

Unambiguous detection of speciated stabilized Criegee intermediates via gas phase derivatization followed by detection using mass spectrometry

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Ozonolysis of unsaturated volatile organic compounds proceeds via formation of primary ozonides followed by decomposition leading to Criegee intermediates (CI). Their internal energy, buffer gas density and temperature and number of internal degrees of freedom affect their unimolecular lifetime. Stabilized CI (sCI) have sufficient long lifetimes that their fate is determined by trace gases present in the atmosphere. Due to the lack of reliable measurement techniques – especially for larger CI – their role in atmospheric chemistry still remains largely ambiguous.

We present results from an effort trying to close this observational gap by utilizing gas phase derivatization of sCIs followed by detection of the formed complexes with chemical ionization mass spectrometry. Our results suggest that the reactions of, e.g., Hexafluoroacetone (HFA) with a number of sCIs (ranging from CIs containing 2 to 10 carbons) are sufficiently fast so that complete conversion can be achieved when adding HFA at ppm levels – largely independent from the exact reaction rate and the amount of HFA introduced beyond that threshold. Using proton transfer reaction time-of-flight mass spectrometry (PTR-ToF), the protonated covalently bound complexes show little to none fragmentation, have unique mass defects and can therefore be clearly separated from other protonated species.

We further highlight both analytical and technical challenges accompanied with the implementation of a detection scheme along this route, comprising a broad range of sCIs present at typically minute atmospheric concentrations.