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Water vapor enhancement of the HNO_3 yield in the HO_2 + NO reaction and its impact on the atmospheric composition

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We have previously observed a minor channel forming nitric acid (1b) in the reaction of HO_2 with NO [1]:

$HO_2 + NO \rightarrow OH + NO_2$ (1a); $HO_2 + NO \rightarrow HNO_3$ (1b)

We have further determined the HNO_3 yield, $\beta = k_{1b}/k_{1a}$, of reaction (1) over the whole pressure and temperature ranges of the troposphere[2]. This yield increases from 0.5% near the earth surface to 0.9% in the upper troposphere (UT). The integration of these laboratory data in a 2D and a 3D model has been shown to have a significant impact on the tropospheric concentrations of HOx, NOx, HNO_3 and ozone species, specially in the tropical UT [3].

The previously observed water vapour enhancement of the nitric acid yield in reaction (1)[1], has been better quantified recently. The experiments have been carried out using the same turbulent flow reactor coupled to a chemical ionisation mass spectrometer (CIMS) for the analysis of both radical and molecular species. In the CIMS measurements special care was taken to discriminate between the water effect on the ion source processes and that on HNO_3 formation in reaction (1). A significant H_2O enhancement of the nitric acid yield has been measured. For instance, at 298K and 200 Torr, an enhancement factor of about 8 has been found at 50% relative humidity. Under these conditions, a rate constant 40 times higher than k_{1b} was derived for the reaction:

$HO_2 \bullet H_2O + NO \rightarrow HNO_3 + H_2O$ (1bw)

assuming that the water enhancement is due to this reaction between the $HO_2 \bullet H_2O$ complex and NO. The integration of these new data in a 0D model indicates that H_2O significantly increases the impact of HNO_3 formation in reaction (1) on the atmospheric composition, in particular near the earth surface as a HNO_3 source and HOx loss process.

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