Supporting Information

Kinetics of Heterogeneous Reactions of Ozone with Representative PAHs and an Alkene at the Air-Ice Interface at 258 and 188 K

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The Uptake Coefficient

Adsorption of gaseous molecules is usually efficient due to the highly dynamic nature of the ice surface[1] but is not, in general, the rate determining step of a heterogeneous chemical reaction; thus the adsorption equilibrium is typically described by an air–ice partitioning coefficient K_{O_3}.[2]

Table S1. The partitioning coefficients obtained at 258 and 188 K[a]

	$K_{O_3}^{258\,K}$ / cm^{-3}	$K_{O_3}^{188\,K}$ / cm^{-3}
DPE[b]	$(1.5 \pm 0.04) \times 10^{-15}$	$(4.1 \pm 0.1) \times 10^{-8}$
STI	n.d.[c]	n.d.[c]
PER	$(9.2 \pm 0.6) \times 10^{-13}$	$(1.3 \pm 0.3) \times 10^{-11}$
ANT	$(3.3 \pm 0.1) \times 10^{-10}$	$(1.1 \pm 0.2) \times 10^{-9}$

[a] Calculated by fitting of the Langmuir–Hinshelwood equation to the data. [b] Determined in our previous study.[3] [c] Not determined; the K_{O_3} values could not be determined with confidence because reliable $\ln(c_S / c_S^0)$ data could not be obtained at the highest $[O_3]_g$.

The apparent uptake coefficients, γ, which describes the probability that a gaseous molecule undergoing a kinetic collision with a surface is taken up (reacts),[4] were calculated according to the following equation:[5, 6]

$$\gamma = \frac{4k^{\mathrm{I}}_{\max} K_{\mathrm{O_3}}}{\sigma_{\mathrm{S}} v_{\mathrm{O_3}} (1 + K_{\mathrm{O_3}} [\mathrm{O_3}]_{\mathrm{g}})} \qquad \text{Eq S1}$$

where σ_{S} is the substrate cross-section (estimated for DPE[7] and STI: 6×10^{-15} cm^2 molecule^{-1}, and ANT[8] and PER: 8×10^{-15} cm^2 molecule^{-1}); $v_{\mathrm{O_3}}$ is the ozone mean thermal velocity (here: 2.88×10^4 cm s^{-1} at 188 K; 3.37×10^4 cm s^{-1} at 258 K). γ decreases with increasing $[\mathrm{O_3}]_{\mathrm{g}}$; the values of $k^{\mathrm{I}}_{\max}$, $K_{\mathrm{O_3}}$, and $[\mathrm{O_3}]_{\mathrm{g}}$ were calculated based on an approximation that the data obtained at 188 K can be explained by the Langmuir–Hinshelwood model (see the main text), and must be taken with caution.

Lifetimes

The lifetime τ of the studied compounds for a typical atmospheric ozone concentration in polar areas (50 ppbv) at both 258 and 188 K were estimated from the equation:[9]

$$\tau = ([\mathrm{O_3}]^{1/2} + [\mathrm{O_3}]_{\mathrm{g}}) / k^{\mathrm{I}}_{\max} . [\mathrm{O_3}]_{\mathrm{g}} \qquad \text{Eq S2}$$

where $[\mathrm{O_3}]$ = 50 ppbv ≈ 1.2×10^{12} molecules cm^{-3}, $[\mathrm{O_3}]^{1/2}$ is the ozone concentration when surface coverage is 0.5. The $[\mathrm{O_3}]^{1/2}$ values of STI, PER and ANT were estimated from the LH dependences: STI: 2.0×10^{14} molecules cm^{-3}; DPE: 2.0×10^{14} molecules cm^{-3} (258 K), 1.0×10^{14} molecules cm^{-3} (258 K); PER: 4.0×10^{15} molecules cm^{-3} (258 K), 4.5×10^{15} molecules cm^{-3} (188 K); ANT: 3.0×10^{15} molecules cm^{-3} (258 K), 3.5×10^{15} molecules cm^{-3} (188 K).

Figures S1–S6. Determination of the observed rate constants k_{obs} by plotting $\ln(c_S/c_S^0)$ against reaction time using a weighted-least-squares method (where c_S^0 is the initial substrate S concentration and c_S those obtained at the different reaction times). Ozone concentrations, $[O_3]_g$, and k_{obs} values are shown. Average values and error bars representing the standard deviation are given.

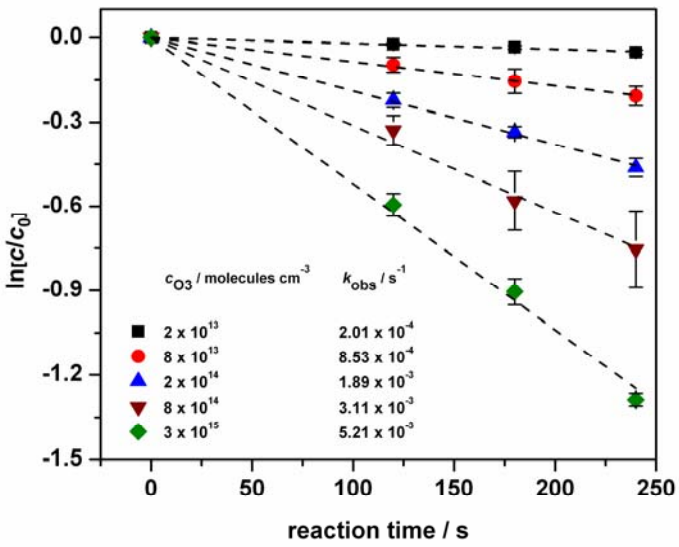

Figure S1. STI (258 K)

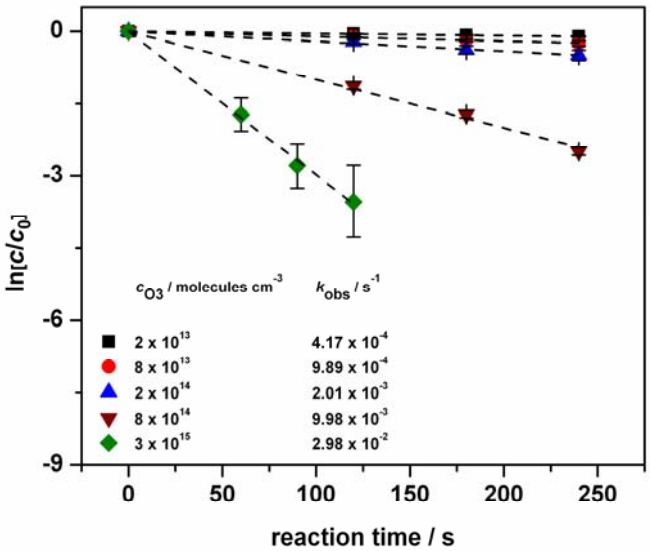

Figure S2. STI (188 K)

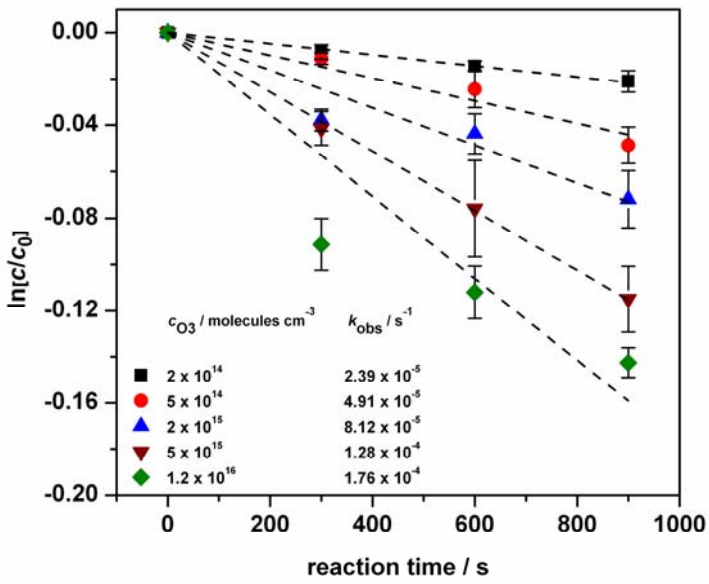

Figure S3. ANT (258 K)

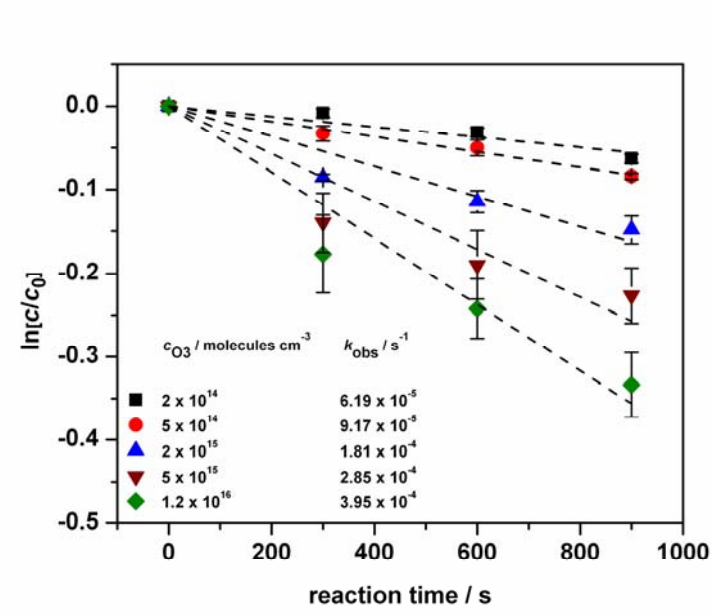

Figure S4. ANT (188 K)

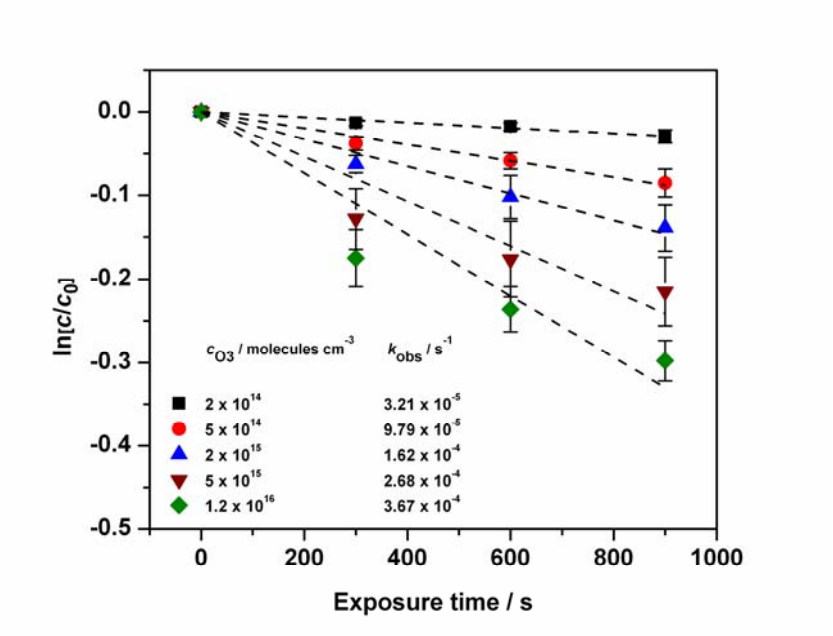

Figure S5. PER (258 K)

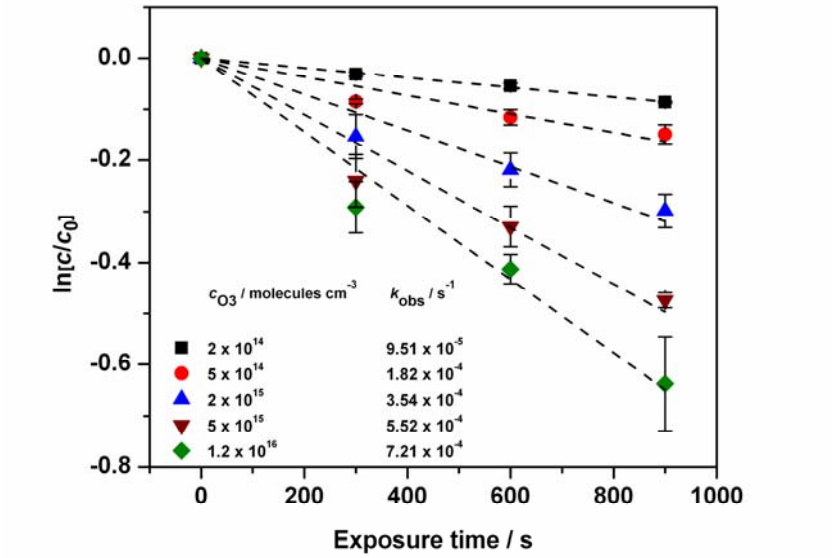

Figure S6. PER (188 K)

References

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