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Aqueous-phase reactivity of polyfunctional organic nitrates under atmospheric conditions

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Organic nitrates ($RONO_2$) are relevant compounds in the atmosphere as they are involved in the NO_x spread, and thus they are related to the O_3 and SOA production. For this reason, the study of the reactivity of $RONO_2$ has a huge importance for achieving proper atmospheric pollutants predictions. So far, the studies of these compounds have only been focused on their fates in the gas phase, however, most of the $RONO_2$ are highly functionalized, with a relevant presence in the condensed phases.

The present work deals with the atmospheric reactivity of several $RONO_2$ within the aqueous phase. We will present our methodology, including direct photolysis and OH-oxidation, validated with two commercial alkyl nitrates in the aqueous phase. A complete study has been performed by following the reaction with a wide variety of analytical techniques (LC-UV, LC-MS, GC-MS, IC, PTR-MS, NO_x and EPR) covering the evolution of the compounds and intermediate reactants in the aqueous-phase and it is exchange with the gas-phase.

For OH-oxidation, we have determined precise kinetic rate constants by a new competitive kinetics method that can be used for other relevant molecules that partition between the gas and the aqueous phase. We have elucidated the mechanisms which take place in the reactions and have identified the main reactions products. The results show the extent to which the aqueous processing differs from the gas-phase reactivity. The formation of highly oxidised compounds have been found, thus implicating the connexion between SOA formation and aqueous phase reactivity. After validation, this procedure is applied to more functionalized and atmospherically relevant $RONO_2$ such as those derived from biogenic compounds.

The results show the relevance of multi-phase studies of polyfunctional $RONO_2$ in the atmosphere.