



Oxidation of Sulfur Dioxide via Multifunctional Organic Hydroperoxides in Cloud Droplets

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Oxidation of sulfur dioxide (SO_2) to sulfate in the atmosphere contributes to particulate matter (PM) formation. Hydrogen peroxide (H_2O_2) is considered to be the main oxidant of SO_2 hence the main sulfate source in cloud and fog water. Even though atmospheric oxidation of SO_2 by organic peroxides with one functional group, such as methylhydroperoxide and peroxyacetic acid, has been investigated,¹ the oxidation via multifunctional organic hydroperoxides has not been examined. We investigate the oxidation of SO_2 by the primary low- NO_x isoprene oxidation products: the two main isomers of isoprene hydroxyl hydroperoxide (1,2-ISOPOOH and 4,3-ISOPOOH).² Moreover, we examine the oxidation of SO_2 by hydroxymethyl hydroperoxide. These compounds are expected to be the most important organic hydroperoxides present in clouds due to their high Henry's law constants and as they are the most abundant multifunctional hydroperoxides^{2,3,4}. The multifunctional organic hydroperoxides were synthesized and an ion chromatography system was used to quantify the sulfate produced, and nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) utilized to analyze the secondary products produced. pH dependence was also investigated over the cloud pH range of 3 to 6 and compared with the reaction of SO_2 with H_2O_2 . The results indicate that the reactions mechanisms are different than that of the reaction of H_2O_2 with SO_2 . Model simulations in GEOS-Chem, updated with the kinetics of the atmospheric oxidation of SO_2 via the multifunctional organic hydroperoxides, show that while this pathway is a minor source of sulfate globally, it can be locally significant (>50% of total sulfate production) in regions with high isoprene emissions. In regions such as the Southeast USA where the atmospheric conditions are moving towards pre-industrial levels with respect to NO_x , but SO_2 is still emitted, the oxidation of SO_2 via the multifunctional organic hydroperoxides is of high importance.

Reference:

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