

An isotopic view on ionising radiation as a source of sulphuric acid

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Sulphuric acid is an important factor in aerosol nucleation and growth. It has been shown that ions enhance the formation of sulphuric acid aerosols, but the exact mechanism remains undetermined. Furthermore some studies have found a deficiency in the sulphuric acid budget, suggesting a missing source. In this study the production of sulphuric acid from SO₂ through a number of different pathways is investigated. The production methods are standard gas phase oxidation by OH radicals produced by ozone photolysis by UV light, liquid phase oxidation by ozone, and gas phase oxidation initiated by gamma rays. The distributions of stable sulphur isotopes in the products and substrate were measured using isotope ratio mass spectrometry. All methods produced sulphate enriched in ³⁴S and we find a

³⁴S value of 8.7 permil for the OH reaction. Only UV light (Hg emission at 253.65 nm) produced a clear nonmass-dependent excess of ³³S of around 0.3 permil. The pattern of isotopic enrichment produced by gamma rays is similar, but not equal, to that produced by aqueous oxidation of SO₂ by ozone. This, combined with the relative yields of the experiments, suggests a mechanism in which ionising radiation may lead to hydrated ion clusters that serve as nanoreactors for S(IV) to S(VI) conversion.

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