Methylmercury Speciation and Dimethylmercury Production in Sulfidic Solutions

Challenge
• Decades of research have been devoted to understanding methylmercury (MeHg) formation and degradation, but little is known about the formation of dimethylmercury (DMeHg) in aquatic systems.

Approach and Results
• Combined complementary experimental and computational approaches to examine MeHg speciation and DMeHg formation in sulfidic solutions
  • Log K for $2\text{CH}_3\text{Hg}^+ + \text{HS}^- \leftrightarrow (\text{CH}_3\text{Hg})_2\text{S} = 26.0$
  • $(\text{CH}_3\text{Hg})_2\text{S}$ decomposes slowly to DMeHg and HgS
  • DFT calculations suggest a likely mechanism in excellent agreement with experimental rate measurements.

Significance and Impact
• In natural systems with relatively high MeHg/sulfide ratios (e.g., the oxic/anoxic interface), DMeHg may be produced, warranting further investigation.


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The article was selected by the handling Editor as one of the top 10% of papers published in Environmental Science: Processes and Impacts. This selection is based on the exceptionally positive referee reports that the manuscript received during peer review, along with the Editor’s assessment of the significance and impact of the paper. The paper was chosen as a HOT paper recommended by our handling Editors in this collection: rsc.li/espi-hot

Abstract
Alkylated mercury species (monomethylmercury, MeHg, and dimethylmercury, DMeHg) exhibit significant bioaccumulation, and pose significant risks to ecosystems and human health. Although decades of research have been devoted to understanding MeHg formation and degradation, little is known about DMeHg formation in aquatic systems. Here, we combine complementary experimental and computational approaches to examine MeHg speciation and DMeHg formation in sulfidic aqueous solutions, with an emphasis on the formation and decomposition of the binuclear bis(methylmercuric(II)) sulfide complex (CH$_3$Hg)$_2$S. Experimental data indicate that the reaction 2CH$_3$Hg$^+$ + HS$^-$ = (CH$_3$Hg)$_2$S has a log $K = 26.0$ +/- 0.2. Thus, the binuclear (CH$_3$Hg)$_2$S 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 (SRB). Our finding of a significant abiotic removal mechanism for MeHg in sulfidic solutions through the formation of relatively insoluble (CH$_3$Hg)$_2$S suggests careful reexamination of reported “oxidative demethylation” of MeHg by SRB and perhaps other obligate anaerobes. We provide evidence for slow decomposition of (CH$_3$Hg)$_2$S 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$_3$Hg)$_2$S 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$_3$Hg)$_2$S formation. In natural systems with relatively high MeHg/[H$_2$S]$_T$ ratios (the oxic/anoxic interface, for example), DMeHg production may be observed, and warrants further investigation.