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On the formation of hydroxyxacetone in the ozonolysis of terpenes

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Terrestrial vegetation releases a great variety of volatile organic compounds (VOC) into the atmosphere. Monoterpenes, like myrcene, ocimene and terpinolene contribute significantly to this global biogenic VOC emission. In the atmosphere, monoterpenes rapidly undergo oxidation reactions by OH radicals (mainly during the daytime), NO_3 radicals (mainly during the nighttime) and O_3 to form multifunctional oxidation products. The products of these reactions are likely to be of low volatility and hence might lead to secondary organic aerosol (SOA) formation.
In the present study, we report results from a series of chamber experiments performed in the LEAK chamber at TROPOS in which the formation of carbonylic compounds obtained from myrcene, ocimene and terpinolene O_3 reactions with and without an OH radical scavenger have been measured. During the experiments the consumption of the monoterpene as well as the formation of gas-phase products was monitored using a proton transfer reaction mass spectrometer (PTR-MS). Ozone concentration was measured by an O_3 monitor. In addition to the products observed by means of the PTR-MS by their m/z values, an identification of hydroxyacetone by its DNPH derivative was performed.
Besides the expected carbonylic compounds like acetone and the respective C7H10O compound the formation of hydroxyacetone in the ozonolysis has been observed. The emergence of the gas-phase product hydroxyacetone as direct result of the myrcene ozone reaction will be mooted, because hydroxyacetone seems to be formed directly from the Criegee radical (dimethyl carbonyl oxide). Such a rearrangement of a Criegee radical is different from the currently discussed reaction pathways. The assumption that hydroxyacetone is directly formed in the ozonolysis of myrcene, ocimene and terpinolene is confirmed by the fact that the experiments with OH scavenger revealed also the formation of hydroxyacetone.