



Water independent SO₂ oxidation by Stabilised Criegee Intermediates from Biogenic Alkenes

Mike Newland (1), Andrew Rickard (2), Luc Vereecken (3), Mat Evans (2), Amalia Muñoz (4), Milagros Ródenas (4), and William Bloss (1)

(1) University of Birmingham, United Kingdom (m.j.newland@bham.ac.uk), (2) National Centre for Atmospheric Science, Wolfson Atmospheric Chemistry Laboratories, University of York, UK, (3) Max Planck Institute for Chemistry, Mainz, Germany, (4) Instituto Universitario CEAM-UMH, EUPHORE Laboratories, Spain

Biogenic VOCs account for about 90% of global VOC emissions and these are dominated by the unsaturated hydrocarbons: isoprene (600 Tg yr⁻¹) and monoterpenes (100 Tg yr⁻¹). Stabilised Criegee Intermediates (SCI) are thought to be formed in the atmosphere mainly from reactions of unsaturated hydrocarbons with ozone. SCI have been shown in laboratory experiments to rapidly oxidise SO₂ ($k > 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and NO₂ ($k = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$), providing a potentially important gas phase oxidation route for these species in the atmosphere.

The importance of the SCI reaction with trace gases has been shown in modelling work to be critically dependent on the ratio of the rate constants for the reaction of the SCI with these trace gases and with H₂O. Such modelling work has suggested that the SCI + SO₂ reaction is only likely to be important in regions with high alkene emissions, e.g. forests, and that elsewhere SCI are likely to be almost entirely quenched by reaction with water, thus negating their importance as trace gas oxidants. However, it has been shown in laboratory experiments with small SCI that the reaction rate of SCI with water is structure dependent, with *anti*-CH₃CHOO reacting fast with H₂O ($k > 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$), and *syn*-CH₃CHOO reacting orders of magnitude slower ($k < 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$).

Here we present results from a series of ozonolysis experiments performed at the EUPHORE atmospheric simulation chamber in Valencia. These experiments measure the loss of SO₂, in the presence of various biogenic alkenes (isoprene and three monoterpenes: α -pinene, β -pinene and limonene), as a function of water vapour. The SO₂ loss shows a dependence on relative humidity for all systems studied, decreasing with increasing relative humidity. However, for all species, there also appears to be a fraction of the SO₂ loss that shows a much lower sensitivity to relative humidity.

We quantify the relative rates of reaction of the SCI produced in the ozonolysis of these biogenics with water and SO₂, and their decomposition rates. The results suggest that the alkenes studied produce a mixture of SCIs with widely varying reactivity towards H₂O under atmospheric conditions. This behaviour is likely dependent on structure, in agreement with direct observations of the small SCI CH₃CHOO, and suggests that different SCIs have different fates in the atmosphere.

The impact of these observations for the identity, abundance and behaviour of SCIs expected to predominate in regions dominated by biogenic emissions, and their scope to act as atmospheric oxidants for other trace gases, is discussed.