

Multiphase reactivity of organic nitrates in the atmosphere

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Organic nitrates (RONO₂) are secondary species in the atmosphere formed from the reaction between NO_x and Volatile Organic Compounds (VOC). RONO₂ are considered as NO_x sinks and reservoirs, and thus they play a key role in the chemical transport of pollutants. While their gas-phase chemistry has been studied, and has been reported to lead to NO_x recycling pathways, their reactivity in condensed phases is far from being understood. However, these compounds represent an important fraction of organic matter in condensed phases.

This work studied, for the first time, the aqueous-phase photolysis and ·OH oxidation of eight RONO₂: 5 alkyl nitrates, and 3 polyfunctional organic nitrates. Their aqueous-phase kinetics were determined, and the main reaction products and mechanisms were identified and elucidated.

The kinetic results showed that RONO₂ is less reactive in the aqueous phase than in the gas phase. The photolysis of RONO₂, previously reported as a relatively fast sink for atmospherically relevant RONO₂ in the gas phase, is extremely impeded in the aqueous phase due to very low quantum yields. The aqueous-phase ·OH oxidation of RONO₂ was also found to be slower than the gas-phase reaction. Nevertheless, aqueous-phase ·OH oxidation was determined to be the major chemical sink for RONO₂ that partition significantly into the aqueous phase as isoprene and terpene nitrates.

The identification of reaction products showed that RONO₂ reactivity substantially differs from the gas phase. While RONO₂ recycle ·NO₂ to the atmosphere through gas-phase chemistry, in the aqueous phase, HNO₂ and HNO₃ are directly formed. This is of special relevance since their partition to the aqueous phase implies a sink of ·NO₂, and thus a less effective pathway in the transport of pollution. Nevertheless, this reactivity is a potential source of HONO, an important precursor of ·OH radicals for which atmospheric formation is complex and far from being understood.

Overall, this work shows that RONO₂ reactivity in condensed phases should be considered in atmospheric chemistry transport models to better assess the oxidizing capacity of the atmosphere and the distribution of pollution at the regional and global scales.