Missing SO₂ oxidant in the coastal atmosphere? Evidence from high resolution measurements of OH and atmospheric sulfur compounds

Berresheim et al., Atmos. Chem. Phys. Discuss., 14, 1159-1190, 2014

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The authors describe measurements of OH and H₂SO₄ at the Mace Head atmospheric research station which indicate an unknown oxidant responsible for the oxidation of SO₂ in the atmosphere. Calculated concentrations of H₂SO₄, based only on SO₂ oxidation by OH, were lower than observations by a factor of ~5. A number of potential additional oxidants of SO₂ are considered in the manuscript, including stabilised Criegee intermediates. However, calculations regarding oxidation of SO₂ by Criegee intermediates are focussed on the C₂ Criegee intermediate (CH₃CHOO). While the authors do comment on our recent results regarding CH₂OO + SO₂ kinetics,¹ and the formation of CH₃OO following solar photolysis of CH₂I₂,² we believe this could be explored further.

Owing to the experimental techniques used in our work, we were able to report a lower upper limit for the rate coefficient for CH₂OO + H₂O than has been reported previously³ (k_{CH2OO+H2O} < 9 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} for our work¹), and lower than that reported for the corresponding syn-CH₃CHO + H₂O reaction (we note that the reaction between anti-CH₃CHO and H₂O has been observed, with k_{anti-CH3CHO+H2O} = 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}). Oxidation of SO₂ by CH₂OO may therefore be more significant than indicated by the calculations reported for CH₃CHO (similarly, the calculated impact of syn-CH₃CHO is very dependent on the upper limit for k_{syn-CH3CHO+H2O}).

Moreover, our work has shown that solar photolysis of CH₂I₂ yields ~17% CH₂OO at atmospheric pressure, providing a route for Criegee intermediate formation not involving ozonolysis reactions. Previous measurements of CH₂I₂ have indicated that CH₂I₂ photolysis is the dominant source of atmospheric I atoms at Mace Head.⁴,⁵ A photolysis source of CH₂OO could explain the observed diurnal profile of the missing oxidant. Additionally, given the dependence of CH₂I₂ emissions on tidal activity,⁴,⁵ a significant photolytic source of CH₂OO from CH₂I₂ could explain the observed increases in the activity of the missing oxidant at low tide.

References


