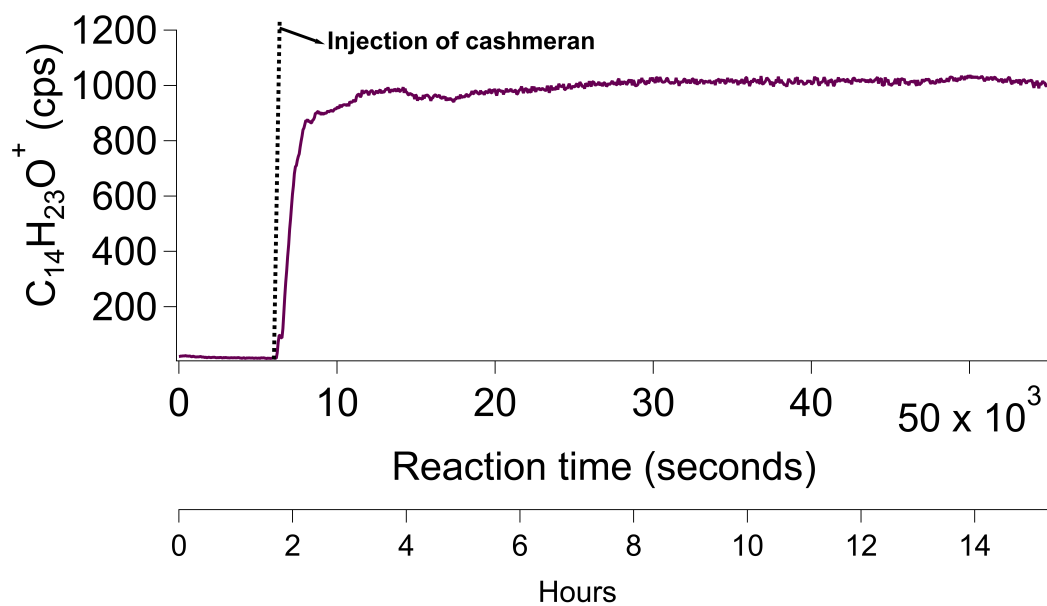
Figure S5: The time series of cashmeran's signal measured by the Vocus showed the stability of the compound in the 8 m^3 smog chamber beyond the duration of a typical kinetic experiment.
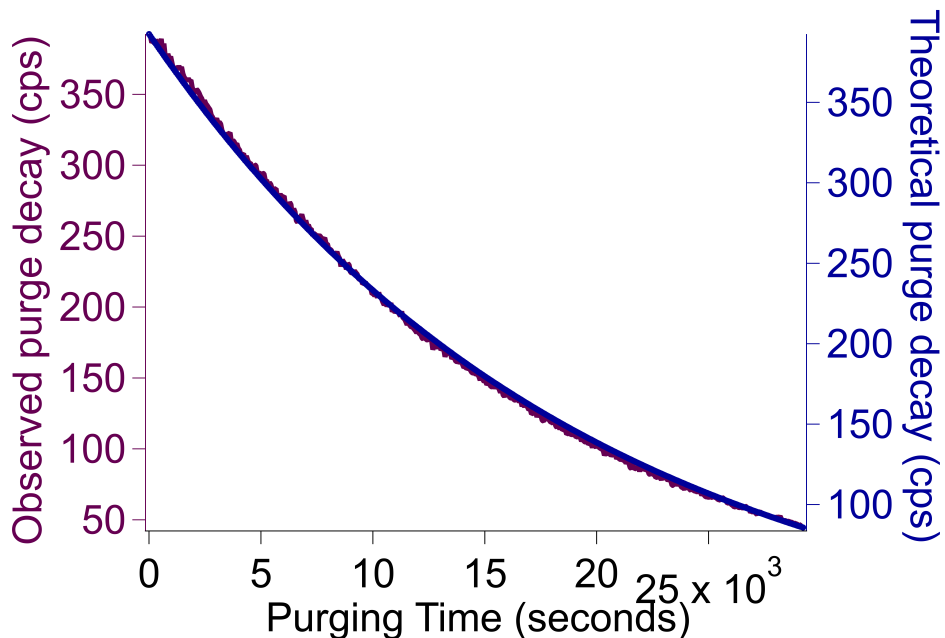
Figure S6: The time series of the decay of $C_{14}H_{23}O^+$ within the smog chamber during a purging experiment was perfectly fitted by the pump's flow at 14 LPM. The excellent overlay confirms that cashmeran is removed from the smog chamber under first-order rate conditions and emphasizes minimal wall chemistry during the kinetic experiments.

Wall loss is a crucial consideration in chamber oxidation experiments, particularly as the volatility of the studied compounds decreases.[2] Due to significant wall loss and the long reaction time of cashmeran with O_3, we transitioned from a 450 L pillow bag[3] to an 8000 L smog chamber with a surface-area-to-volume ratio of 3 m^{-1}. We did not observe significant wall losses in the 8000L, highlighting the importance of large chambers for experiments with SVOCs. For comparison, Zein et al. studied the ozonolysis of guaiacol, a less volatile aromatic compound with a similar rate constant to cashmeran, in an 8000 L poly(methyl methacrylate) chamber, and also found wall loss to be negligible.[4] While not exhaustive, we have compiled additional examples of negligible wall loss during kinetics experiments (Table S1).

Table S1: Wall loss comparison during gas-phase kinetics across different compounds and chamber sizes of selected experiments. This list is not exhaustive.

References	Chamber type & size	Molecules studied
Grira et al[5]	Teflon chamber, 300 L	Cis-2-penten-1-ol (C5H10O)
		trans-2-hexen-1-ol, trans-3-hexen-1-ol, cis-3-hexen-1-ol (C6H12O)
		1-octen-3-ol, Trans-2-octen-1-ol (C8H16O)
Zein et al[4]	Poly(methyl methacrylate) chamber, 8000 L	Catechol (C6H6O2)
		Guaiacol (C7H8O2)
Heine and Borduas-Dedekind[3]	PFA bag, 450 L	Dimethyl selenide (CH3SeCH3)
		Dimethyl diselenide (CH3SeSeCH3)
Magneron et al[6]	FEP Teflon bag, 140L	Hexylene glycol (C6H14O2)
		Diacetone alcohol (C6H12O2)
This study	PFA Teflon, 8000 L	Cashmeran (C14H22O)

5. Observed increase of musk compounds during perfume analysis
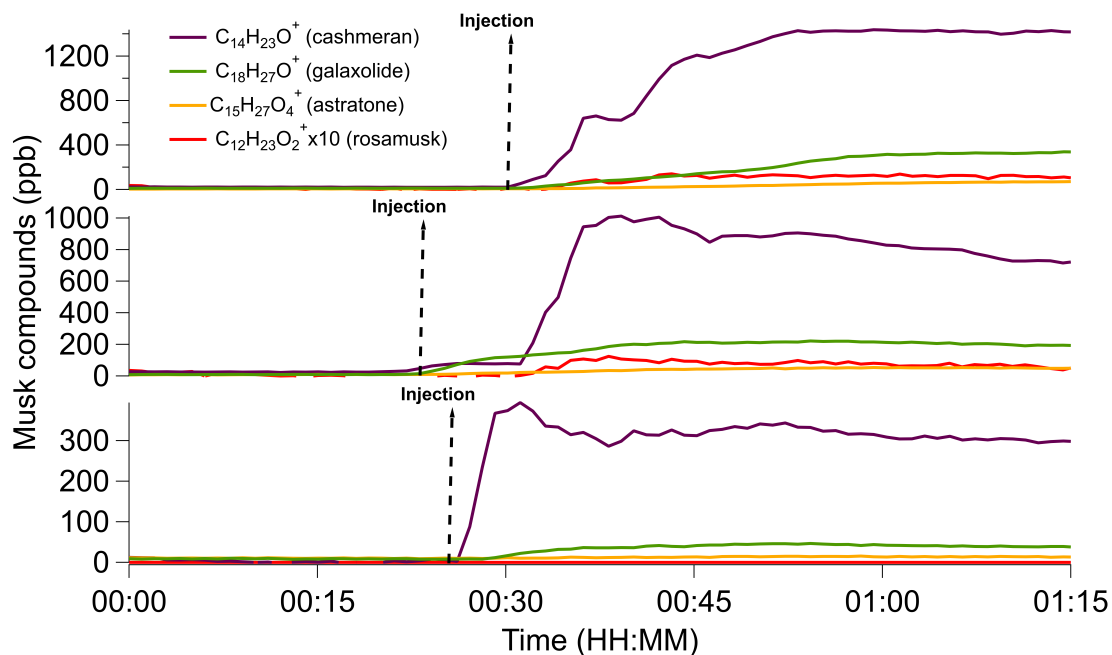
Figure S7: The time series of musk compounds was monitored by the Vocus upon injection of 10, 5, and 2 μl of perfume into the chamber shown in the top, middle, and bottom panels respectively. The dashed black line indicates when the injection occurred and time 0 s was when the instrument started measuring.

6. Pseudo-first order reactions
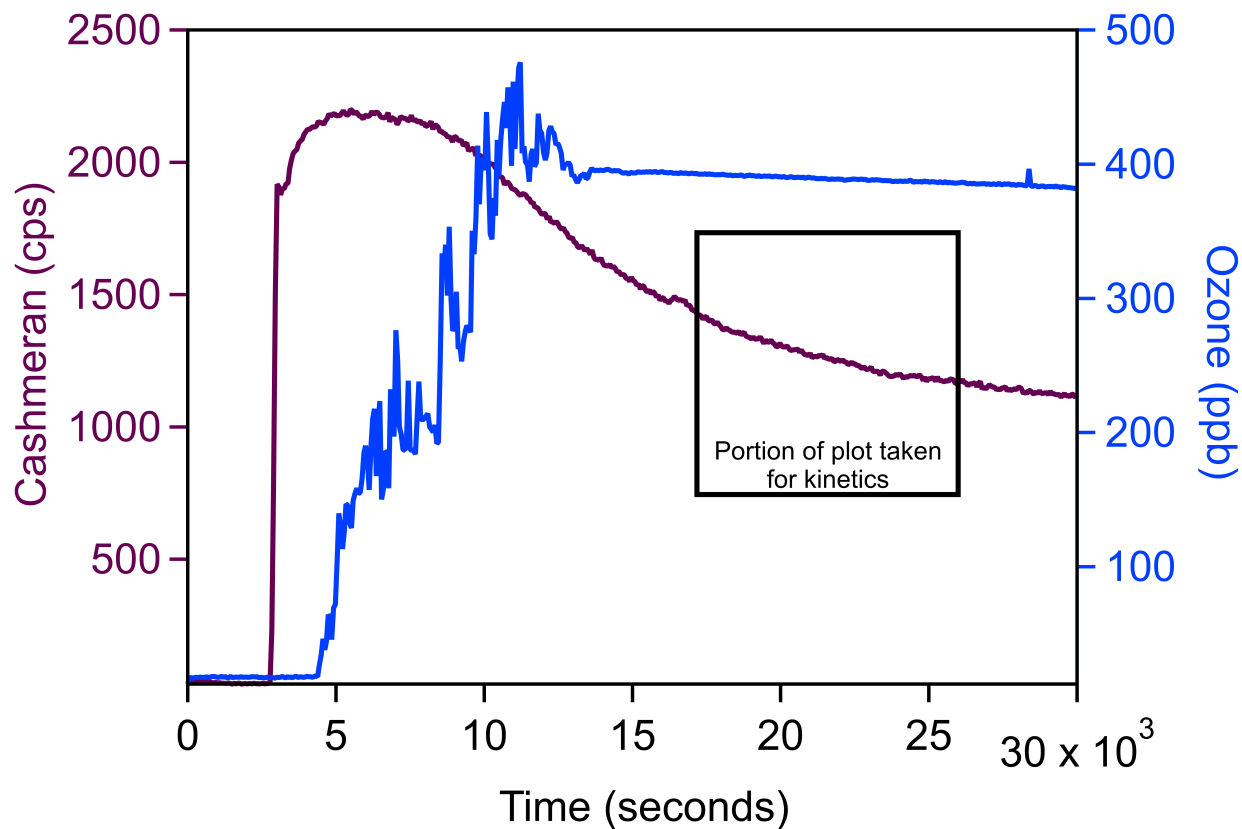
Figure S8: This graph represents a typical time series obtained during an ozonolysis experiment in air where cashmeran was injected first followed by O_3. The red rectangle highlights the data used for pseudo-first order rate kinetics. Under our experimental conditions, the lifetime of cashmeran was 4 days against 400 ppbv of O_3, hence the necessity of working with a large 8 m^3 chamber to avoid wall losses.

7. SOA formation in ozonolysis experiments occurs only in particle-free air and is due to the presence of cashmeran
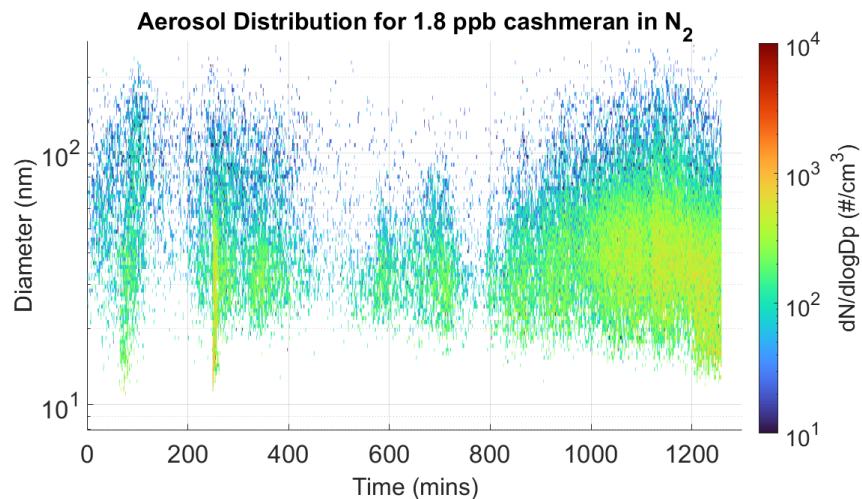
Figure S9: Organic aerosol number concentration (dN/dlogDp) plot as a function of size and time for ozonolysis experiment done under N_2 at 1.8 ppb of cashmeran and 585 ppb of O_3
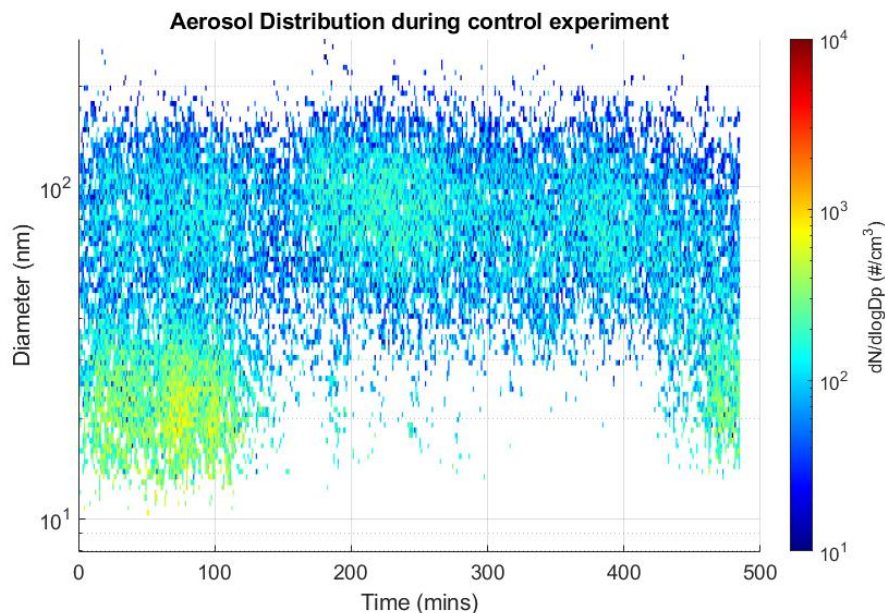
Figure S10: Organic aerosol number concentration (dN/dlogDp) during a control experiment is shown as a function of size and time. Cashmeran was absent from the smog chamber in this particular control experiment. 400 ppb of O_3 and 33 ppb of cyclohexane were introduced into the chamber.

8. Mass yield calculation of musk compounds in perfume

The mass yield of a musk compound was obtained by dividing its mass in the gas phase as measured by the Vocus, m_{musk} in grams, by the total mass of perfume injected into the chamber, $m_{perfume}$ in grams according to equation below:

$$\text{mass yield } (\%) = \frac{m_{musk}}{m_{perfume}} \tag{1}$$

The total mass of perfume was calculated based on its density, 0.83 g cm^{-3}, and the volume injected in the chamber (Table S1). To determine the mass of the musk compound, we first calculated the number concentration of the musk compound present in the bag under experimental conditions using the ideal gas law. We then converted this concentration to mass using the molecular weight of the compound and the volume of the chamber (Table S1).

Table S2: Mass yield values of musk compounds determined from perfume analysis. The density of the perfume was determined to be 0.83 g cm^{-3} and the volume of the chamber was 8×10^6 cm^{-3} (or 8000 L).

| Compound	Volume of perfume injected (μl)	Total mass of perfume (μg)	Mixing ratios of musk compound (ppb)	Mass of musk compound (μg)	Mass ratio (%)
Cashmeran	2	1660	0.35	5.5	0.33
	5	4150	0.08	15	0.36
	10	8300	0.22	24	0.29
Galaxolide	2	1660	0.073	0.9	0.05
	5	4150	0.010	4.3	0.10
	10	8300	0.050	6.3	0.08
Astratone	2	1660	0.012	0.4	0.02
	5	4150	0.004	1.0	0.02
	10	8300	0.011	1.1	0.01
Rosamusk	2	1660	0.000	0.0	0.000
	5	4150	0.003	0.1	0.003
	10	8300	0.002	0.2	0.002

9. Result output of cashmeran's reactivity with OH radicals and O$_3$ from Atmospheric Oxidation Program

- **SMILES**: O=C(C(=C(C(C1C)(C)C)CC2)C1(C)C)C2

- **Chemical name**: 4H-Inden-4-one, 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-

- **Molecular formula**: $C_{14}H_{22}O$

- **Molecular weight**: 206.33 g mol^{-1}

Summary

Hydroxyl Radicals at 25°C (AOP v1.92)

- Hydrogen Abstraction = 9.2057×10^{-12} cm^3 molecule^{-1} sec^{-1}

- Addition to Olefinic Bonds = 99.0000×10^{-12} cm^3 molecule^{-1} sec^{-1}

- **Overall OH Rate Constant = 108.2057×10^{-12} cm^3 molecule^{-1} sec^{-1}**

Ozone Reaction at 25°C (AOP v1.91)

- **Overall Ozone Rate Constant = 1.137500×10^{-17} cm^3 molecule^{-1} sec^{-1}**

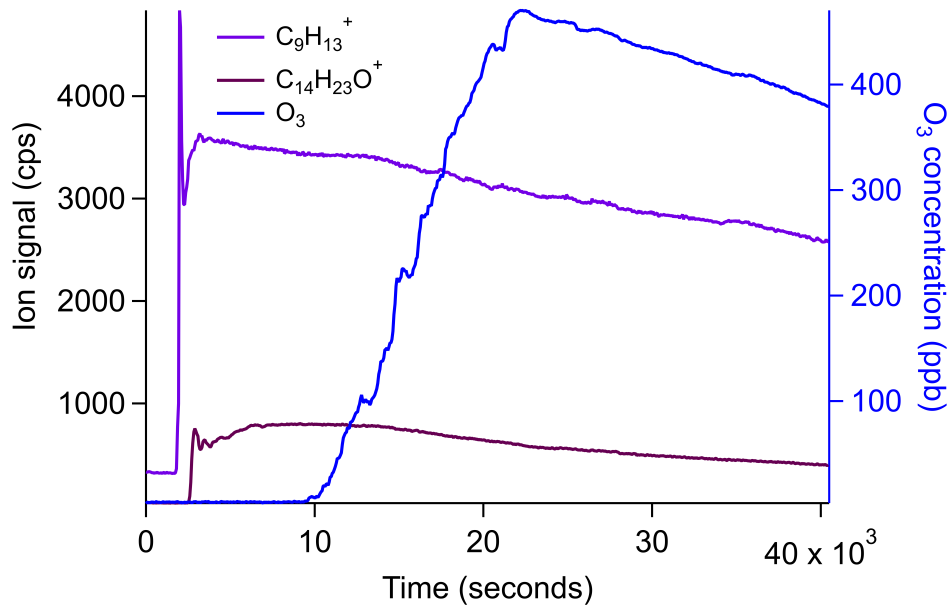# 10. Estimating OH radicals concentration from 1,3,5-trimethylbenzene decay

Figure S11: The time series of cashmeran and 1,3,5-trimethylbenzene during an ozonolysis experiment in air was conducted to estimate the production of secondary OH radicals.
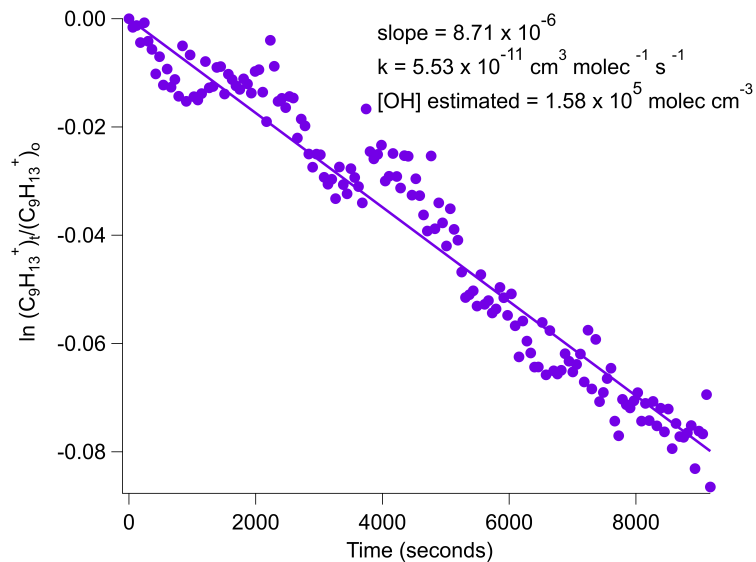
Figure S12: The kinetic trace depicts the decay of 1,3,5-trimethylbenzene during ozonolysis. The data was pre-averaged by 1-minute intervals. We used the literature value of k(1,3,5-trimethylbenzene + OH radicals) = 5.53×10^{-11} cm^3 $molec^{-1}$ s^{-1} to calculate the concentration of OH radicals.[1] The steady-state concentration of OH radicals was calculated to be 1.58×10^5 molec cm^{-3}.

11. Gas phase oxidation product
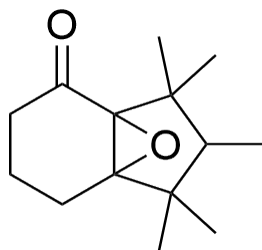
Figure S13: The proposed structure of $C_{14}H_{23}O_2^+$ is an epoxide.
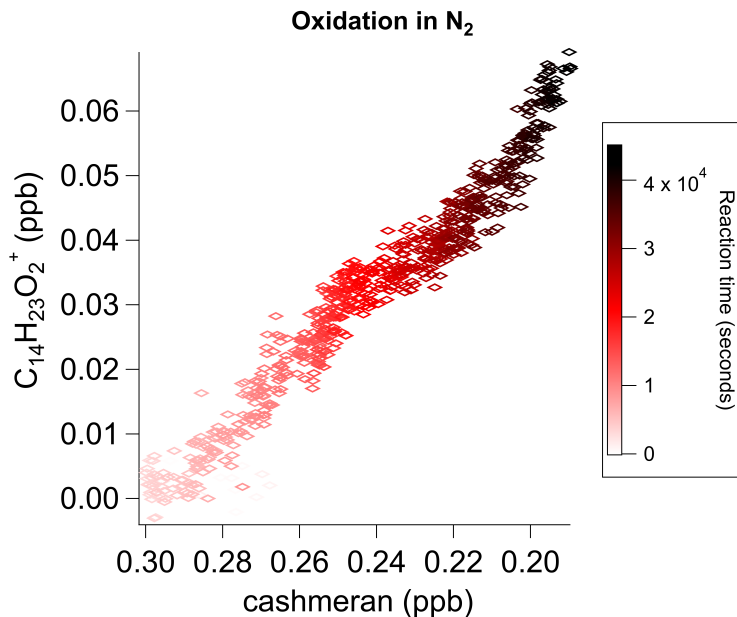
Figure S14: The correlation between $C_{14}H_{23}O_2^+$ and cashmeran as a function of time in N_2 suggests that the oxidation product is likely a first generation product.
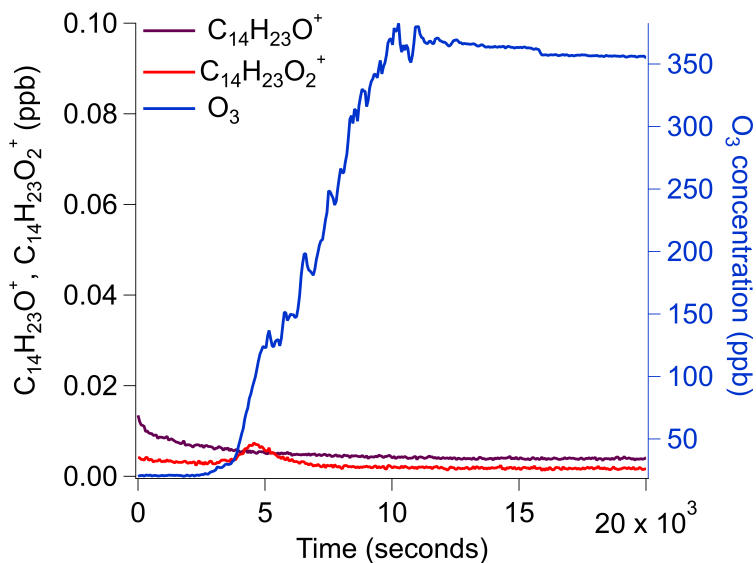
Figure S15: Timeseries data from a control experiment in which no cashmeran was introduced into the chamber. We show that the high concentration of O_3 and duration of experiments are enough to remove any artifacts of our species of interest (cashmeran and its oxidation product, $C_{14}H_{23}O_2^+$).

12. UV-Visible measurement of cashmeran

Figure S16: The absorbance spectrum of cashmeran has a characteristic peak at 320 nm. We therefore expect photolysis chemistry to also play a role in cashmeran's atmospheric fate. In addition, this absorbance hindered our ability to make rate constant measurements of OH radicals + cashmeran by photolysing hydrogen peroxide.
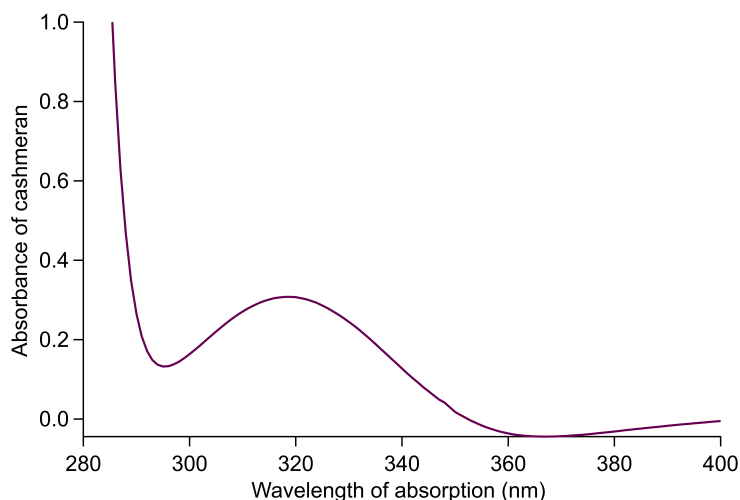
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(2) Kenagy, H. S.; Heald, C. L.; Tahsini, N.; Goss, M. B.; Kroll, J. H. Can we achieve atmospheric chemical environments in the laboratory? An integrated model-measurement approach to chamber SOA studies. *Science Advances* **2024**, *10*, eado1482, Publisher: American Association for the Advancement of Science.

(3) Heine, P. A.; Borduas-Dedekind, N. The Ozonolysis of Methylated Selenide Compounds in the Atmosphere: Isotopes, Kinetics, Products, and Mechanisms. *Environmental Science & Technology* **2023**, *57*, 13079–13087, Publisher: American Chemical Society.

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