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Chemistry of Stabilized Criegee Intermediates in the CLOUD Chamber

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Abstract. In atmospheric conditions the oxidation of sulphur dioxide to sulphuric acid in gas phase has been considered to be determined by the concentration of hydroxyl radical. Recently the significance of stabilized Criegee intermediate as an oxidizer of sulphuric acid has been brought out. In this study we investigated the oxidation of sulphur dioxide in the CLOUD chamber in conditions where the hydroxyl radical was removed. The concentration of formed sulphuric acid was measured with a chemical ionization atmospheric pressure interface time-of-flight mass spectrometer and it was compared with the calculated yield of sulphuric acid.

Keywords: α -pinene ozonolysis, stabilized Criegee intermediates, chamber experiment

PACS: 92.60 Mt, 82.33 Tb

INTRODUCTION

Oxidation of trace gases is an important but yet unclear part of the atmospheric chemistry. Until recently the understanding has been that the main oxidants are hydroxyl radical (OH^\bullet), ozone (O_3) and nitrate radical (NO_3^\bullet)¹, hydroxyl radical dominating during the daytime and nitrate radical during the night. The oxidation of sulphur dioxide has been determined by the concentration of OH but the measurements have implied that there is not enough OH to produce all the oxidation products that had been detected². Lately the importance of the stabilized Criegee intermediate (sCI) as an oxidizer of SO_2 has been under discussion³.

The sCI forms in the gas-phase reaction between ozone and olefin (Figure 1). In our study we produced sCI using α -pinene as a precursor it being one of the most abundant monoterpenes in the atmosphere especially in the boreal forest. Sulphuric acid is a key compound in the initial step of new particle formation so its formation from sulphur dioxide by an oxidation reaction has a significant role in atmospheric chemistry.

In this study we investigated the ability of sCI to oxidize SO_2 in well-defined conditions of CLOUD chamber. We calculated the amount of sCI produced by the precursors and the concentration of sulphuric acid formed from the reaction of sCI with SO_2 .

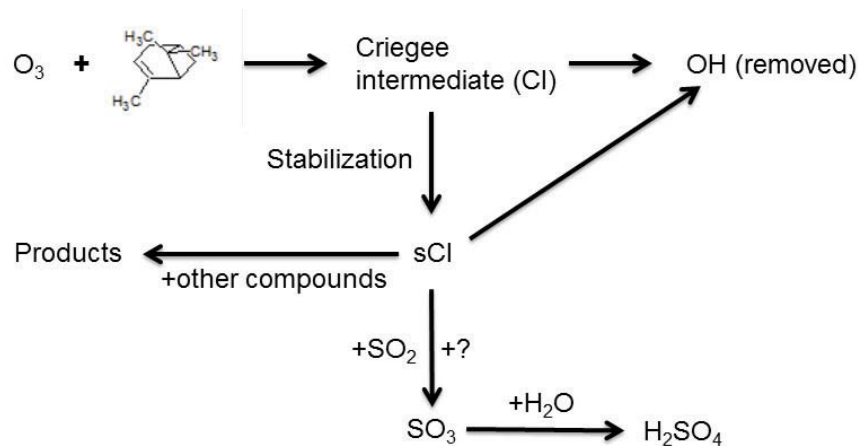


FIGURE 1. Proposed mechanism for the formation of the stabilized Criegee intermediate from ozone and α -pinene¹. In CLOUD experiments produced OH was scavenged by adding hydrogen into the chamber.

METHODS

The steady state concentration of stabilized Criegee intermediates produced from α -pinene and ozone is defined in Eq. 1 where Y equals the yield of sCI, k_I is the rate coefficient and k_{loss} is the inverse of the lifetime of the sCI, dominated by the thermal decomposition of sCI in the sub-second time scale³.

$$[sCI] = \frac{Y \cdot k_I \cdot [O_3] \cdot [\alpha\text{-pinene}]}{k_{loss}} \quad (1)$$

The steady state concentration of sulphuric acid produced by sCI is calculated according to the Eq. 2 where k_2 stands for the rate coefficient of the reaction between sCI and SO_2 and WL is the wall loss rate for sulphuric acid.

$$[H_2SO_4] = \frac{k_2 \cdot [sCI] \cdot [SO_2]}{WL} \quad (2)$$

The values for rate coefficient k_2 , Y and k_{loss} have been determined experimentally in Leibniz-Institute for Tropospheric Research⁴.

The CLOUD (Cosmics Leaving OUtdoor Droplets) chamber is an advanced laboratory setup located in CERN that is used to study the formation and growth of aerosol particles⁵. We investigated gas-phase ozonolysis experiments for α -pinene in the CLOUD chamber in the autumn 2012. These sCI measurements were done in neutral conditions using high electric fields to remove formed ions from the chamber. During these measurements the concentration of 0.1% H_2 was added to the chamber to work as an OH-scavenger. OH was removed using this technique and the only oxidizer left in the chamber was O_3 . The concentration of ozone was kept constant during measurements while the concentration of α -pinene varied between 100 ppt and 1600

ppt. The concentration of SO_2 was around 63-72 ppb for all the experiments except one test with lower concentration (17 ppb). All the experiments were done at ~ 278 K. The sulphuric acid concentration was measured by Atmospheric Pressure interface Time Of Flight mass spectrometer that had an x-ray Chemical Ionization inlet (CI-API-TOF)^{6,7}.

RESULTS

When calculating the concentration of sulphuric acid produced by sCI only the wall loss of sulphuric acid was taken into account so the loss of sulphuric acid into clusters and particles is probably one reason causing the differences between measured and calculated values. Bearing those losses in mind the measured sulphuric acid concentrations match the range of the calculated ones (Figure 2). Other sources of error in calculated and measured values include differences in temperature and maybe concentrations of gases – including SO_2 and H_2O – between the present and the previous⁴ study. Nevertheless, these results support the range of experimentally achieved values for k_2 , Y and k_{loss} and highlight the importance of sCI as an atmospheric oxidizer.

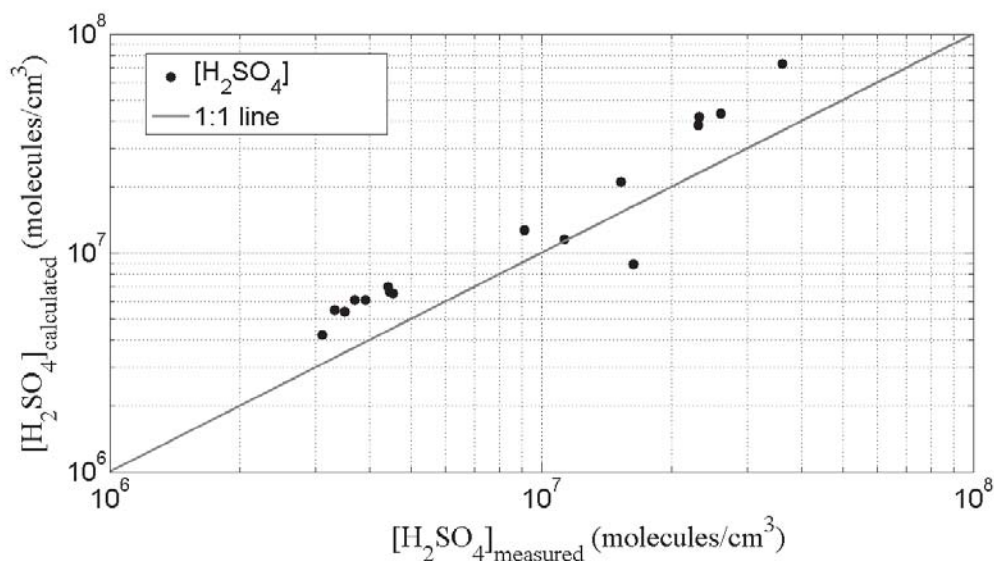


FIGURE 2. Calculated sCI produced sulphuric acid concentrations as a function of the measured concentrations.

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