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Biomolecular Insights into Mercury Transformations

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Decades of research have been devoted to understanding monomethylmercury (MeHg) formation and degradation, but little is known about the formation of dimethylmercury (DMeHg) in aquatic systems. We combined complementary experimental and computational approaches to examine the formation and decomposition of the binuclear bis(methylmercuric(II)) sulfide complex $(CH_3Hg)_2S$. We obtained a log K value of 26.0 +/- 0.2 for the reaction $2CH_3Hg^+ + HS^- = (CH_3Hg)_2S$. Thus, the binuclear $(CH_3Hg)_2S$ complex is likely to be the dominant MeHg species under high MeHg concentrations typically used in experimental investigations of MeHg degradation by sulfate-reducing bacteria. We provide evidence for slow decomposition of $(CH_3Hg)_2S$ to DMeHg and HgS, with a first-order rate constant $k = 1.5 \pm 0.4 \times 10^{-6}$ h^{-1}. Quantum chemical calculations suggest that the reaction proceeds by a novel mechanism involving rearrangement of the $(CH_3Hg)_2S$ complex facilitated by strong Hg–Hg interactions that activate a methyl group for intramolecular transfer. Predictions of DMeHg formation rates under a variety of field and laboratory conditions indicate that this pathway for DMeHg formation will be significant in laboratory experiments utilizing high MeHg concentrations, favoring $(CH_3Hg)_2S$ formation. In natural systems with relatively high MeHg/$[H_2S]T$ ratios, DMeHg production may be observed, warranting further investigation.

Microorganisms that produce MeHg use corrinoid cofactors to perform the methylation reaction. To enable accurate simulations of corrinoid-dependent systems, we developed CHARMM force field parameters for several corrinoids developed from quantum mechanical calculations. We provide parameters for corrinoids in three oxidation states, Co^{3+}, Co^{2+}, and Co^{1+}, and with various axial ligands. The resulting parameters were validated by assessing their agreement with quantum chemical calculations and by analyzing MD simulation trajectories of several corrinoid proteins for which X-ray crystal structures are available. In each case, we obtained excellent agreement with the reference data. This approach is readily adaptable for developing parameters for simulating other corrinoids or large biomolecules.