Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

FT-IR calibration method

Up to now no calibrated SQT FT-IR spectra or absorption cross sections are available in the literature. These information were needed for the determination of SQT concentrations by means of FT-IR spectroscopy. The experimental setup used for calibration is shown in Fig. S 1. The plugged flask including the SQT (without the other parts of the setup) was weighed at a high-precision balance (precision: ± 0.01 mg) before and after flushing 100 cm^3 min^{-1} (STP) nitrogen through the flask for one hour resulting in a mass difference Δm of the SQT. Directly after leaving the flask, the outflow was diluted with 9900 cm^3 min^{-1} (STP) air and pumped continuously through a long-path FT-IR spectrometer (pathlength: 20 m). Spectra in the range 3500 – 750 cm^{-1} with a resolution of 8 cm^{-1} were recorded repetitively after each 5 minutes. For more instrumental details, see section 2.2.

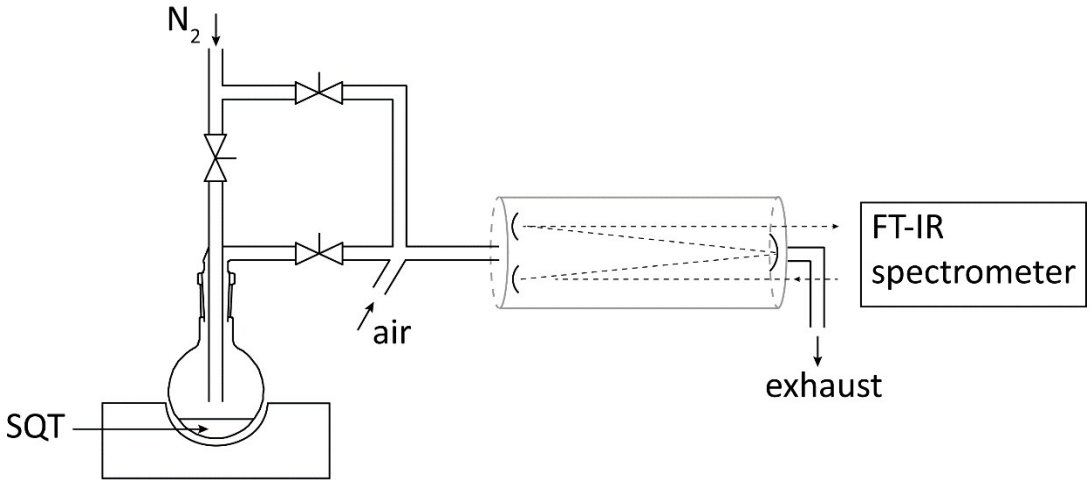

Fig. S 1 Experimental setup of the gravimetrical calibration of SQT FT-IR spectra.

The SQT concentration [SQT] in the gas flow entering the FT-IR spectrometer is calculated from the measured mass difference Δm according to equation (VI) using a flow of 10000 cm^3 min^{-1} (STP), a flow time t = 60 min and M_{SQT} = 204 g mol^{-1}.

$$[SQT] = \frac{\Delta m \quad N_A}{flow \cdot t M_{SQT}} \qquad \text{(VI)}$$

The procedure was repeated at least five times. The standard deviation was calculated from the deviation of Δm and a 2σ interval is given as the error limit. FT-IR spectra with the corresponding SQT concentrations are shown in Fig. S 2.

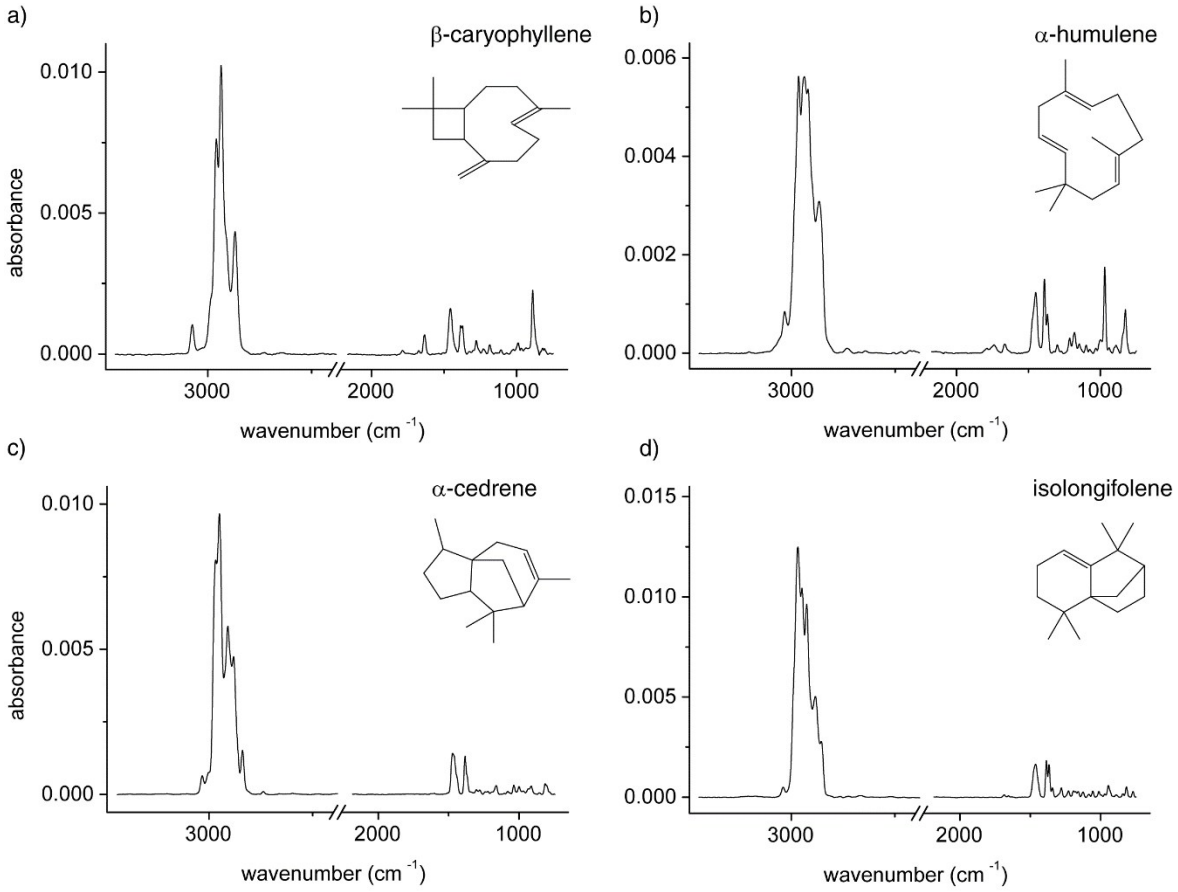

Fig. S 2FT-IR spectra (resolution: 8 cm^{-1}, 1000 scans, 3500 - 750 cm^{-1}, path length: 20 m) of the four SQTs with the following concentrations (unit: molecule cm^{-3}): [β-caryophyllene] = (7.7 ± 0.9) · 10^{12}, [α-humulene] = (8.8 ± 1.0) · 10^{12}, [α-cedrene] = (7.8 ± 1.0) · 10^{12}, [isolongifolene] = (1.1 ± 0.1) · 10^{13}, error limit: 2σ. The spectral range of 2400 - 2250 cm^{-1} is cut out due to the strong CO_2 absorption.

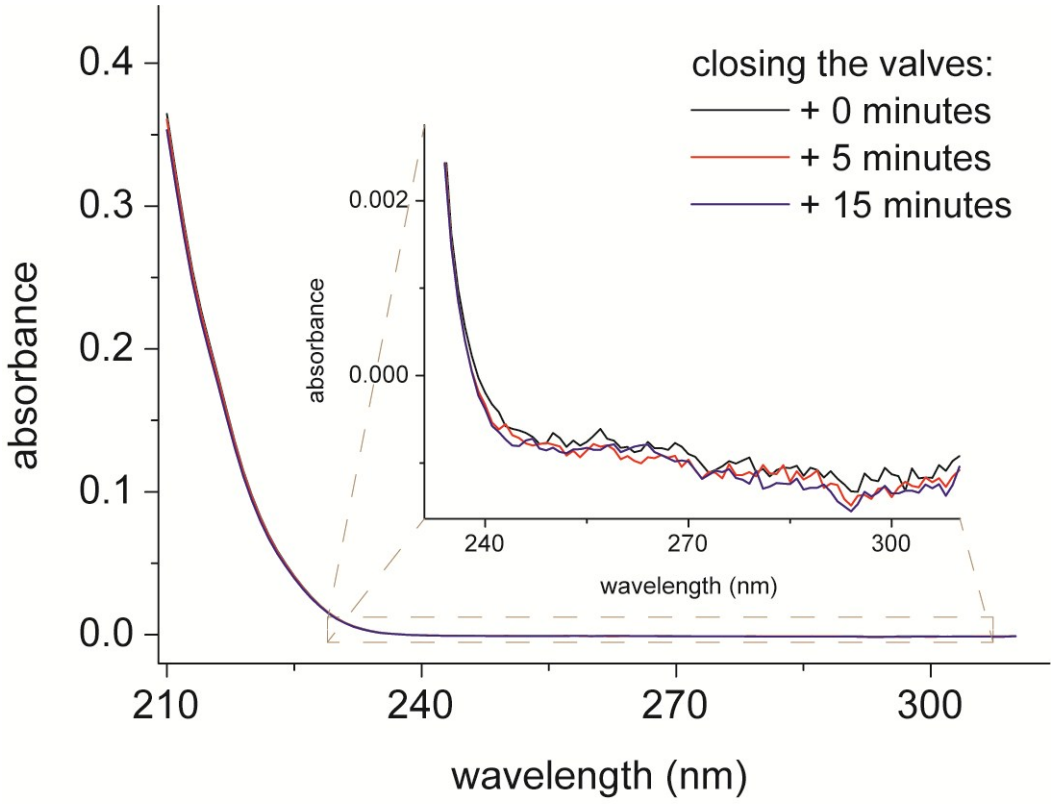

Fig. S 3UV spectra of β-caryophyllene in the stopped-flow experiment. [β-caryophyllene] = $2 \cdot 10^{14}$ molecule cm^{-3}. Experimental data 0 (black), 5 (red) and 15 (blue) minutes after closing the valves of the UV cell. For better visibility, the inner plot shows the zoomed range of the spectrum as marked in the original plot.

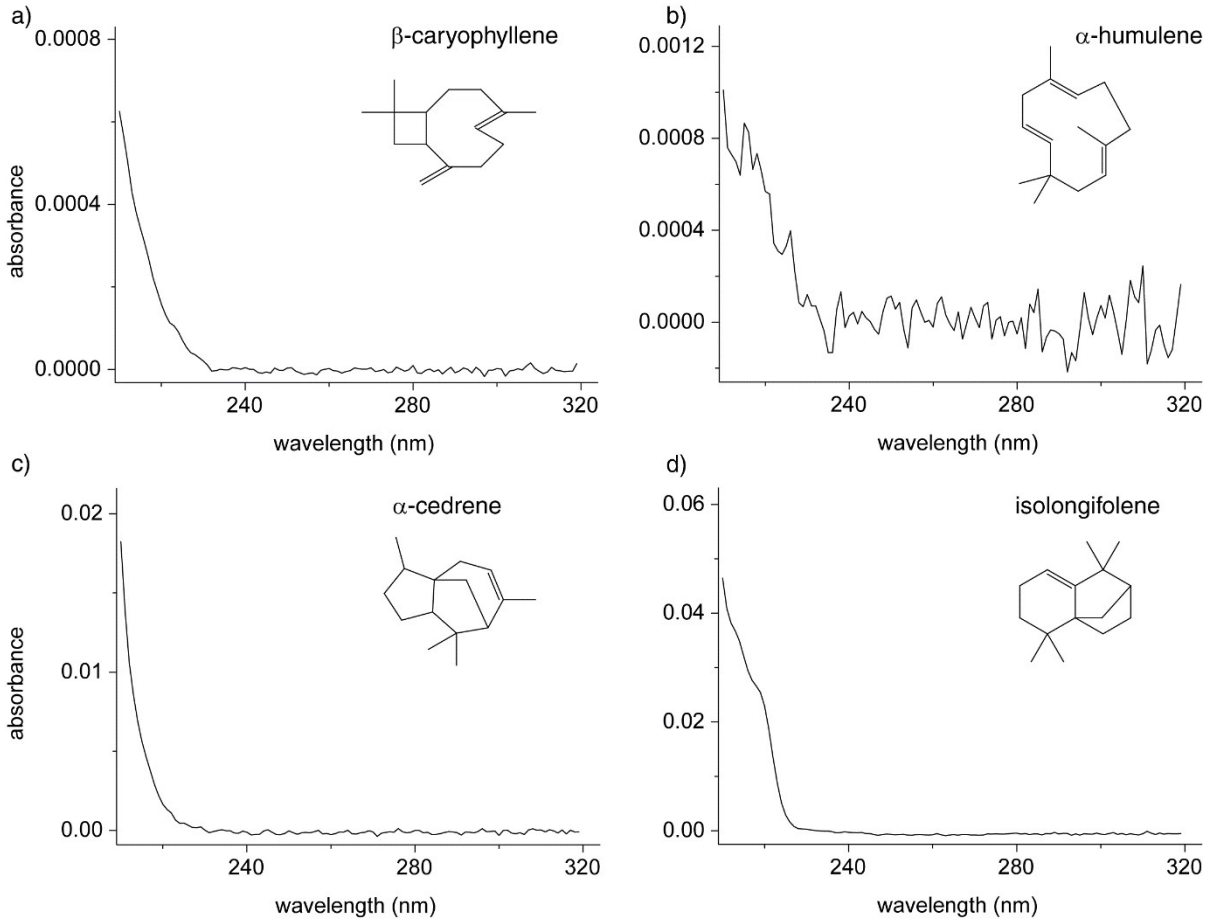

Fig. S 4UV spectra of the four SQTs in the range 210 - 320 nm with the following concentrations (unit molecule cm^{-3}): [β-caryophyllene] = (5.9 ± 0.5) · 10^{11}, [α-humulene] = (9.0 ± 0.6) · 10^{11}, [α-cedrene] = (2.0 ± 0.2) · 10^{13}, [isolongifolene] = (1.0 ± 0.1) · 10^{14}. The concentrations were determined by means of FT-IR spectroscopy measuring in parallel to the experiments with UV absorption spectroscopy.

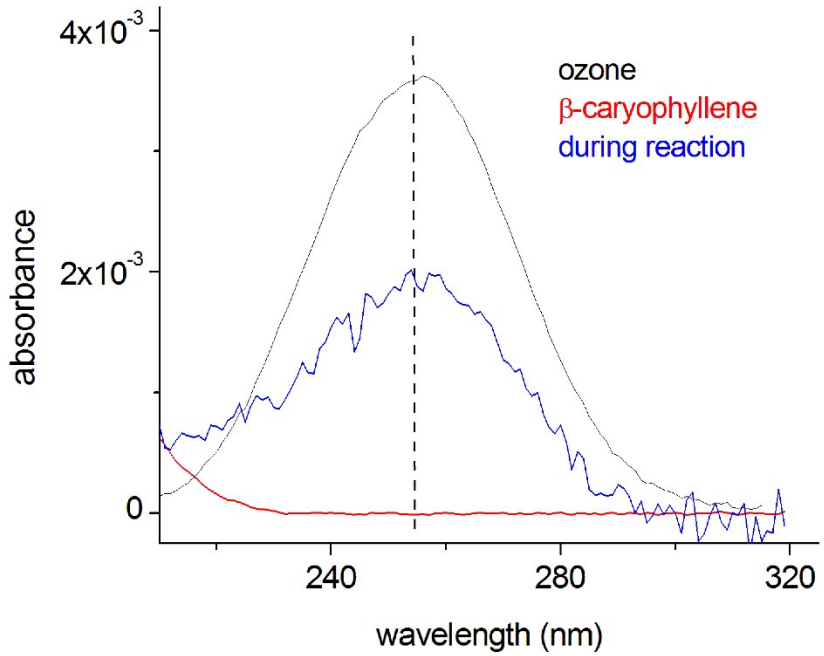

Fig. S 5 Experimental data of the UV spectra of ozone (black, $[O_3]$ = 7.8 · 10^{11} molecule cm^{-3}), β-caryophyllene (red, [β-caryophyllene] = 5.9 · 10^{11} molecule cm^{-3}) and during the reaction of ozone with β-caryophyllene (blue). The dashed line shows the wavelength of the strongest ozone absorption at λ = 254 nm. Neither β-caryophyllene itself nor reaction products distort the detection of ozone at λ = 254 nm.

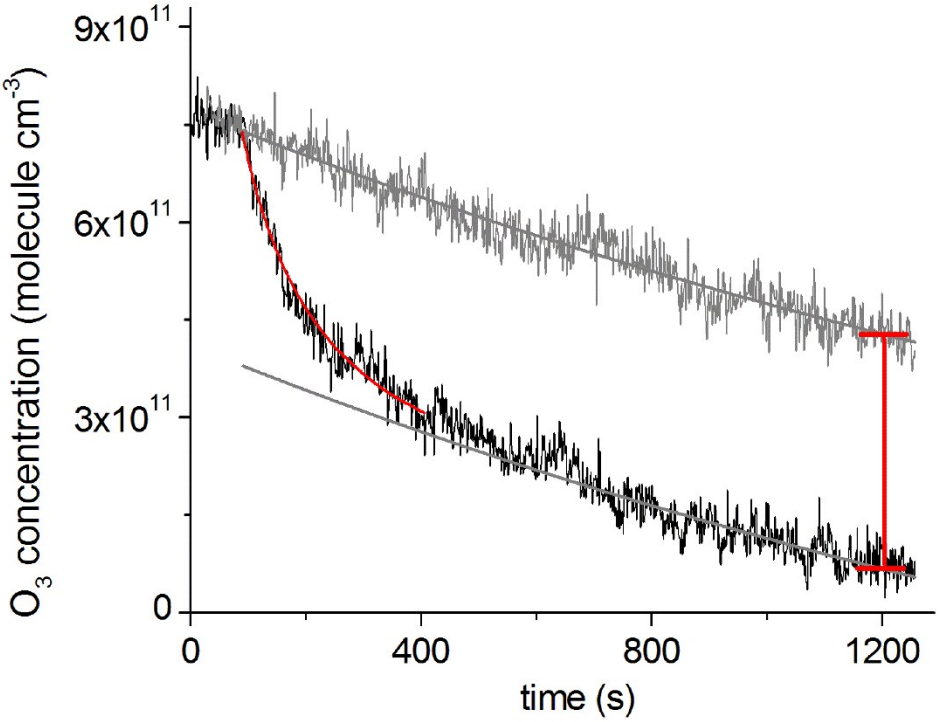

Fig. S 6 Experimental data of the stopped-flow experiment of ozone in the absence (grey) and presence (black) of β-caryophyllene. [β-caryophyllene] = $4.7 \cdot 10^{11}$ molecule cm^{-3}, [O_3] = $7.4 \cdot 10^{11}$ molecule cm^{-3} and [C_3H_8] = $2 \cdot 10^{16}$ molecule cm^{-3} (OH radical scavenger). The experimental data for long reaction time indicate an additional ozone consumption beside the wall loss of $\Delta[O_3] = 3.6 \cdot 10^{11}$ molecule cm^{-3}, in line with a 1:1 stochiometry (reacted [O_3] per reacted [SQT]), The amount of ozone that has disappeared additionally to the wall loss ($\Delta[O_3]$) is slightly lower than the initial β-caryophyllene concentration and agrees with the fitted line from parameter estimation (in red).

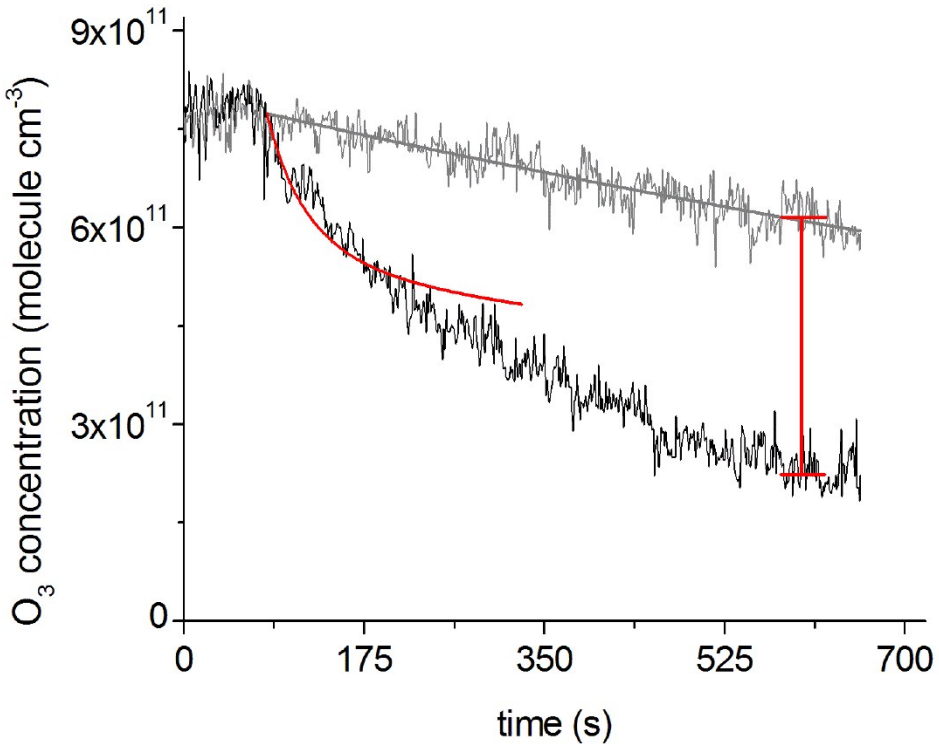

Fig. S 7 Experimental data of the stopped-flow experiment of ozone in the absence (grey) and presence (black) of α-humulene. [α-humulene] = 2.4 · 10^{11} molecule cm^{-3}, [O_3] = 7.8 · 10^{11} molecule cm^{-3} and [C_3H_8] = 2 · 10^{16} molecule cm^{-3} (OH radical scavenger). The ozone consumption of $\Delta[O_3]$ = 4 · 10^{11} molecule cm^{-3} exceeds the initial α-humulene concentration, and hence, the 1:1 stochiometry is not fulfilled.The red line shows the best fit result from parameter estimation. It doesn't show a good agreement with experimental data and hence supports the assumption that secondary reactions distort the measurements.

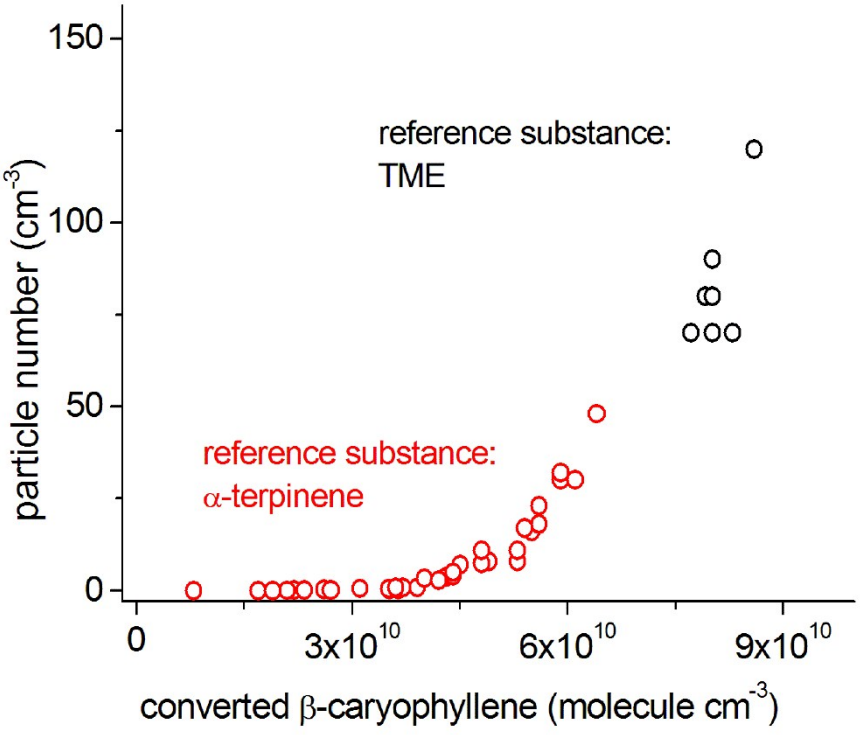

Fig. S 8 Particle formation from the reaction of ozone with β-caryophyllene and a reference substance. [β-caryophyllene] = 1 · 10^{11} molecule cm^{-3}, [O_3] = (1 – 17) · 10^{11} molecule cm^{-3}, [C_3H_8] = (1.2 - 2.5) · 10^{15} molecule cm^{-3} and [*i*-C_4H_8] = 3.7 · 10^{15} molecule cm^{-3}. In red, experiments with α-terpinene as reference substance: [α-terpinene] = 2.0 · 10^{10} molecule cm^{-3} and in black, experiments with TME as reference substance: [TME] = 1.0 · 10^{11} molecule cm^{-3}.