Reconciling Disparate Mechanisms for Oxidation of Hg(0) to Hg(II) in the Gas Phase

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Mostly Hg(0) Emitted but Much Hg(II) Deposited

Gas-phase redox affects how readily Hg enters food chain

\[ [\text{Hg (g)}] \approx 2 \text{ ng/meter}^3 \]
\[ = 0.2 \text{ pptv} \]
\[ = 5 \times 10^6 \text{ atoms cm}^{-3} \]

Fish: up to \(~1 \mu g/g (5 \mu M)\)
EPA blood Ref Dose: 29 nM
Rain: \(~50 \text{ pM}\)
Ocean: \(~1 \text{ pM}\)
Hg Health Effects and Sources

Neurotoxin
- Hatter’s shakes
- Minimata Disease (1953-now)
- Fetal damage

Major Sources
- Gold refining
- Combustion

EPA/DAI KUROKAWA
Competing Mechanisms for Hg(0) to Hg(II)

**One-Step by OH and Ozone**  
(CMAQ-Hg)

- \[ \text{Hg} + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2 \quad \Delta H^\circ = +20 \text{ kcal/mole} \]
- \[ \text{HO} + \text{Hg} \rightarrow \text{HOHg} \rightarrow \text{HgO} + \text{HO}_2 \quad \Delta H^\circ = -11 \text{ kcal/mole} \]

**Two-Step (by Br, Cl, and OH)**  
(GEOS-Chem)

\[ \text{X}^\bullet + \text{Hg} \leftrightarrow \text{XHg}^\bullet \rightarrow \text{XHgY} \]

- \( \text{X}^\bullet = \text{Br, Cl, OH} \)
- \( \text{•Y} = \text{NO}_2, \text{HO}O, \text{ROO}, \text{BrO}, \ldots \)

From computations (& flash photolysis LIF experiments)

Can’t explain observations in continental boundary layer.

!!! \[ \text{HgO (g)} \rightarrow \text{Hg} + \text{O} \quad \Delta H^\circ = +4 \text{ kcal/mol} \]
Two-Step Oxidation by Br versus OH

\[ \text{X}^- + \text{Hg} \rightarrow \text{XHg}^- \rightarrow \text{XHgY} \quad \text{X}^- = \text{Br, Cl, OH} \]

\[ \cdot \text{Y} = \text{NO}_2, \text{HOO, ROO, BrO, ...} \]

\[ \text{Br} + \text{Hg} \rightarrow \text{BrHg}^- \rightarrow \text{BrHgY} \quad \sim 90\% \]

\[ \text{OH} + \text{Hg} \rightarrow \text{HOHg}^- \rightarrow \text{HOHgY} \quad < 5\% \]

\[ \text{Lab} [\cdot \text{Y}] \]

\[ \text{Tropospheric} [\cdot \text{Y}] \]

\[ \text{HOHgY} \quad \sim 100\% \]

Dibble et al. *JPC A* (2020)
Effects of $\text{HOHg}^\bullet + \text{O}_3$

$\text{HOHg}^\bullet + \text{O}_3 \rightarrow \text{HOHgO}^\bullet + \text{O}_2$

$[\text{O}_3] >> [\text{NO}_2]$ or $\Sigma[\bullet Y]$ if $k(\text{HOHg}^\bullet + \text{O}_3)$ high:

$\text{HOHg}^\bullet \rightarrow \text{Hg(II)}$ efficient

$\text{HOHgO}^\bullet$ chemistry:

D.T.H. Edirappulige et al. ms in preparation:
No Barrier in Pot. Energy

Oxidation of HOHg by O3

Effective Core Potential for Hg and Br and aug-cc-pVTZ for other.

Barrier in $G(T) \Rightarrow k(T)$

Gibbs En.  Pot. En.
Rate Constant for BrHg + O\textsubscript{3}

\[ k(\text{BrHg} + \text{O}_3) \text{ from Gomez Martin et al. } \textit{PCCP} \text{ 2022} \]

DFT: CAM-B3LYP-D3BJ

CCSD(T): Energies with DFT data on the reaction path

Graph showing rate constants for BrHg + O\textsubscript{3} as a function of temperature (K) with rate constants at different temperatures (x10^11 cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}).
Rate Constants for BrHg + O$_3$ and HOHg + O$_3$

We recommend k(exp) for HOHg, also.

$k$(BrHg + O$_3$) from Gomez Martin et al. //PCCP 2022

DFT: CAM-B3LYP-D3BJ
CCSD(T): Energies with DFT data on the reaction path
Together, OH and Ozone Oxidize Hg(0)

Profiles from CMAQ, 39° N for Eastern United States.

\[ k(\text{HOHg}^\bullet + \text{O}_3) = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

One latitude in Eastern US

With ozone, two step oxidation initiated by OH is efficient.
Together, OH and Ozone Oxidize Hg(0)

Globally

OH $\sim$ 30\% (vs. <1\%) of trop Hg(0) oxidation

$k(\text{HOHg}^\bullet + \text{O}_3) = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

$= 40\%$ of observed $k(295 \text{ K})$

Conclusions

$O_3$ efficiently oxidizes $HOHg\cdot$ (and $BrHg$) to $Hg(II)$

OH and ozone, **together**, convert $Hg(0)$ to $Hg(II)$

Globally: OH-initiation $\sim50\%$ of gross oxidation

Future Directions

Refine $k(HOHg\cdot + O_3)$ and fate of $XHgO\cdot$

Photolysis of $Hg(OH)_2$

Chemistry in/on aerosol

Thank you for your attention!!
Can Other Radicals Initiate Hg(0) Oxidation?

Do other radicals bond strongly to Hg?

F and Cl react with everything else, so [F] and [Cl] too low to remove Hg(0). Bonds to Hg(0) break before reaction with anything else.
Mechanism

Br + Hg + M → hv

BrHg• + M → BrHgOOH

NO₂ → hv

BrHgONO → hv

CO

hn

NO

BrHgO•

Rh

BrHgOH

BrHgONO₂

HOO• → BrHgOOH

O₃ → hv
Mechanism with OH

\[ \text{OH} + \text{Hg} + \text{M} \]

\[ \text{HOHg}^- + \text{M} \]

\[ \text{NO}_2 \]

\[ \text{CO} \]

\[ \text{HOHgONO} \]

\[ \text{HOHgO}^- \]

\[ \text{RH} \]

\[ \text{Hg(OH)}_2 \]

\[ \text{HOHgONO}_2 \]

\[ \text{hv} \]

\[ \text{O}_3 \]
Why not Ozone-Initiated Oxidation of GEM?

Experiments: \( k = 3-80 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)

One-Step mechanism: \( \text{Hg} + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2 \)

Subsequently learned Hg-O bond \(~4\text{ kcal/mole}\)

1) \( \Delta H^\circ \) too + for reported \( k \) to reflect this mechanism

2) \( \text{HgO} \rightarrow \text{Hg} + \text{O} \text{ fast} \Rightarrow \text{GEM would not be removed?!} \)

Explanation? \( \Rightarrow \) surface reactions/catalysis