Missing SO_2 oxidant in the coastal atmosphere? Evidence from high resolution measurements of OH and atmospheric sulfur compounds

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The authors describe measurements of OH and H_2SO_4 at the Mace Head atmospheric research station which indicate an unknown oxidant responsible for the oxidation of SO_2 in the atmosphere. Calculated concentrations of H_2SO_4, based only on SO_2 oxidation by OH, were lower than observations by a factor of ~5. A number of potential additional oxidants of SO_2 are considered in the manuscript, including stabilised Criegee intermediates. However, calculations regarding oxidation of SO_2 by Criegee intermediates are focussed on the C_2 Criegee intermediate (CH_3CHOO). While the authors do comment on our recent results regarding CH_2OO + SO_2 kinetics,[1] and the formation of CH_2OO following solar photolysis of CH_2I_2,[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 CH_2OO + H_2O than has been reported previously[3] ($k_{CH2OO+H2O} < 9 \times 10^{-17}$ cm^{-3} s^{-1} for our work[1]), and lower than that reported for the corresponding *syn*-CH_3CHOO + H_2O reaction (we note that the reaction between *anti*-CH_3CHOO and H_2O has been observed, with $k_{anti\text{-}CH3CHOO+H2O} = 1 \times 10^{-14}$ cm^{-3} s^{-1}). Oxidation of SO_2 by CH_2OO may therefore be more significant than indicated by the calculations reported for CH_3CHOO (similarly, the calculated impact of *syn*-CH_3CHOO is very dependent on the upper limit for $k_{syn\text{-}CH3CHOO+H2O}$).

Moreover, our work has shown that solar photolysis of CH_2I_2 yields ~17 % CH_2OO at atmospheric pressure, providing a route for Criegee intermediate formation not involving ozonolysis reactions. Previous measurements of CH_2I_2 have indicated that CH_2I_2 photolysis is the dominant source of atmospheric I atoms at Mace Head.[4,5] A photolysis source of CH_2OO could explain the observed diurnal profile of the missing oxidant. Additionally, given the dependence of CH_2I_2 emissions on tidal activity,[4,5] a significant photolytic source of CH_2OO from CH_2I_2 could explain the observed increases in the activity of the missing oxidant at low tide.

References

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