

Emission of iodine molecule and iodine monoxide from frozen solutions containing iodide ion

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Iodine oxides are receiving increasing attention in atmospheric chemistry, because it may contribute to ozone depletion and atmospheric particle formation in polar region. Iodine monoxide(IO) generates from the reaction of iodine atom with ozone. Iodine atoms may be formed by photolysis of iodine(I₂) or volatile iodocarbons, the main source of which is oceanic biogenic production. Emission processes from inorganic source are also being proposed, but they are so far unexplained. Iodine compounds were found above, below and within the sea ice of the Weddell Sea, and these measurements show the Weddell Sea as an iodine hotspot. But, the calculated fluxes from biological production of iodocarbons are too small to explain the observed atmospheric IO, and the modelled I₂ is also smaller than the observed I₂. This observation suggests there is an unidentified iodine source. One of the candidates is presumably an inorganic source. In this work, we studied the surface reaction between gaseous ozone and a frozen sodium iodide solution by using cavity ring-down spectroscopy to detect gaseous products, iodine, I₂(g) and an iodine monoxide radical, IO(g).

The I₂(g) and IO(g) emissions were observed during ozonolysis of liquid and frozen NaI aqueous solutions. The concentrations of NaI were typically 1 and 5 mM. The concentrations of flowing O₃(g) were (0.5-4.2)×10¹⁵ molecules cm⁻³. The observed products concentrations were ~10¹¹ molecules cm⁻³ for IO(g) and ~10¹⁴ molecules cm⁻³ for I₂(g). The peak of I₂(g) emission was markedly enhanced on a frozen NaI aqueous solution more than that on a liquid at pH 2. The peak of IO(g) emission was also enhanced on a frozen solution under the same condition. The physical structures of the ice substrates supposedly play an important role in this enhancement. Iodide anions are expected to be excluded from ice matrix during freezing. This exclusion process leads to the formation of concentrated iodide anions at the air-ice interface. In fact, sea ice contains brine microchannels that permit transport of reactants over large distances. It was found that the amounts of I₂(g) and IO(g) produced depend on [NaI], I₂(g) production is markedly enhanced at pH <4, and I₂(g) emission is decreased with decreasing temperature of a frozen NaI solution. Acidification of the brine by atmospheric trace acids could potentially lead to low pH. These results imply that a surface reaction between gaseous ozone and frozen iodide could be responsible for the inorganic source of iodine.

Keywords: iodine, iodine monoxide, ice, ozone, heterogeneous reaction, cavity ring-down spectroscopy