



Branching ratios between the abstraction and addition channels in the reactions of OH radicals with monoterpenes

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Secondary Organic Aerosol (SOA) formation in the atmosphere is described as a mass transfer of volatile organic compound oxidation products with low vapour pressures in particular phases. Among the different aerosol components, the SOA represent an important fraction, but, the fundamental processes governing their physics and chemistry in the atmosphere are poorly understood. So it is important to characterize and understand the mechanisms of their formation.

It is well-known that atmospheric oxidation of monoterpenes is an important process in tropospheric SOA formation. Consequently, the identification and quantification of reaction products from the oxidation of monoterpenes in the gas phase have been receiving great attention over the past years.

However, the atmospheric degradation leads to the formation of a plethora of reaction products and proceeds through a very complex mechanism that is still not fully characterised.

In our study, we have focused on SOA formation from OH + monoterpene reactions and more precisely on the primary oxidation steps of γ -terpinene and d-limonene by OH radicals. Indeed, the primary reaction of monoterpenes with hydroxyl radicals can in principle occur by two reaction pathways: OH-addition and H-abstraction. In this work, we have determined branching ratios of these reactions. Although there seems to be a consensus in the literature that OH-monoterpene reactions proceed almost exclusively by addition, several measurements have shown that in some case H-abstraction can represent up to 30% of the total reaction rate constant. Therefore it is necessary to determine this branching ratio in order to know, in particular, the main peroxy radicals formed and propose a mechanism for the gas phase oxidation of terpene by hydroxyl radicals.

(γ -terpinene + OH) and (d-limonene + OH) reactions have been studied i) at atmospheric pressure, using laser photolysis coupled with UV absorption radical detection, and ii) at low pressure, using discharge-flow reactor coupled to mass spectrometry. Therefore, it has been possible to measure the branching ratios between the abstraction and addition channels at different pressures and to discuss on H-abstraction importance for all reactions of monoterpenes with hydroxyl radicals.

This work has shown that, contrary to the results of the available literature, H-abstraction is a significant reaction pathway for the reaction of monoterpenes with hydroxyl radical. Therefore, oxidation products resulting from the H-abstraction should not be neglected in mechanisms describing the reaction of monoterpene + OH and SOA formation.