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Temperature dependence of alkyl nitrate formation from the reaction of alkyl peroxy radicals with NO

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The reaction of alkyl peroxy radicals (RO_2) with NO is an important intermediate step in the gas-phase degradation of volatile organic compounds (VOC) under tropospheric conditions. The reaction is thought to proceed via formation of a peroxy nitrite intermediate, RO_2NO^*, which can decompose to RO and NO_2 or undergo an internal molecular rearrangement to yield the alkyl nitrate product. An accurate knowledge of the branching ratio for the title reaction is thus important to model ozone formation in the troposphere and to predict the chemistry, hence the environmental impact, of atmospheric VOC emissions.

The dynamics of the chemical mechanism influencing the formation of organic nitrates are not well understood. $RONO_2$ yields have been shown to depend on the size and complexity of the reactant RO_2 and to be a function of temperature and pressure but an accurate quantitative knowledge of this dependence is lacking. Most of the published data, for example, were obtained from the photo-oxidation of VOC precursors, thus were not isomer specific, and the extent of the reported temperature dependence varies over a factor of $\sim$2.

In this work, we have investigated the formation yield of three C_5 pentyl nitrate isomers from the reaction of the corresponding pentyl peroxy radicals with NO at atmospheric pressure over the temperature range (262-305) K. Contrary to previous observations, we observed $RONO_2$ yields increasing along the series primary $<$ secondary = tertiary. Our results also suggest a significant temperature dependence for the formation of nitrates from the reaction of pentyl peroxy radicals with NO, with $RONO_2$ formation increasing almost by a factor of 2 over the studied temperature range.