Comparison between modelling and experimental measurements of Criegee intermediates from the ozonolysis of biogenic and anthropogenic VOCs

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One of the most important reactions in the troposphere is ozonolysis of alkenes contributing to local photochemical smog and global climate change (Vereecken, 2013). Ozonolysis of alkenes occurs with a generally accepted mechanism, in which ozone adds to the double bond of alkenes forming a primary ozonide, which promptly decomposes to form a carbonyl compound and a biradical/zwitterion called Criegee intermediate (CI) (Criegee, 1975). CIs are highly reactive and short-lived and therefore their analysis represents an analytical challenge.

We generated CIs in a flow tube by reacting olefinic compounds with ozone and we stabilised them with the volatile spin trap 5,5-dimethyl-pyrroline N-oxide (DMPO) prior to analysis with proton transfer reaction mass spectrometry (PTR-MS). In a recent study we unambiguously identified the structure of the CI-spin trap adducts formed in the ozonolysis of α-pinene (Giorio et al, submitted). Identification was performed and molecular structures of the adducts were determined with mass spectrometry techniques and nuclear magnetic resonance and supported by density functional theory (DFT) calculations (Giorio et al., submitted).

We have now expanded the study to the ozonolysis of various biogenic alkenes, including β-pinene, limonene and methacrolein, as well as anthropogenic alkenes, including cis-2-hexene and styrene. As an example, for the ozonolysis of β-pinene both of the expected C1 and C9 CIs have been detected. These measurements indicate that the ratio between the yields of the C9 CI- and the C1 CI- DMPO adducts formed in this system is about 0.1, while theoretical estimates with the model "Master Chemical Mechanism" (MCM) 3.3.1 suggest a ratio of 0.7 (considering the stabilised CIs) (Saunders et al., 2003). This difference is likely due to different reaction rates of the two CIs with the spin trap DMPO. Similarly, for limonene, all three masses corresponding to the CIs from ozone attack to both the endo and the exo double bonds have been detected. For all the tested VOCs, experimental measurements were compared with MCM modelling results and discrepancies discussed in terms of stability of the CI-DMPO adducts derived from DFT calculations.

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