

## SUPPORTING INFORMATION

# Determination of the Specific Surface Area of Snow Using Ozonation of 1,1-Diphenylethylene

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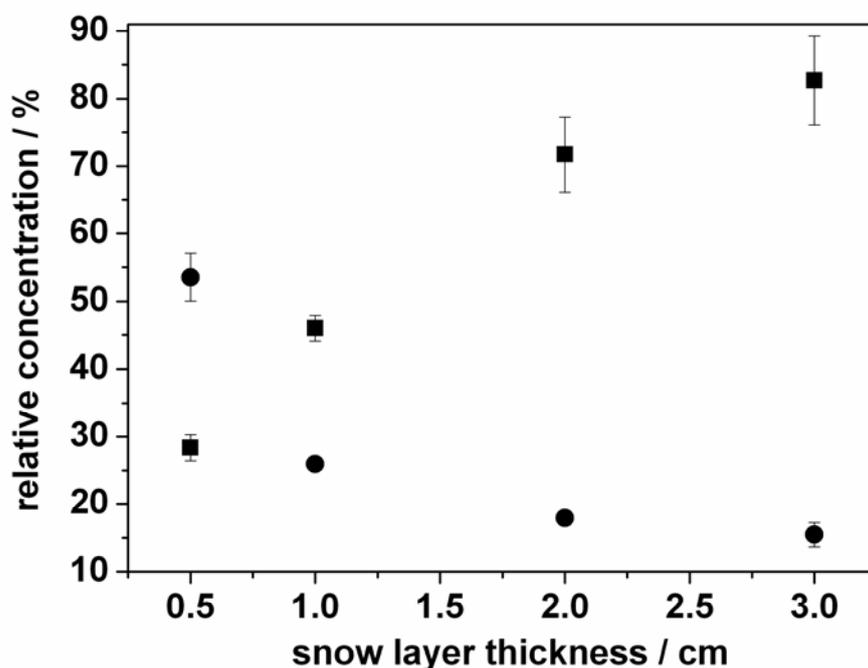
### Experimental

**Materials.** Reagents and solvents (1,1-diphenylethylene, **DPE**; benzophenone, **BP**; potassium iodide; potassium iodate; anhydrous sodium sulfate; dichloromethane) of the highest purity available were used as purchased. Water was purified on an Osmonics 2 and a Millipore Simplicity 185.

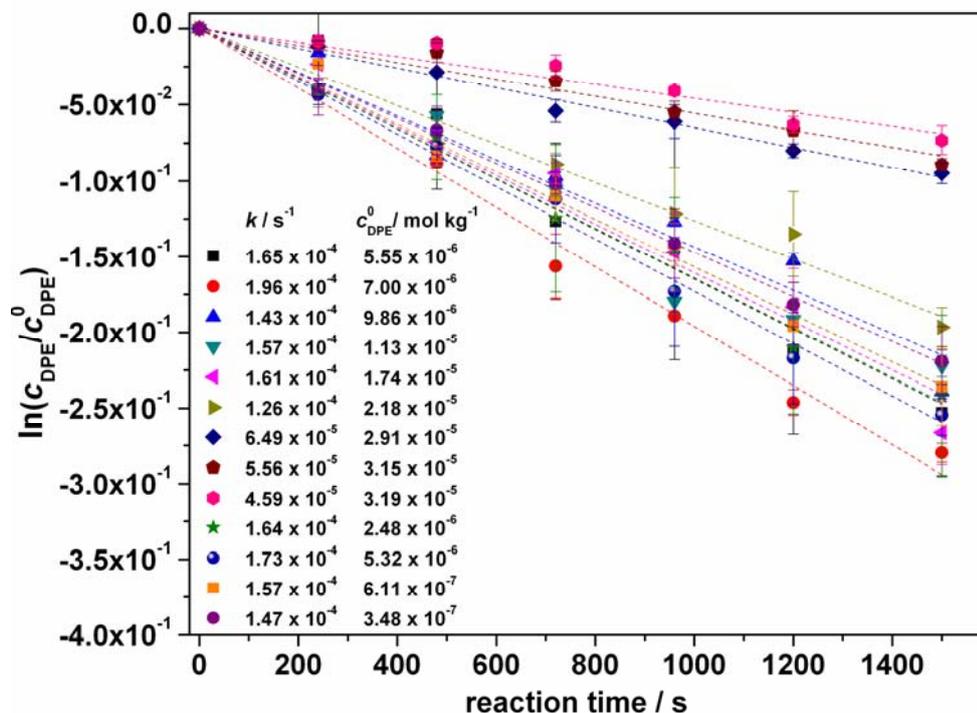
**Instrumentation.** A GC-MS system consisting of a HP 6890 gas chromatograph (Agilent), equipped with a J&W Scientific DB-5MS fused silica column (60 m × 0.25 mm; 0.25 μm stationary-phase film; 5% phenyl/95% methyl-polysiloxane) and a HP 5973 mass selective detector (Agilent), was used; the carrier gas was helium (flow: 1.5 mL min<sup>-1</sup>). Injector and transfer line temperature was 280 °C. Samples (1 μL) were injected in a split mode (1:20) for a full-scan analysis or in a split-less mode (SIM). Initial temperature was 80 °C, held for 1 min, the temperature was raised to 180 °C by 10 min<sup>-1</sup>, then to 300°C by 15 min<sup>-1</sup>; the final temperature was held for 5 min.

**Sample Analyses.** The snow samples (50 g) were melted at 20 °C and extracted with dichloromethane ( $3 \times 15$  mL). The extracts were concentrated under a stream of nitrogen to 10 mL, dried with anhydrous sodium sulfate ( $\sim 5$  g), filtered through glass wool, concentrated to 1 mL under a gentle stream of nitrogen gas, and analyzed directly using GC-MS (Supporting Information). All measurements were based on at least 3 independent experiments, and the relative standard deviation of the mean is given.

**Iodometry.** Ozone was produced using a homemade variable ozone generator. Its concentration inside the desiccator was determined iodometrically using a UV-Vis spectrometry.<sup>1,2</sup>  $O_3$  in the  $O_3/O_2$  stream was passed through a buffered solution of KI. The molar concentrations of triiodide ion formed were determined from the absorbance vs. concentration calibration curve; the number of moles of  $I_3^-$  is equivalent to that of ozone. The values were corrected for KI oxidation by molecular oxygen (when the ozonator lamp is off). The  $O_3$  concentrations were measured always before and after the experiment. The flow tube ozone concentrations were in the range of  $0-1.6 \times 10^{16}$  molecules  $cm^{-3}$  and were controlled by changing the flow rate of  $O_2$  gas as well as by the irradiation flux in the ozone generator.



**Figure S1:** The relative concentrations of **DPE** (■) and **BP** (●) during ozonation of the **DPE** snow samples, when layers of the samples of different thickness were exposed to the same  $O_3$  concentration for the same time (10 min);  $c_{DPE}^0 = 4.7 \times 10^{-6}$  mol  $kg^{-1}$  (sub-monolayer concentration; see the main text);  $c_{O_3} = 10^{16}$  molecules  $cm^{-3}$ ;  $T = -15$  °C; error bars represent the standard deviation.

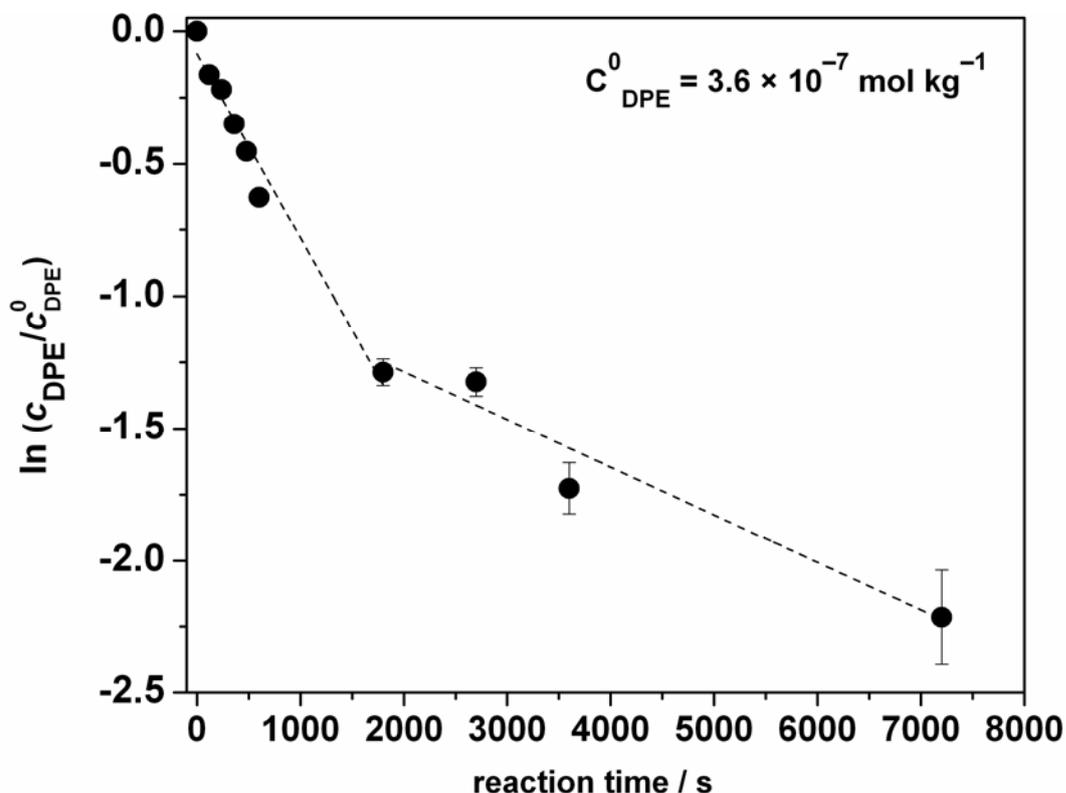


**Figure S2:** Determination of the observed rate constants  $k_{obs}$  by plotting  $\ln(c_{DPE}/c_{DPE}^0)$  vs. reaction time using the least-squares method for different initial snow surface concentrations ( $c_{DPE}^0$ );  $c_{DPE}$  are the **DPE** sample concentrations in the course of ozonation. Average values for the given  $c_{DPE}^0$  are shown; error bars represent the standard deviation.

**Determination of the Specific Surface Area.** The specific surface area (SSA) was determined similarly to the method described in our previous works<sup>3,4</sup> using Equation S1:

$$SSA = c_{DPE}^L \times N_A \times A_{DPE} \quad \text{Eq. S1}$$

where  $c_{DPE}^L$  is the concentration ( $mol\ kg^{-1}$ ; see the main text) related to the monolayer coverage,  $N_A$  is the Avogadro number, and  $A_{DPE}$  is the molecular area of **DPE** calculated from the structure optimized with a DFT method<sup>4</sup> ( $\sim 6 \times 10^{-19}\ m^2$ ).  $A_{DPE}$  was estimated from the molecule volume considering the van der Waals parameters and making the projection onto the surface parallel the molecular plane. Using the concentration  $c_{DPE}^L = 2 \times 10^{-5}\ mol\ kg^{-1}$ , the calculated SSA value is  $72\ cm^2\ g^{-1}$ . This method considers the molecules lying flat on the ice surface.



**Figure S3:** An example of the plot of  $\ln(c_{\text{DPE}}/c_{\text{DPE}}^0)$  vs. time for the initial concentration  $c_{\text{DPE}}^0 = 3.6 \times 10^{-7} \text{ mol kg}^{-1}$ . A longer exposure to ozone was set to obtain high reaction conversions and to show a possible slower kinetic component (see the main text).

## References

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