Kinetic study of the reactions of isoprene hydroxy hydroperoxide radicals and sulfur dioxide and their global-scale impact on sulfate formation

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Isoprene is known to be the most relevant biogenic volatile organic compound (BVOC) which accounts for more than 60% of the total VOC emissions in the global scale. The addition of OH radical to C=C double bonds is one of the main reaction paths of isoprene consumption, which generates six isomers of isoprene hydroxy hydroperoxide radicals (ISOPOOs). The fate of ISOPOOs is divided into two paths: oxidizing air pollutants such as NO to NO₂ etc. or forming ISOPOOHs by reacting with HO₂ which finally leads isoprene epoxydiols (IEPOXs), the precursor of secondary organic aerosols. Previous study revealed the rate constants of the reactions of ISOPOOs and NO, CO, NO₂, etc., but there were no studies which determined the rate constants of ISOPOOs with SO₂ reactions which are finally expected to form sulfate aerosol (SO₄²⁻). In this study, the rate constants of six isomers of ISOPOOs with SO₂ were determined using quantum chemical calculation (QCC) coupling with transition-state theory (TST). QCC was conducted by Gaussian 16 and TST calculation was conducted by the Gaussian Post Processor (GPOP). Further, pressure dependence of SO₄²⁻ formation was evaluated by the Rice-Ramsperger-Kassel-Marcus theory coupling with master equation (RRKM/ME) to determine the rate constants in ambient condition which was conducted by the Steady-State Unimolecular Master-Equation Solver (SSUMES). The results of the optimization of the chemical structure of six isomers of ISOPOOs from QCM, which are shown in the Figure, suggested that 1,2-ISOPOO, 4,3-ISOPOO, Z-1,4-ISOPOO, and Z-4,1-ISOPOO form intermolecular hydrogen bonds by -OH and -OO leading stabilization of the structures and the rate constants with SO₂ reaction were less than 1×10⁻²⁰ cm³ molecule⁻¹ s⁻¹. On the other hand, E-1,4-ISOPOO and E-4,1-ISOPOO do not form intermolecular hydrogen bond, which resulted in the rate constants with SO₂ reaction to be ~1×10⁻¹⁹ cm³ molecule⁻¹ s⁻¹ (more than one order of magnitude higher than other ISOPOOs). Nevertheless, the intermediate products of E-1,4-ISOPOO and E-4,1-ISOPOO with SO₂ reactions (ISOPOOOSO₂) are estimated to be very stable by RRKM/ME calculation, ISOPOOOSO₂ may not decompose into SO₃. On the other hand, ISOPOOOSO₂ formed by 1,2-ISOPOO, 4,3-ISOPOO, Z-1,4-ISOPOO, and Z-4,1-ISOPOO with SO₂ reactions are quite unstable, and immediately decompose into SO₃ which contribute to SO₄²⁻ formation.

The Goddard Earth Observing System Chemistry model (GEOS-Chem v12.9.3) was applied to understand the effect of ISOPOOs + SO₂ reactions to the global SO₄²⁻ concentration in 2019. The calculated period was from Jan. 2018 to Dec. 2019, and the period from Jan. 2018 to Dec. 2018 was treated as the term of spin-off calculation. In terms of emission inventories, EDGAR v4.3 was used for anthropogenic emission, CEDS was used for ship emission, GFED was used for biomass burning, and MEGAN was used for BVOCs emissions with the meteorological inputs from MERRA2. The kinetic parameters obtained by QCC/TST/RRKM/ME calculations were incorporated to the standard chemical mechanism of GEOS-Chem. The results of GEOS-Chem calculation suggested that the concentration of SO₄²⁻ decreases in the middle- to low-latitude regions, and increases in the high-latitude regions. This is because in the middle- to low-latitude regions, intense sunlight and high temperature enhances SO₂ + OH reaction, but ISOPOOs consume SO₂ and the oxidation of SO₂ by OH is interrupted, causing decrease of SO₄²⁻ formation. On the other hand, in high-latitude regions, SO₂ + OH reaction does not efficiently occur because of low sunlight and temperature, and the formation of SO₄²⁻ by the reaction of ISOPOOs + SO₂...
and ISOPOOSO₂'s unimolecular decomposition. The results of this study will contribute to detailing the gas phase chemistry of $\text{SO}_4^{2-}$ formation over global-scale.

Keywords: Isoprene hydroxy hydroperoxide radicals, Fine particulate matter, Sulfate, Quantum chemical calculation, Microcanonical kinetics, Global chemical transport model