



Quantifying the Fate of Stabilised Criegee Intermediates under Atmospheric Conditions

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The products of alkene ozonolysis have been shown in field experiments to convert SO_2 to H_2SO_4 . One fate of H_2SO_4 formed in the atmosphere is the formation of sulphate aerosol. This has been reported to contribute -0.4 W m^{-2} to anthropogenic radiative forcing via the direct aerosol effect and can also contribute to the indirect aerosol effect, currently one of the greatest uncertainties in climate modelling.

The observed SO_2 oxidation has been proposed to arise from reactions of the carbonyl oxide, or Criegee Intermediate (CI), formed during alkene ozonolysis reactions, with SO_2 . Direct laboratory experiments have confirmed that stabilised CIs (SCIs) react more quickly with SO_2 ($k > 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) than was previously thought.

The major sink for SCI in the troposphere is reaction with water vapour. The importance of the $\text{SO}_2 + \text{SCI}$ reaction in H_2SO_4 formation has been shown in modelling work to be critically dependent on the ratio of the rate constants for the reaction of the SCI with SO_2 and with H_2O . Such modelling work has suggested that the $\text{SCI} + \text{SO}_2$ reaction is only likely to be important in regions with high alkene emissions, e.g. forests.

Here we present results from a series of ozonolysis experiments performed at the EUPHORE atmospheric simulation chamber, Valencia. These experiments measure the loss of SO_2 , in the presence of an alkene (ethene, cis-but-2-ene and 2,3-dimethyl butene), as a function of water vapour. From these experiments we quantify the relative rates of reaction of the three smallest SCI with water and SO_2 and their decomposition rates. In addition the results appear to suggest that the conversion of SO_2 to H_2SO_4 during alkene ozonolysis may be inconsistent with the $\text{SCI} + \text{SO}_2$ mechanism alone, particularly at high relative humidities.

The results suggest that SCI are likely to provide at least an equivalent sink for SO_2 to that of OH in the troposphere, in agreement with field observations. This work highlights the importance of alkene ozonolysis not only as a non-photolytic source of HO_x but additionally as a source of other important atmospheric oxidants and moves towards quantifying some of the important sinks of SCI in the atmosphere.