Supplementary material

SO_2 oxidation and nucleation studies at near-atmospheric conditions in outdoor smog chamber

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Figure S1

We performed many experiments to observe the relationships between SO₂ decay and RH for both the SO₂ only-day or only-night and the propylene–NO_x–SO₂ systems. Fig. S1, below, shows the relationship between SO₂ decay and RH in (a) the SO₂-day, (b) SO₂-night and (c) SO₂-propylene-NO_xphotochemistry system. Several pathways of SO₂ decay may occur in the chamber: loss to the walls, gas phase reactions with OH or other radicals, and aqueous phase reactions with H₂O₂. In the absence of active photochemistry, reactions via the latter channels are thought to be minor. Our night-time experiments showed no evidence of particle nucleation, and since the dilution rate is $\sim 1-1.5$ % h⁻¹ most of the SO₂ is assumed to be lost to the chamber walls. This SO₂ wall loss appears to be a function of RH (Fig. S1b). During the daytime, the reaction with OH radical leads to the particle nucleation for the SO_2 only system. It is also well known that nitrous acid (HONO) is an important precursor for OH radicals in environmental chambers (Carter et al.^[1]), which would be formed either from the dark reaction of NO₂ and adsorbed water on chamber walls (Finlayson-Pitts et al.^[2]), or from a photo-enhanced HONO production (Rohrer et al.^[3]). Thus, multiple pathways for SO₂ decay are present for the SO₂ only daytime experiments, and higher decay rates were observed (Fig. S1a) relative to the night-time experiments. For the SO₂-propylene-NO_x system, other photochemical pathways, such as H_2O_2 , RO_2 can mediate SO_2 decay. This (



Fig. S1. Trends for SO₂ decay and RH for: (a) SO₂ only, day; (b) SO₂ only, night; (c) SO₂–NO_x–propylene, day.

Figure S2

We modelled the propylene– NO_x system by using a kinetics Carbon Bond box model (CBIV, Gery et al.^[4]) with our own SO₂ chemistry. The model suggests a significant level of H₂O₂ is generated in the gas phase. The time series for relevant measurement data and model results are shown in Fig. S2.



Fig. S2. Measurement and model results of one SO_2 -NO_x-propylene experiment.

References

[1] W. Carter, R. Atkinson, A. Winer, J. Pitts Jr, Evidence for chamber-dependent radical sources: impact on kinetic computer models for air pollution. *Int. J. Chem. Kinet.* **1981**, *13*, 735. <u>doi:10.1002/kin.550130805</u>

[2] B. Finlayson-Pitts, L. Wingen, A. Sumner, D. Syomin, K. Ramazan, The heterogeneous hydrolysis of NO₂ in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism. *Phys. Chem. Chem. Phys.* **2003**, *5*, 223. <u>doi:10.1039/b208564j</u>

[3] F. Rohrer, B. Bohn, T. Brauers, D. Brüning, F. Johnen, A. Wahner, J. Kleffmann, Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR. *Atmos. Chem. Phys.* **2005**, *5*, 2189. doi:10.5194/acp-5-2189-2005

[4] M. W. Gery, G. Z. Whitten, J. P. Killus, M. C. Dodge, A photochemical kinetics mechanism for urban and regional scale computer modeling. *J. Geophys. Res.* **1989**, *94*, 12925. <u>doi:10.1029/JD094iD10p12925</u>