

## Experimental study on the heterogeneous reaction of gaseous OH radical with aqueous DMSO: Determination of the $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ production ratio

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The oxidation of dimethyl sulfide (DMS) emitted from ocean (~ 45 Tg S per year) is a global source of cloud condensation nuclei. Hydrophobic DMS is mostly oxidized in the gas-phase into  $\text{H}_2\text{SO}_4(\text{g}) + \text{DMSO}(\text{g})$  (dimethyl sulfoxide), whereas water-soluble DMSO is oxidized into  $\text{SO}_4^{2-} + \text{CH}_3\text{SO}_3^-$  (methane sulfonate) on water surfaces.  $R = \text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$  ratios therefore indicate the extent of DMSO heterogeneous oxidation if  $R_{\text{het}} = \text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$  for  $\text{DMSO}(\text{aq}) + \cdot\text{OH}(\text{g})$  were determined. Here, products and intermediates of the oxidation of aqueous DMSO initiated by gas-phase hydroxyl radicals,  $\text{OH}(\text{g})$ , at the air-water interface were directly detected by mass spectrometry in a novel setup under various experimental conditions. Exposure of millimolar DMSO aqueous microjets to ~ 10 ns  $\text{OH}(\text{g})$  pulses from the 266 nm laser flash photolysis of  $\text{O}_3(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})/\text{N}_2(\text{g})$  mixtures yielded an array of interfacial intermediates/products, including  $\text{CH}_3\text{SO}_3^-$  and  $\text{HSO}_4^-$ , that were unambiguously and simultaneously identified in situ by mass spectrometry. We determined  $R_{\text{het}} = 2.7$  from the heterogeneous OH-oxidation of DMSO on aqueous aerosols for the first time. The nearly quantitative production of  $\text{H}_2\text{SO}_4(\text{g})$  (that leads to  $\text{SO}_4^{2-}$ ) in the oxidation of DMSO in the gas-phase versus the  $R_{\text{het}} \sim 2.7$  value determined at the air-water interface means that  $R = \text{CH}_3\text{SO}_3^-/\text{nss-}\text{SO}_4^{2-}$  variations in the aerosol, particularly in remote locations, should arise from the competition between the gas-phase versus the heterogeneous DMSO oxidation pathways. The present study reveals that interfacial OH-oxidation processes play a more significant role in the generation and growth of atmospheric aerosol over ocean than previously envisioned.

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