Supplement of Atmos. Chem. Phys., 19, 5805–5833, 2019
https://doi.org/10.5194/acp-19-5805-2019-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer

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1 Case of high $\mathrm{Cl_y}$

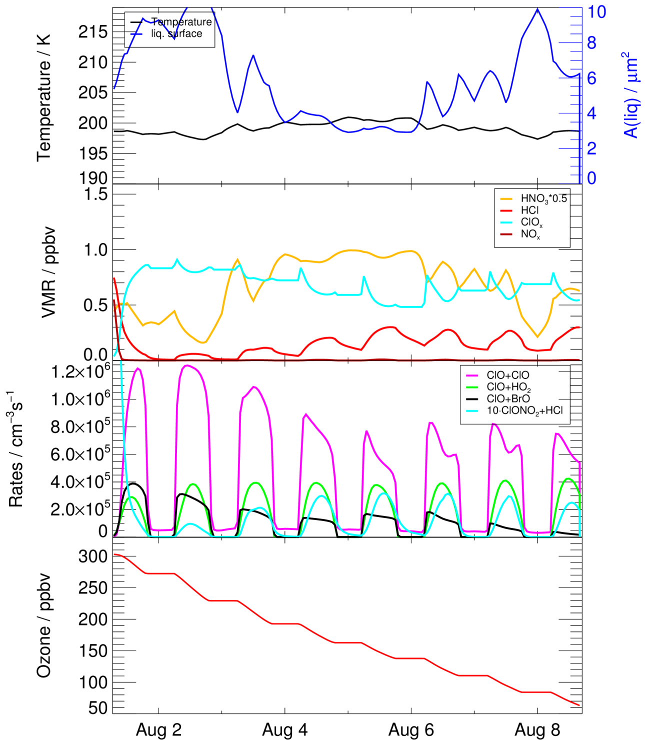

Figure 1: Behaviour under "Case of high Cl_y" conditions assuming high values for Cl_y and NO_y (see Tab. 1). Presented is the volume mixing ratio of ozone, temperature, liquid surface density, mixing ratio of $\mathrm{HNO_3}$ (scaled by 0.5), HCl, ClO_x and NO_x and reaction rates of reactions essential for chlorine activation and catalytic ozone loss cycles ($\mathrm{ClONO_2 + HCl}$) and the reactions ClO+BrO, ClO+ClO and $\mathrm{ClO + HO_2}$. The x-axis ticks refer to 00:00 local time (06:00 UCT) of that day.

Comparing the standard case and the high Cl_y case using 15 ppmv water vapour conditions, in the high Cl_y case more inactive chlorine is converted into active ClO_x on the first day of the simulation (Fig. 1). This higher ClO_x mixing ratio results in faster catalytic ozone loss cycles with peak values of $3.9 \cdot 10^5\,cm^{-3}s^{-1}$ for the reaction $ClO+HO_2$, $2.0 \cdot 10^5 cm^{-3}s^{-1}$ for the reaction ClO+BrO and $10.9 \cdot 10^5 cm^{-3}s^{-1}$ for ClO+ClO on 3 Aug 2013. Since the Cl_y-mixing ratio is much higher than in the standard case, the catalytic ozone loss cycles are dominated by the ClO-Dimer cycle and result in a much larger ozone loss than in the standard case assuming realistic Cl_y and NO_y mixing ratios.

2 Reduced Br_y Case

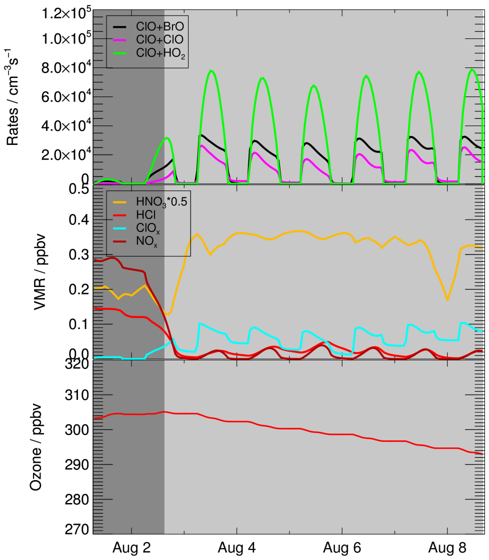

Figure 2: Impact of a Br_y reduction on the ozone loss process. The volume mixing ratio of ozone, the mixing ratio of HNO_3 (scaled by 0.5), HCl, ClO_x and NO_x and reaction rates of reactions essential for chlorine activation and catalytic ozone loss cycles ($ClONO_2$ + HCl) and the reactions ClO+BrO, ClO+ClO and ClO + HO_2. The x-axis ticks refer to 00:00 local time (06:00 UCT) of that day.

In the case of reduced Br_y, the catalytic ozone destruction in the ClO-BrO-cycle (ClO + BrO) is reduced (Fig. 2), while the rates of further reactions , which yield catalytic ozone loss, (ClO+ClO and ClO+HO_2) are similar to those of the standard case. This results in a reduced ozone destruction in the 0.5 Br_y case regarding the standard case.

3 Extended time period

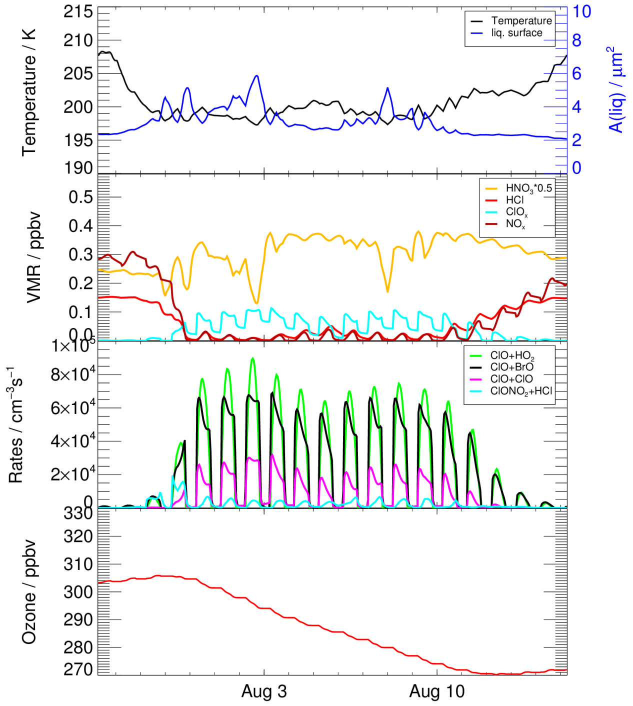

Figure 3: Temperature and chemical behavior for the 19-day simulation. Temperature, liquid surface area, the mixing ratio of ozone, HNO_3 (scaled by 0.5), HCl, ClO_x and NO_x and reaction rates of reactions essential for chlorine activation ($ClONO_2 + HCl$) and catalytic ozone loss cycles ($ClONO_2 + HCl$) and the reactions ClO+BrO, ClO+ClO and ClO + HO_2 are shown for the 19-day simulation. The x-axis ticks refer to 00:00 local time (06:00 UCT) of that day.

On 27 July 2013, the 19-day simulation starts at a temperature of 208 K (Fig. 3, right), decreasing until 29 July 2013 to lower than 200 K. The temperatures remain lower than 201 K until 11 August and increase to over 205 K on 14 August 2013.

Assuming a water vapour mixing ratio of 15 ppmv, chlorine activation occurs on 30 July 2013, after the temperatures fall below 200 K (Fig. 3, right). The mixing ratio of NO_x remains low and ClO_x remains high until 11 August, when the heterogeneous reaction rate of ($ClONO_2 + HCl$) decreases due to higher temperatures. For this reason chlorine activation cannot anymore be maintained. Thus, the time span holding a ClO_x mixing ratio high enough for the occurrence of catalytic ozone loss cycles comprises 14 days and ozone destruction stops on 12 August.