



The photochemistry of CH_2I_2 , CH_2BrI and CH_2ClI in seawater

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Iodine plays a fundamental role in the chemistry of the marine boundary layer, by catalysing tropospheric ozone destruction and contributing to new particle formation in the daytime marine atmosphere. Recent observations suggest that the photolabile iodocarbons CH_2I_2 , CH_2ClI and CH_2BrI may be a significant source of iodine atoms to the coastal marine boundary layer. Little is known of the transformations that iodocarbons undergo in seawater; yet an understanding of their degradation and reaction routes is fundamental in order to predict their sea-to-air fluxes. Here we present some results from laboratory photochemical experiments carried out with CH_2I_2 , CH_2BrI and CH_2ClI .

Irradiations were carried out with a 1 kW Xe lamp, optically filtered to simulate the solar spectrum at the earth's surface. The wavelength-dependence of CH_2I_2 photolysis rates was determined with a 1 kW Xe lamp coupled to a monochromator. Halocarbon concentrations in the samples were analysed by purge-and-trap gas chromatography / mass spectrometry.

All three compounds were observed to follow first-order removal kinetics on irradiation. Photolytic lifetimes varied from 12 minutes for CH_2I_2 to 13 hours for CH_2ClI in natural seawater at a solar zenith angle = 0° . Photolysis of CH_2I_2 in artificial and natural seawater generated CH_2ClI and iodide. The sunlight-normalised CH_2I_2 photolysis rates showed a maximum around 320 nm. Photolysis rates decrease quickly with depth in oceanic waters, and even in the clearest waters photo-degradation of CH_2I_2 is reduced by a factor of 10 at a depth of 20 m. Our results suggest that a fraction of CH_2I_2 produced at or transported to the ocean surface would be photolysed

before evading into the atmosphere. On the other hand, the longer aquatic photolytic lifetime of CH_2ClI would allow this compound to vent to the atmosphere, and indeed CH_2ClI has been detected in the remote marine atmosphere.