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Nitric acid formation in the HO_2 + NO reaction: parametrisation in the pressure and temperature ranges of the troposphere

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

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

The branching ratio β = k_{1b}/k_{1a} for the new reaction (1b) was found to range from *ca* 0.2 to 0.8 from 300 K to 200 K, at a pressure of 200 Torr. This reaction is a chain termination process which can significantly influence the troposheric concentrations of HOx (OH, HO_2), NOx, NOy and related species. Further experiments have shown that the branching ratio β was also pressure dependent; this ratio has been investigated in the temperature and pressure ranges 220-310K and 100-600 Torr, respectively, in order to provide a parametrisation for modelling of the tropospheric composition. The experiments have been carried out in a turbulent flow reactor coupled to a chemical ionisation mass spectrometer for the analysis of both radical and molecular species. The detection sensitivity for the key HNO_3 species has been increased by amplification of the HNO_3 formation in the reactor by adding CO and O_2 to the flow of the co-reactants HO_2 and NO and of N_2 used as carrier gas. A complete and consistent set of β values have been determined in the temperature and pressure ranges mentioned above. The best fit of the parametrisation to the experimental plots could be expressed as: β(P,T) = a /T + $b\times$P – c, where a, b and c are fixed parameters. The experimental data will be presented in details as well as model calculations from other groups showing the impact of this new reaction on the tropospheric composition.

[1] N. Butkovskaya et al., J. Phys. Chem. A 109, 6509, 2005.