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# Chemistry of Stabilized Criegee Intermediates in the CLOUD Chamber

Nina Sarnela<sup>a</sup>, Mikko Sipilä<sup>a</sup>, Tuija Jokinen<sup>a</sup>, Heikki Junninen<sup>a</sup> and the CLOUD collaboration

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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:**  $\alpha$ -pinene ozonolysis, stabilized Criegee intermediates, chamber experiment

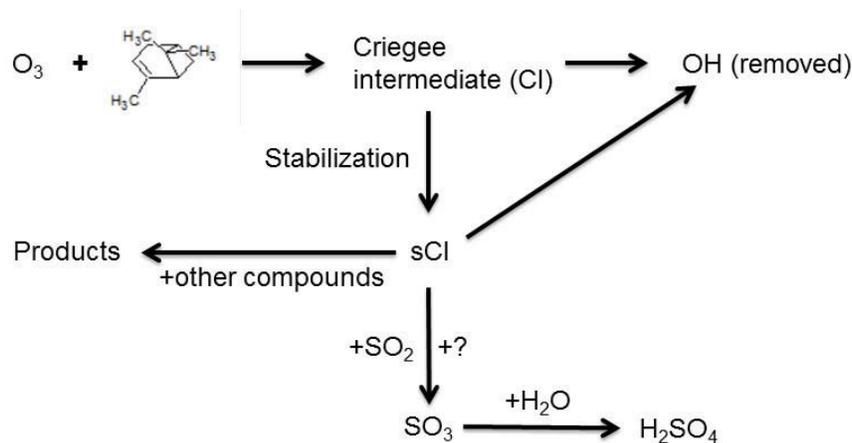
**PACS:** 92.60 Mt, 82.33 Tb

## 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 ( $\text{OH}^\bullet$ ), ozone ( $\text{O}_3$ ) and nitrate radical ( $\text{NO}_3^\bullet$ )<sup>1</sup>, 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 detected<sup>2</sup>. Lately the importance of the stabilized Criegee intermediate (sCI) as an oxidizer of  $\text{SO}_2$  has been under discussion<sup>3</sup>.

The sCI forms in the gas-phase reaction between ozone and olefin (Figure 1). In our study we produced sCI using  $\alpha$ -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  $\text{SO}_2$  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  $\text{SO}_2$ .



**FIGURE 1.** Proposed mechanism for the formation of the stabilized Criegee intermediate from ozone and  $\alpha$ -pinene<sup>1</sup>. In CLOUD experiments produced OH was scavenged by adding hydrogen into the chamber.

## METHODS

The steady state concentration of stabilized Criegee intermediates produced from  $\alpha$ -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 scale<sup>3</sup>.

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

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.

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

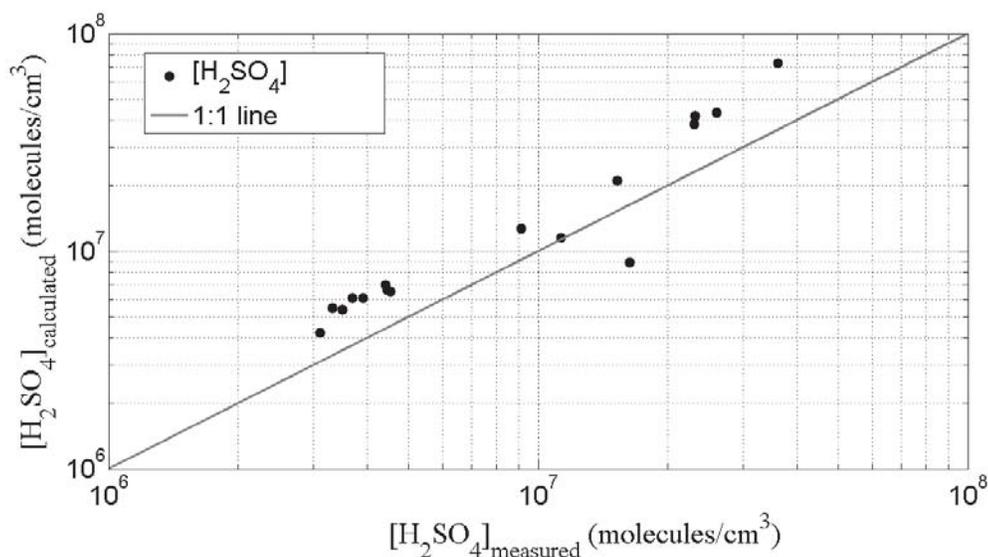
The values for rate coefficient  $k_2$ ,  $Y$  and  $k_{loss}$  have been determined experimentally in Leibniz-Institute for Tropospheric Research<sup>4</sup>.

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 particles<sup>5</sup>. We investigated gas-phase ozonolysis experiments for  $\alpha$ -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  $\alpha$ -pinene varied between 100 ppt and 1600

ppt. The concentration of  $\text{SO}_2$  was around 63-72 ppb for all the experiments except one test with lower concentration (17 ppb). All the experiments were done at  $\sim 278$  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)<sup>6,7</sup>.

## 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  $\text{SO}_2$  and  $\text{H}_2\text{O}$  – between the present and the previous<sup>4</sup> 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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