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Formation of small alkyl nitrates in RO_2 + NO reaction and its significance in gas phase tropospheric chemistry

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The OH-initiated oxidation of VOCs produces ozone and other photooxidants in the presence of NO_x through a chain mechanism involving the HO_x (OH, HO_2) and RO_2 chain carrier radicals. The efficiency of this mechanism is reduced by reaction of these radicals with NO_x which produce NO_x "reservoir" or "sink" species. In particular, reaction of peroxy RO_2 radicals with NO forming $RONO_2$ can be a significant chain termination step. This latter is minor channel (b) of the peroxy radical + NO reaction which proceeds mainly through the chain propagation channel (a):

$RO_2 + NO \rightarrow RO + NO_2$ (a)

$\rightarrow RONO_2$ (b)

In case of alcane precursors R is the alkyl group R=C_nH_{2n+1}. Up to now, the yield of nitrate in the above reaction has been systematically determined only for alkyls with $n \geq 5$ [1]. The branching ratio $\beta = k_b/k_a$ for smaller alkyls do not exceed a few percent at atmospheric pressure, and such data can be obtained using appropriate experimental methods, in particular, the turbulent flow reactor coupled with a chemical ionisation mass spectrometer (TFR-CIMS) [2,3]. In our experiments using this technique, the working pressure and temperature ranges in the flow reactor were 50-600 Torr and 220-300 K, respectively. The combination of CIMS analysis in positive (PTR) and negative (F- NICI) mode allows a selective and sensitive detection of the species, in particular RONO and $RONO_2$, produced at very low concentrations. The data to be presented include the formation yields of $RONO_2$ in the reactions of short chain alkyl peroxy radicals (CH_3O_2, $C_2H_5O_2$ and iso-$C_3H_7O_2$) with NO, as a function of pressure and temperature. At T = 298 K and atmospheric pressure, β = 2.4, 3.3 and 4.0 %, respectively, for reaction of NO with CH_3O_2, $C_2H_5O_2$ and iso-$C_3H_7O_2$.

Even with the very low branching ratios obtained reaction (b) is expected to significantly influence the VOC/NO_x/ozone chemistry and related tropospheric composition at both regional and global scales. This effect can be assessed by integrating the provided parametrisation equations of β as a function of pressure and temperature into chemistry-transport models.

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