

Reactivity of Unsaturated Oxygenated VOC with NO₃ Radical

B. Picquet-Varrault, M. Scarfogliero and J-F. Doussin

LISA, CNRS and University Paris 12&7, 61 Av. Général de Gaulle, 94010, Créteil, France

Oxygenated volatile organic compounds are widely emitted into the troposphere by both anthropogenic (use as solvents in paints, pharmaceutical process synthesis, adhesives) and biogenic sources (). When released into the troposphere, they can undergo either photolysis or oxidation by OH and NO₃ radicals and by ozone. The nitrate radical is formed by reaction of NO₂ with ozone and has been observed and shown to be an important oxidant during night time. Since NO₃ is very efficiently photolysed in sunlight and reacts rapidly with NO which is a predominantly daytime species, it can not accumulate during the day. For this reason, its daytime reactivity was considered to be negligible for many years. But recently, and have shown that for highly reactive VOC, NO₃-oxidation was not a negligible process during the day. For example, NO₃-oxidation of α -pinene in the presence of NO_x contributes to 10-40% of the total daytime oxidation rate.

Unsaturated oxygenated VOC, because of their unsaturation and the potential activation effect of the oxygenated function are suspected to be very reactive. Hence, their reactivity with NO₃ may contribute significantly to their loss process even during the day. However one can observe that there is a strong lack of kinetic and mechanistic data concerning NO₃-oxidation processes in comparison to those involving OH radicals in the literature. Therefore, in order to precisely evaluate the implication in nighttime and daytime chemistry of these compounds, new kinetic and mechanistic data for their reactivity toward NO₃ are absolutely needed.

To improve our knowledge of these processes and to provide a consistent experimental database for predictions by SAR, we choose a “systematic” approach aiming at studying the influence of VOC molecular structure (nature of the oxygenated function, length and branching of the alkyl chain) on their reactivity. Hence, series of unsaturated oxygenated VOC (esters, ethers, alcohols, carbonyls, ...) are studied.

First kinetic and mechanistic experiments on series of four vinyl ethers and three unsaturated esters have been performed. Experiments were carried out under atmospheric conditions (295 \pm 3K, atmospheric pressure) in the simulation chamber of LISA made of a Pyrex reactor (6 meters long, volume 977 litres). Analysis were performed using two *in-situ* spectrometric devices, a FTIR spectrometer and a UV-visible spectrometer, both coupled to multi-reflection White-cells (infrared path length: 156 m, UV-visible path length: 72 m). In particular, UV-visible spectrometry was used to monitor NO₃ concentrations during the experiments for absolute rate determinations.

Kinetic and mechanistic results will be presented and reactivity of studied compounds will be discussed with respect to their chemical structure.

References