‘Sizing’ heterogeneous chemistry in the conversion of gaseous dimethyl sulfide to atmospheric particles

The oxidation of biogenic dimethyl sulfide (DMS) emissions is a global source of cloud condensation nuclei. The amounts of the nucleating H\textsubscript{2}SO\textsubscript{4}(g) species produced in such process, however, remain uncertain. Hydrophobic DMS is mostly oxidized in the gas-phase into H\textsubscript{2}SO\textsubscript{4}(g)+DMSO(g) (dimethyl sulfoxide), whereas water-soluble DMSO is oxidized into H\textsubscript{2}SO\textsubscript{4}(g) in the gas-phase but into SO\textsubscript{4}\textsuperscript{2-} + MeSO\textsubscript{3}\textsuperscript{-} (methane sulfonate) on water surfaces. Thus, R=MeSO\textsubscript{3}\textsuperscript{-}/non-sea-salt-SO\textsubscript{4}\textsubscript{2-} ratios would therefore gauge both the strength of DMS sources and the extent of DMSO heterogeneous oxidation if R\text{het}= MeSO\textsubscript{3}\textsuperscript{-}/SO\textsubscript{4}\textsubscript{2-} for DMSO(aq) + ·OH(g) were known. Here we report that R\text{het}=2.7, a value obtained from online electrospray mass spectra of DMSO (aq) + ·OH(g) reaction products, which quantifies the MeSO\textsubscript{3}\textsuperscript{-} produced in DMSO heterogeneous oxidation on aqueous aerosols for the first time. On this basis, the inverse R-dependence on particle radius in size-segregated aerosol collected over Syowa station and Southern oceans is shown to be consistent with the competition between DMSO gas-phase oxidation and its mass accommodation followed by oxidation on aqueous droplets. Geographical R variations are thus associated with variable contributions of the heterogeneous pathway to DMSO atmospheric oxidation, which increase with the specific surface area of local aerosols.

Biography

Agustín J Colussi is a Senior Research Scientist at CALTECH since 1998 and has published more than 200 papers in environmental physical chemistry.

ajcoluss@caltech.edu