

New insights into the cool flame oxidation of terpenes and surrogates: detection of highly oxygenated, polyunsaturated, and aromatic products using very high-resolution mass spectrometry

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Terpenes are hydrocarbons naturally released by vegetation. They constitute a large fraction of volatile organic chemicals present in the troposphere. In addition, because of their high-energy-density, this class of chemical compounds could be used as biojet fuel. Cetane numbers of monoterpenes have been determined to be of the order of 20. Then, one could also use them as drop-in fuels to reduce the carbon footprint in transportation. However, the use of terpenes as biofuel or drop-in fuel would undoubtedly contribute to increasing their concentration in the troposphere through unburnt fuel emissions and evaporation during transport and refueling. While the kinetics of oxidation of terpenes under troposphere-relevant conditions has been the topic of numerous studies, a good understanding of the multiple oxidation routes has not been reached yet. The chemical kinetics of combustion of this class of chemicals has not received much attention to date since only burning velocity in air and impact on ignition have been reported in the literature.

Recently, we tried to better characterize the autoxidation products of terpenes under cool-flame conditions. We investigate the formation of highly oxidized products, aromatics and polyunsaturated products. We carried out oxidation experiments in a jet-stirred reactor at 1 bar. Oxidation products were characterized using high-resolution mass spectrometry and soft ionization (+/- heated electrospray ionization –HESI– and +/- atmospheric pressure chemical ionization –APCI). As an example, we will present results for limonene-O₂-N₂ and α -pinene-O₂-N₂ mixtures oxidized in a jet-stirred reactor at 1 bar, in the cool flame regime, and fuel-lean conditions. Results obtained under the same conditions for a simple surrogate will be presented. Samples of the reacting mixtures were collected, dissolved in acetonitrile, and analyzed by Orbitrap mass spectrometry after flow injection or chromatographic separation by ultra-high-performance liquid chromatography and soft ionization. H/D exchange using D₂O and reaction with 2,4-dinitrophenylhydrazine were performed for probing the existence of hydroxy, hydroperoxy, and carbonyl functions in the products, respectively. A very large set of oxidation products, including highly oxygenated organic products with five and more oxygen atoms, was observed. Aromatic and polyunsaturated products were detected. Van Krevelen plots computed oxidation state of carbon and degree of unsaturation in products were used to rationalize the results.

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