Atmos. Chem. Phys. Discuss., 13, C4653–C4655, 2013
www.atmos-chem-phys-discuss.net/13/C4653/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Key chemical NO_x sink uncertainties and how they influence top-down emissions of nitrogen oxides" *by* T. Stavrakou et al.

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Received and published: 10 July 2013

We would like to thank Dr. Gottschaldt for his very useful comment, which contributed to improve our manuscript.

We did a similar sensitivity study, but restricted to the HNO3-forming channel of the HO2+NO reaction (see www.atmos-chem-phys.net/13/3003/2013/). OH mixing ratios are strongly affected by this reaction and it would be ineresting to see some absolute values (e.g. global mean OH concentration) for the different simulations of Stavrakou et al. for comparison. Comparing modelled OH to observation based estimated might

also provide an additional test for the various modifications to the chemical mechanism.

The impact of the HNO_3-forming channel on OH is indeed substantial. Table 1 now includes the calculated methane lifetime with respect to OH-oxidation in the troposphere for each sensitivity simulation. The impact of the HNO_3-forming channel in HO_2+NO is found to be very dependent on the assumed temperature- and pressure-dependence of the rate k_w of the reaction NO + HO_2•H_2O → HNO_3. In our simulation BUTKO2, k_w is taken equal to its value measured by Butkovskaya et al. (2009). In Gottschaldt et al. (2013), as well as in our newly added sensitivity simulation (BUTKO3), the rate is taken equal to 42 times the reaction rate in dry conditions, which is strongly T- and p-dependent. Although the two assumptions lead to identical rates at the experimental conditions of Butkovskaya et al. (2009), the overall rate in real tropospheric conditions is a factor 2–3 higher in BUTKO3 compared to BUTKO2.

We adapted the discussion of the results as follows:

"Overall, the relative contribution of this reaction to the global tropospheric NOx sink amounts to 12% in the case of BUTKO1 scenario, and reaches 26–43% when water-assistance is taken into account (BUTKO2-3). As a result, the global NOx lifetime is reduced by 18, 32 and 75% in BUTKO1, BUTKO2 and BUTKO3 respectively, compared to the base run, whereas the lifetime of methane due to reaction with OH in the troposphere (8.1 years in MINLOSS) is increased to 9.2, 10.6 and 14.3 years (i.e. by 14, 31 and 76%), respectively. These results imply a very large uncertainty associated to the temperature and pressure dependence of the rate k_w in humid conditions. The methane lifetime changes are slightly larger than the lifetime increases (11% and 50% without and with H_2O-assistance, respectively) estimated in the modelling study of Gottschaldt et al. (2013) which adopted the same T- and p-dependence of k_w as in our BUTKO3 simulation. Part of the discrepancy with that study might be due to the lower equilibrium constant for the complexation of HO_2 adopted by Gottschaldt et al.

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(2013)."

Note that we now use the JPL recommendation for the equilibrium constant (Sander et al., 2011).

References

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