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Solar radiation induced photolysis of dihalomethanes in water and seawater

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The surface ocean is an important source of reactive organic iodine compounds to the marine boundary layer. While the gas phase photochemistry of these compounds has been widely studied, the fate of organic iodine in seawater is less well-characterised. Rates and products of the photodissociation of low concentrations of CH₂I₂, CH₂IBr and CH₂ICl in water, salt water (0.5 M NaCl) and seawater in natural sunlight have been determined by Ultraviolet-visible absorption spectroscopy and purge-and-trap GC-MS analyses. Photolysis leads to formation of iodide (I^{-}) and, in salt and seawater environments, production of CH_2XCl (where X = Cl, Br, or I). Thus CH_2ICl was produced during CH₂I₂ photolysis, CH₂BrCl from CH₂IBr photolysis and CH₂Cl₂ from CH₂ICl. Formation of these chlorine-atom substituted products may be via direct reaction of Cl⁻ or equivalent (e.g. NaCl) with either (A) the isodihalomethane photoisomer or associated ion pair (e.g. CH_2I^+ — I^-) or (B) the initially produced CH_2I^{\bullet} photofragment. Apparent quantum yields for photolysis were estimated and found to exhibit only small differences in water, 0.5 M NaCl and seawater. A radiative transfer model was used to calculate seasonal values of CH₂I₂, CH₂IBr and CH₂ICl photolysis in surface seawater at mid-latitudes (50°N). Implications for CH₂ICl and I⁻ production in the surface ocean are discussed.