



## **Interfacial chemistry of aqueous sulfur/iodide aerosol microdroplets in gaseous ozone**

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The intermediates  $\text{ISO}_3^-$  ( $m/z = 207$ ) and  $\text{IS}_2\text{O}_3^-$  ( $m/z = 239$ ) generated in aqueous (iodide - thiosulfate) microdroplets traversing dilute ozone gas plumes at atmospheric pressure are detected via online electrospray mass spectrometry within 1 ms, and their stabilities gauged by collision-induced dissociation. The simultaneous detection of anionic reactants and the  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{IO}_3^-$  and  $\text{I}_3^-$  products as a function of experimental conditions provides evidence of unique interfacial reaction kinetics. Although ozone reacts  $\sim 3$ - $4$  times faster with  $\text{I}^-$  than  $\text{S}_2\text{O}_3^{2-}$  in bulk solution, only  $\text{S}_2\text{O}_3^{2-}$  is apparently oxidized in  $[\text{I}^-]_o/[\text{S}_2\text{O}_3^{2-}]_o = 10$  microdroplets below  $[\text{O}_3(\text{g})] \sim 50$  ppm. The sulfite to sulfate and iodide to triiodide and iodate oxidations in the interfacial layers of aqueous thiosulfate or mixed thiosulfate and iodide microdroplets briefly exposed to dilute  $\text{O}_3(\text{g})$  gas mixtures are also investigated. S(IV) oxidation kinetics in sodium thiosulfate solutions, where the rates are proportional to  $[\text{S(IV)}][\text{O}_3(\text{g})]$  in the ranges investigated, correspond to a surface-specific reaction.  $\text{I}_3^-/\text{IO}_3^-$  yields based on interfacial  $\text{I}^-$  losses exceed their stoichiometric limits in the presence of excess S(IV), revealing that interfacial  $\text{I}^-$ .