

GC-MS Studies of Iron-Catalyzed Decomposition of Isoprene Hydroxy Hydroperoxide (ISOPOOH) in the Aqueous Phase

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Organic hydroperoxides (ROOHs) are components of the atmospheric aqueous particles originating from reactions of volatile organic compounds (VOC) in the gas phase¹. ISOPOOH is the most important representative of ROOH and is produced through the oxidation of isoprene (C₅H₈) under low NO_x conditions. Isoprene reacts with hydroxyl radicals in the atmosphere, producing organic peroxy radicals (RO₂) after oxygen addition. In low-NO, HO₂-dominated conditions, RO₂ reacts with hydroperoxyl radicals (HO₂), resulting in the formation of ISOPOOH.¹ Their hydrophilicity allow the rapid uptake into the aqueous phase such as fogs, droplets of clouds, or liquid aerosols. The decomposition of the peroxides in the aqueous phase is accelerated by dissolved iron.² Although the mechanistic aspects of the Fenton reaction³ and the fate of ROOHs⁶ have been widely studied, there is still considerable interest in elucidating the influence of pH on the system⁵.

The present study investigates the decomposition of atmospherically relevant peroxides and hydroperoxides, specifically H₂O₂ and isoprene hydroxy hydroperoxides (ISOPOOH), by the Fenton reaction. The study focuses on the amount of radical products formed at different pH values. The quantification of OH radical yield was conducted through the application of 2-propanol-d₈ as a radical scavenger. Subsequently, the formation of acetone- d₆ from the reaction mixtures comprising ISOPOOH and Fe(II) or containing H₂O₂ and Fe(II), was assessed via gas chromatography-mass spectrometry (GC-MS) analysis. Additionally, the k_{2nd} value for the reaction between Fe(II) and ISOPOOH was also determined. The second-order reaction constant for the reaction between Fe(II) and ISOPOOH at pH = 4.5-4.8 was determined to be $k_{2nd} = 65.1 \pm 9.2 \text{ L mol}^{-1} \text{ s}^{-1}$. A kinetic model was developed to provide an explanation the pH-dependent observations. The results obtained will contribute to a better understanding of the decomposition of atmospherically relevant H₂O₂ and ROOHs in aqueous-phase by the Fenton reaction. The experiments on pH dependence will aid in the evaluation of radical yields and composition under cloud and aerosol conditions.

References

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