

MASS-DEPENDENT AND -INDEPENDENT MERCURY ISOTOPE FRACTIONATION DURING GAS-PHASE OXIDATION OF ELEMENTAL MERCURY VAPOR BY THE ATOMIC HALOGENS CL AND BR

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Introduction

Reactive halogen species are key oxidants of gaseous Hg⁰ making up the bulk of atmospheric Hg and considered having an important influence on the atmospheric residence time and dispersion of this toxic element. Stable Hg isotope analysis is an emerging tool to investigate sources, transport and transformation of airborne Hg, however field sample data interpretation is hampered due to a lack of information on the isotopic fractionation involved in major atmospheric transformation pathways (Sonke, Heimbürger, & Dommergue, 2013). This study presents the first measurements of Hg stable isotope fractionation during gas-phase oxidation of Hg⁰ vapor by the halogen atoms X* (X = Cl, Br).

Methods

Photolysis experiments were performed in 160 L collapsible Teflon-film chambers including initial air mixtures of Hg⁰ vapor (3 to 12 ppbv) and halogen atom precursor (50 ppmv CCl₃C(O)Cl and CHBr₃, respectively) at atmospheric pressure (750±1 Torr) and room temperature (298±3 K). The average Cl and Br atom concentration ranges $(0.3 - 1.5) \times 10^8$ and $(0.4 - 2.3) \times 10^{10}$ atoms cm⁻³ during the study. The rates of reaction between Hg⁰ and Cl* and between Hg⁰ and Br* of $(1.8 \pm 0.5) \times 10^{-11}$ and $(1.6 \pm 0.8) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively, were determined by using a relative rate technique involving light hydrocarbons with known rate coefficients as references. The relative consumption of the reference compounds and Hg⁰ was measured using a gas chromatograph with flame ionization detection and a cold vapor atomic fluorescence spectrophotometric (CVAFS) detection, respectively. In a set of experiments with Cl and Br atoms without organic references, the degree of conversion Hg⁰ → HgX₂ measured as $f_R = [\text{Hg}^0]_t / [\text{Hg}^0]_0$ by CVAFS was systematically varied by the duration of photolysis time. After an experiment reached the stipulated f_R , the reaction mixture was evacuated from the chamber into a wet chemical Hg speciation train consisting of a series of impingers to separately capture

the Hg reactant and product(s). All impinger solutions were analyzed for total Hg concentration using dual stage Au amalgamation and CVAFS detection and Hg isotopic ratios were determined by MC-ICP-MS.

Results

Significant mass-dependent fractionation (MDF), and mass-independent fractionation (MIF) of the odd isotopes (¹⁹⁹Hg and ²⁰¹Hg) were observed during Hg⁰ oxidation by both halogen atoms. Heavier isotopes are preferentially enriched in the remaining Hg⁰ during Cl[•] initiated oxidation, whereas they are enriched in the HgBr₂ product during oxidation by Br[•]. The latter inverse kinetic isotope effect is plausibly linked to a pre-equilibrium in the Hg + Br[•] system due to a slower oxidation of reaction intermediate ·HgX and a faster dissociation of ·HgX into reactants at room temperature. The measured fractionation factors for ²⁰²Hg/¹⁹⁸Hg during Cl[•] and Br[•] initiated oxidation are $\alpha^{202/198} = 0.99941 \pm 0.00006$ (2 σ) and 1.00074 ± 0.00014 (2 σ), respectively. The odd isotopes becoming increasingly enriched in the reactant Hg⁰ during the course of oxidation with nearly a three-fold higher magnitude of $\Delta^{199}\text{Hg}$ produced in the Cl[•] initiated reaction (up to ~1.2‰). An $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.61 ± 0.30 (2 σ) during oxidation of Hg⁰ by Br atoms suggests that Hg-MIF is most plausibly introduced by the nuclear volume effect (NVE) (Wiederhold et al., 2010; Zheng & Hintelmann, 2010). In contrast, the Hg⁰ + Cl[•] reaction produced a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ -slope of 1.88 ± 0.17 (2 σ), which in addition to a high degree of odd-mass-number isotope MIF impels impact from mass-independent fractionation effects other than NVE. Interestingly, this reaction also exhibits significant MIF of ²⁰⁰Hg ($\Delta^{200}\text{Hg}$, up to -0.17‰ in the reactant), which to our knowledge, is the first physico-chemical process up to now identified to trigger ²⁰⁰Hg anomalies that being frequently detected in atmospheric samples.

References

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