# ECHAM5 simulations with the HO$_2$ + NO → HNO$_3$ reaction

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ABSTRACT: A HNO$_3$-forming channel of the HO$_2$ + NO reaction recently found in laboratory measurements (Butkovskaya et al., 2005, 2007) may significantly alter the concentration of HNO$_3$, NO$_x$, O$_3$ and other trace gases in the tropopause region. This region is also significantly affected by air traffic NO$_x$ emissions. Cariolle et al. (2008) adopted a pressure- and temperature dependent parameterisation of the rate constant to assess the impact of the HO$_2$ + NO -> HNO$_3$ reaction on trace gas concentrations in a 2-D stratosphere-troposphere model, and a 3-D tropospheric chemical transport model. We implemented the parameterisation of Cariolle et al. (2008) into the 3-D stratosphere-troposphere chemistry-climate model ECHAM5 / MESSy. Here we present results of our test runs, in support of planned studies of the effects of aircraft emissions on atmospheric chemistry.

## 1 BACKGROUND

The concentration of ozone in the upper troposphere and lower stratosphere region (UTLS) is mainly controlled by the reactive NO$_x$ and HO$_x$ cycles (figure 1).
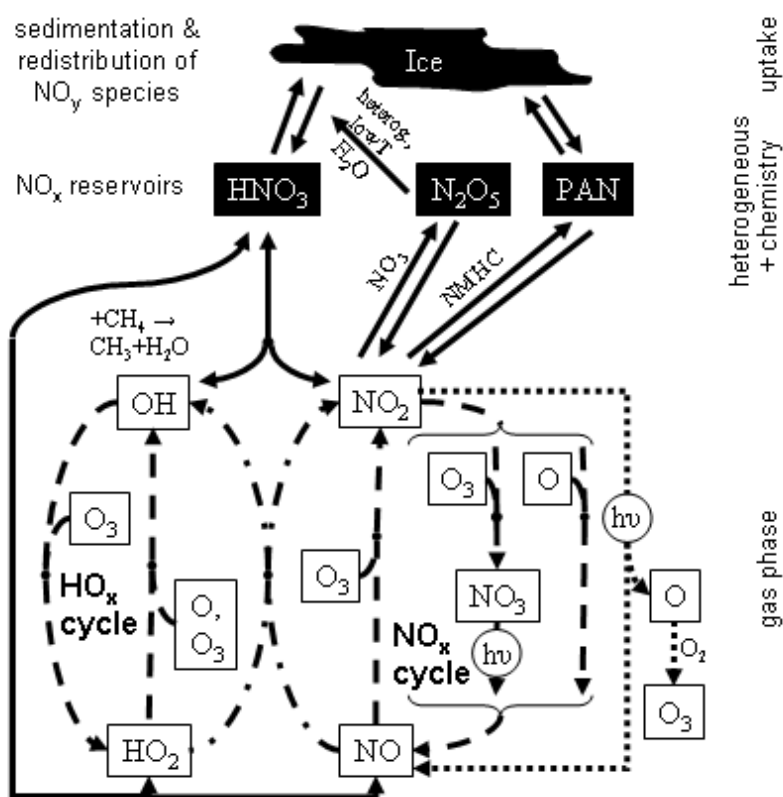


Figure 1. Major reactions in the UTLS involving ozone, methane NO$_x$, NO$_y$ and HO$_x$. Solid lines represent reservoir reactions, dotted lines show reaction paths of ozone production, dashed paths indicate ozone destruction, and dash dot is neutral with respect to ozone.

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Aircraft NO$_x$ emissions peak in the UTLS. Considering gas phase chemistry, the NO$_x$ effect on ozone changes sign in the altitude range between about 12 and 18 km (Søvde et al., 2007). Below the tipping point, the ozone destructing NO$_x$ cycle is bypassed via peroxy radicals. NO$_x$ emissions lead to increased ozone production. Peroxy radicals and NO$_2$ photolysis are less important at higher altitudes. There aircraft NO$_x$ emissions intensify the NO$_x$ cyle, enhancing ozone destruction. NO$_x$ may be removed from the system by heterogeneous reactions, but also by the recently discovered HNO$_3$-forming channel of the HO$_2$ + NO reaction (Butkovskaya et al., 2005, 2007):

$$k_1; \quad HO_2 + NO \rightarrow NO_2 + OH \tag{1}$$

$$k_2; \quad HO_2 + NO \rightarrow HNO_3 \tag{2}$$

with the rate constants $k_1$ and $k_2$.
The HO$_2$ + NO conversion has been assumed to have a temperature-dependent rate constant (Sander et al., 2003),

$$k_0 = k_1 + k_2 = 3.5 \cdot 10^{12} \cdot \exp\left(\frac{250}{T}\right) \tag{3}$$

with temperature $T$ in [K]. In the following we study the effects of three different combinations of $k_1$ and $k_2$ on UTLS gas phase chemistry, extending the work of Cariolle et al. (2008).


## 2   BASE MODEL

We use the global chemistry-climate model ECHAM5 (Roeckner et al., 2003) / MESSy (Jöckel et al., 2006). Dynamics and chemistry are fully coupled. Our runs are based on the setup of Jöckel et al. (2006), but using MESSy version 1.6, with T42 / L90 resolution and the top layer centered at 0.01 hPa. Gas phase chemistry was calculated with the MECCA1 chemistry module (Sander et al., 2005), consistently from the surface to the stratosphere. However, the runs presented here were originally designed to find a parameterisation for correcting upper stratospheric chemistry in low resolution models. Therefore our chemical mechanism has full stratospheric complexity, but neglects the NMHC, sulfur, and halogen families in the troposphere. The initial conditions correspond to January 1978 and we evaluated twelve months, starting November 1978.
Figures 2a show the 12-month average of the zonal mean mixing ratios for HNO$_3$, NO$_x$ and O$_3$, in the base model, run A. Reaction 1 is included with $k_1 = k_0$ (equation 3). The HNO$_3$-forming channel (reaction 2) is ignored here, i.e. $k_2 = 0$.


## 3   EFFECTS OF THE HO2 + NO → HNO3 REACTION

Simulation B differs to the base run just in $k_1$ and $k_2$:

$$k_2 = \frac{k_0 \cdot \beta}{1 + \beta} \tag{4}$$

$$k_1 = k_0 - k_2 \tag{5}$$

with pressure $p$ [Pa] in

$$\beta(p,T) = 0.01 \cdot \left(\frac{530}{T} + p \cdot 4.8 \cdot 10^{-6} - 1.73\right). \tag{6}$$

Hence both reaction rates depend on temperature and pressure in this case. Equation 6 was proposed by Cariolle et al. (2008). It is based on an empirical fit to measurements and valid for dry conditions, in the range 93 - 800 hPa and 223 - 298 K. They noted deviations from equation 6 for temperatures above 298 K.
Figures 2b show the differences $d$ between run B and the base model. The results are noisy, because both runs, A and B, were dynamic. They had all couplings between chemistry and meteorology switched on. Running the ECHAM model in a chemistry transport mode would have been better

suited for our sensitivity runs B and C, but this option was not available. Given the exploratory nature of this study, we believe the present approach is acceptable. Due to the different dynamics in both runs, a low background value in one model might coincidentally fall together with a high value in the other model. The biggest effects on $HNO_3$, $NO_x$ and $O_3$ correlate with rather small background mixing ratios. To filter out some noise, and to avoid random division by numbers close to zero, we normalized all values $d$ by the locally highest background value:

$$d = \frac{v_B - v_A}{\max(v_A, v_B)} \cdot 100\% \tag{7}$$

$v_A$ and $v_B$ are the zonal mean mixing ratios of the same species, in the base run and model B, respectively. We get similar variations to the base model as Cariolle et al. (2008). They show results for March only. However, in another attempt to reduce noise, we evaluated 12 months instead of just March. Results for March display a similar pattern as the yearly mean, in our runs.

Inclusion of the $HNO_3$ forming channel results in a general $HNO_3$ increase, prompting an overall $NO_x$ decrease. As expected, ozone correlates with $NO_x$ variations below ≈12 km, while there is anticorrelation above ≈18 km.

Cariolle et al. (2008) applied equation 6 up to an altitude of 30 km, although it is only based on measurements for pressures corresponding to an altitude of about 15 km. Therefore we did not expect any problems for lower pressures and applied equation 6 up to 0.01 hPa (39 km). Similar to Cariolle et al. (2008), we get a locally pronounced $HNO_3$ increase about 15 km over the equator, followed by a region of smaller effects and another increase from 25 km upwards. However, in our model we note the biggest relative $HNO_3$ increase above 30 km. It remains unclear if this effect is real, an artefact due to the extrapolation of equation 6, or due to the very low background concentration in that altitude.
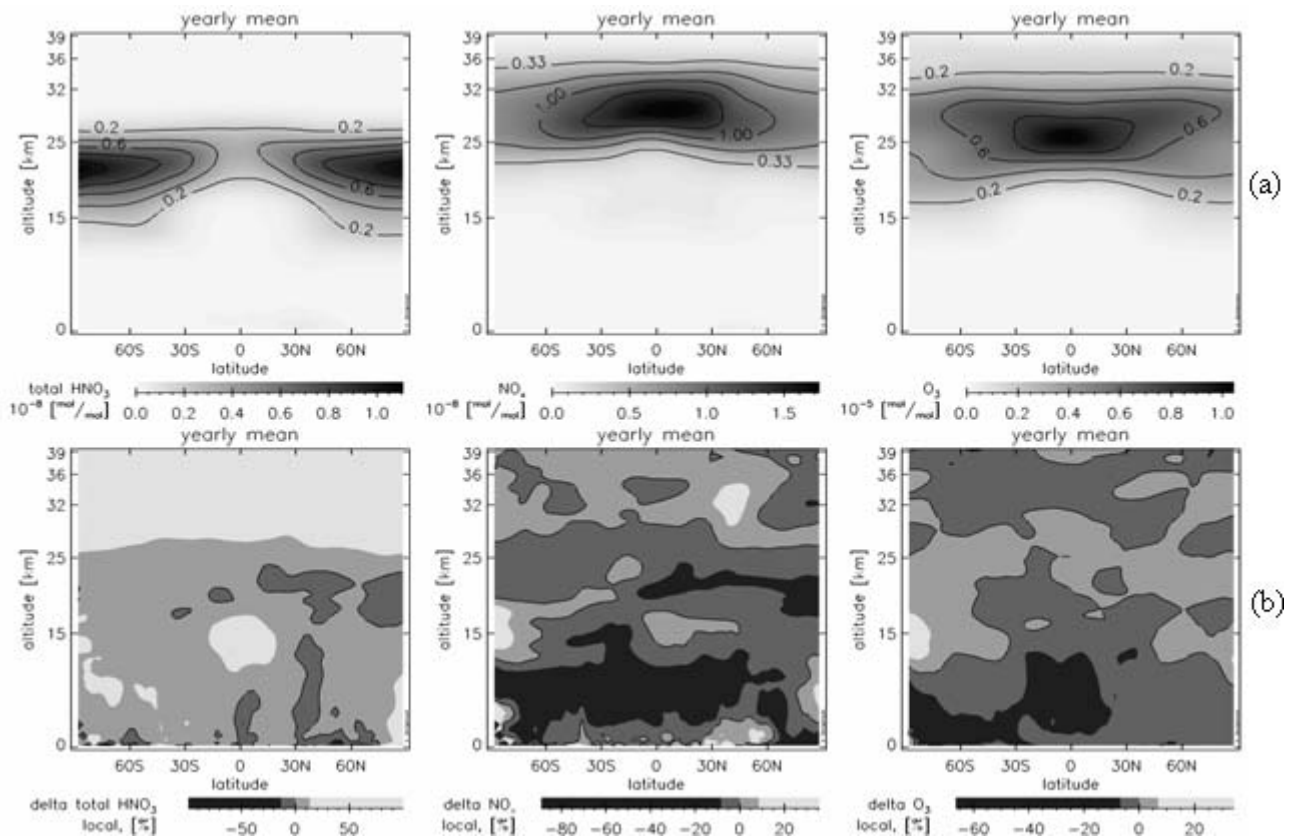


Figure 2: (a) Annual mean values of the zonal average concentrations of $HNO_3$, $NO_x$ and $O_3$ in base run A, without $HO_2 + NO \rightarrow HNO_3$ reaction; (b) Run B: deviations from A after inclusion of the dry $HNO_3$ reaction

## 4 CONCLUSIONS

The HNO$_3$ forming channel of the HO$_2$ + NO reaction has the potential to alter UTLS chemistry significantly. Adding the dry HO$_2$ + NO → HNO$_3$ reaction to our model resulted in a general increase of HNO$_3$, a decrease of NO$_x$ and related effects on ozone. The spatial pattern of variations confirms the results of Cariolle et al. (2008). However, it is not clear if the parameterisation used for the reaction rate is valid above 15 km. Measurements under stratospheric conditions are needed. At any rate, it is important to confirm the data set presented by Butkovskaya et al. (2005, 2007) by independent laboratory studies. A better noise reduction strategy and refined tropospheric chemistry in the model might be useful to study the impact of this reaction in more detail.

## 5 ACKNOWLEDGEMENTS

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