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Interactions of gaseous HNO3 and water with individual and mixed alkyl self-assembled monolayers at room temperature.

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Additions and corrections

A new mechanism for ozonolysis of unsaturated organics on solids: phosphocholines on NaCl as a model for sea salt particles

Federico Karagulian, A. Scott Lea, Christopher W. Dilbeck and Barbara J. Finlayson-Pitts

Phys. Chem. Chem. Phys., 2008, **10**, 528–541 (DOI: 10.1039/B712715D). ***Amendment published 20th November 2012.***

There was an error in converting the data on the time dependence of the secondary ozonide (SOZ) absorbance (Fig. 10) to rates of SOZ formation as a function of O_3 (Fig. 12). This affects the values of the rate constants reported in the paper. However, the overall conclusions regarding the reaction mechanism and the effects of water and irradiation remain valid. Corrections for the kinetics are summarized below.

Kinetics section

Fig. 10 is correct but Fig. 12 should be replaced by the following Figure:

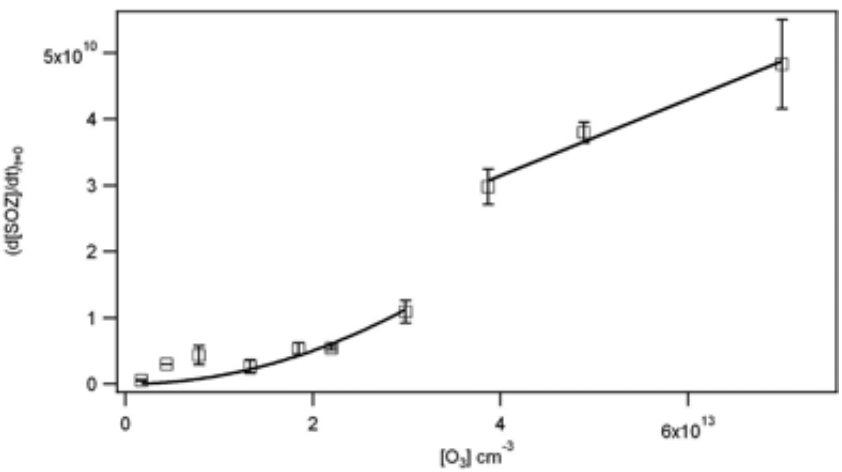

Fig. 12. Initial rates of formation of SOZ (molecule cm^{-2} s^{-1}) as a function of gas phase ozone concentration. Solid lines are the fits based on a first order dependence on ozone at high concentrations, and a second order dependence at low concentrations as described in the text.

As in the original paper, at high ozone concentrations, the rate of formation of SOZ is linear in ozone and approaches $k_1[O_3][OPPC]$. From the slope of the line at ozone concentrations from (3.9–7.0) × 10^{13} molecules cm^{-3}, $k_1[OPPC] = (5.8 \pm 1.6) \times 10^{-4}$ (2*s*). Using an OPPC concentration of 3.2×10^{13} OPPC cm^{-2}, a value for k_1 of $(1.8 \pm 0.5) \times 10^{-17}$ cm^3 $molecule^{-1}s^{-1}$ is derived. This corresponds to a reaction probability of $\gamma = 6 \times 10^{-8}$. However, because of the non-linearity of SOZ formation over the range of ozone concentrations studied, the effective reaction probability varies. For example, converting the measured rate of SOZ formation at an ozone concentration of 2.3×10^{13} molecule cm^{-3} (0.9 ppm) to an effective reaction probability gives $\gamma = 3 \times 10^{-8}$. This order of magnitude is similar to that expected from the gas phase ozonolysis of alkenes, not higher as originally stated. This is attributed to the OPPC forming a non-fluid layer on the NaCl substrate, rather than a fluid, more porous and dynamic film as for OPPC on an aqueous substrate.

Fitting the data in Fig. 12 at lower O_3 concentrations (<3 × 10^{13} molecule cm^{-3}) to the form $k_1k_4[O_3]^2[OPPC]/k_2$ as described in the original paper gives the fit shown in revised Fig. 12, from which a value is obtained for the ratio $k_4/k_2 = (2.2 \pm 0.9) \times 10^{-14}$ cm^3 $molecule^{-1}$ (2*s*). Independent values of k_4 and k_2, and hence the lifetime of POZ with respect to thermal decomposition, could not be derived from the data.

With water vapor addition

Fig. 13 shows the corrected dependence of SOZ on the water vapor concentration. The steep drop-off with increasing water indicates that the Criegee intermediate and/or the POZ are efficiently trapped by even small amounts of water. Eqn (VIII) of the original paper indicates that if water dominates the loss of the CI or POZ, the rate of SOZ formation should depend on the inverse water concentration to the first power for either CI or POZ reacting with water, or to the second power for both CI and POZ reacting with water. The dependence in Fig. 13 is best matched by variation of d[SOZ]/d*t* with $[H_2O]^2$, suggesting that both the CI and POZ are trapped by water. Given the complexity of the mechanism, rate constants for the individual steps involved cannot be extracted.

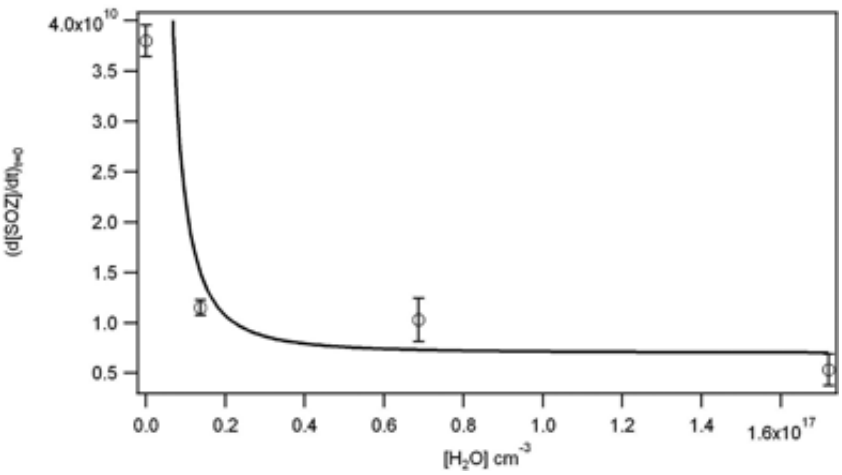

Fig. 13. Initial rate of formation of SOZ as a function of water vapor concentration at an O_3 concentration of 5 × 10^{13} molecule cm^{-3}. The line is of the form $(d[SOZ]/dt)_{t=0} = A + B/[H_2O]^2$.

Note that while the rate of SOZ formation decreases with water vapor concentration, the overall rate may not. As seen in Fig. 7 in the original paper, while the yield of SOZ decreases with water vapor, those of the carbonyl products increase. The loss of $–CH_2–$ groups at 2919 and 2850 cm^{-1} is also seen to increase with water vapor concentration, indicating a shift towards more volatile products such as the nine carbon aldehyde and/or acid that are removed in the gas stream.

Conclusions and atmospheric implications

Because unique values of the rate constants (except for k_1) cannot be derived from the data, the individual estimated lifetimes in Table 4 are withdrawn. For a value of $k_1 = (1.8 \pm 0.5) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} which can be derived from the revised data, the lifetime of OPPC with respect to the ozone reaction at 100 ppb O_3 is 6 hours. From the ratio $k_4/k_2 = (2.2 \pm 0.9) \times 10^{-14}$ cm^3 $molecule^{-1}$, under dry conditions 5% of the POZ will react with O_3 at 100 ppb O_3, with the rest decomposing to form CI and RCHO. The lifetime will be proportionally shorter, and the fraction of POZ reacting directly with O_3 larger, as the ozone concentration increases. Given the rapid decline in SOZ in the presence of even small amounts of water vapor (revised Fig. 13), trapping of the CI and POZ by water under tropospheric

conditions is likely to dominate the chemistry.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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