



Quantum chemical investigation on the catalytic mechanism of vanadium iodoperoxidase and the iodination of common organic compounds

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Atmospheric iodine has received considerable attention in the two past decades due to both its potential role in the catalytic destruction of ozone (1) and its contribution to the formation of cloud condensation nuclei (2). It is generally assumed that iodine in the atmosphere has a natural origin since no anthropogenic sources are known. Seaweeds and marine phytoplankton release iodocarbons. In addition, IO and even I₂, a major source of particle formation in coastal areas, are also detectable in the atmosphere above kelp beds. However, the reasons why iodocarbons are released by seaweeds and the mechanisms involved in their production remain largely unknown. It is currently well established that the general catalytic role of halide oxidation in marine algae is actually played by vanadium-dependent haloperoxidases enzymes, although relevant details such as protonation states of the vanadate cofactor or even key steps in the mechanism are still unknown. In this contribution, we focus on the iodoperoxidase VIPO enzyme. Quantum calculations on the vanadate cofactor were combined with structural analyses on a reliable three-dimensional model of the VIPO protein to investigate the steps along the catalytic mechanism that lead to the release of halide oxidation products. In addition, iodination reactions of several common organic compounds selected to account for representative volatile and non-volatile iodocarbons were thermodynamically studied by means of high-level ab initio correlated calculations. Free energies of reactions with the three possible iodinating species produced by the enzyme, namely HOI, I₂, and I₃⁻ were calculated. Our results show that only hypoiodous acid give rise to clearly exoergonic iodination of organic substrates.

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