

Molecular Structure and Functional Group Arrangements of Organic Ligands Control Photochemical Reduction of Mercury

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Photochemical reduction of mercury (as Hg(II) species) is one of the most important pathways of elemental Hg(0) production in natural and contaminated open waters and plays a key role in Hg cycling in the environment. This redox transformation is affected by aqueous ionic species, among which the aromatic moieties of naturally dissolved organic matter (DOM) are thought to be the most important because of their light-absorbing characteristics. However, the exact mechanism by which DOM mediates the photochemical reduction of Hg(II) is not yet clear owing to our incomplete understanding of the structural arrangement and stoichiometry of reactive functional groups in DOM. In this study, DOM analogs including salicylic acid, 4-hydrobenzoic acid, anthranilic acid, 4-aminobenzoic acid, and phthalic acid were used to systematically investigate the role of functional groups and their steric arrangements in photochemical reduction of Hg(II). We show that the photochemical reduction rates of Hg(II) are influenced not only by the neighboring functional groups but also their positioning on the aromatic benzene ring structure. The reduction rate was found to increase in the order of anthranilic acid > salicylic acid > phthalic acid by varying neighboring functional groups from amine to hydroxyl then to carboxyl on benzoic acid. The substitution position of the functional groups affected reduction rates in the order: anthranilic acid > 4-aminobenzoic acid and salicylic acid > 4-hydroxybenzoic acid. Analyses of ultraviolet (UV) light absorbance of these DOM analogs indicate that the Hg(II) reduction rate is positively correlated to their UV absorption. The reduction rate was also found to depend on the concentration of the organic compounds, suggesting that the secondary reaction mechanism is mainly responsible for the photochemical reduction of Hg(II) in these systems. These observations shed additional light to the understanding of the role of DOM in Hg photoredox transformation and geochemical cycling in the environment.