

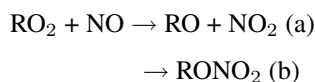


Formation of small alkyl nitrates in $\text{RO}_2 + \text{NO}$ reaction and its significance in gas phase tropospheric chemistry

Georges Le Bras (1), Nadia Butkovskaya (1), and Alexandre Kukui (2)

(1) Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE), CNRS, Orléans, France (georges.lebras@cnrs-orleans.fr), (2) Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS, Guyancourt, France.

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):



In case of alkane precursors R is the alkyl group $\text{R}=\text{C}_n\text{H}_{2n+1}$. 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 , $\text{C}_2\text{H}_5\text{O}_2$ and iso- $\text{C}_3\text{H}_7\text{O}_2$) with NO, as a function of pressure and temperature. At $T = 298$ K and atmospheric pressure, $\beta = 2.4, 3.3$ and 4.0 %, respectively, for reaction of NO with CH_3O_2 , $\text{C}_2\text{H}_5\text{O}_2$ and iso- $\text{C}_3\text{H}_7\text{O}_2$.

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.

1. R. Atkinson, Phys. Chem. Ref. Data, Monograph No. 2, 1994.
2. N. Butkovskaya, A. Kukui, G. Le Bras, J. Phys. Chem. A, 114, 956, 2010.
3. N. I. Butkovskaya, A. Kukui, G. Le Bras, Z. Phys. Chem, 224, 1025, 2010.