

Supporting Information for

Modeling the OH-Initiated Oxidation of Mercury in the Global Atmosphere Without Violating Physical Laws

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Analysis of the experiment of Sommar et al on the kinetics of OH + Hg

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Figure S2. Annually averaged [Br]:[OH] ratio. (Left) spatial variation at ground level for the entire globe. (Right) variation with altitude and latitude averaged over longitude.

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Table S1. Bond lengths (R, in Å) and angles (A, in degrees), rotational constants (cm^{-1}) for OH and HOHg using couple clusters with various basis sets and correlating all (Full) electrons or with a frozen core (FC).

Species	Parameter	AVTZ	AVQZ	AwCVTZ(FC)	AwCVTZ(Full)	ΔCV	AVQZ+ ΔCV
OH	R(OH)	--	0.9706	0.9729	0.9721	-0.0007	0.9699
HOHg	R(HgO)	2.1129	2.1060	2.1116	2.1087	-0.0029	2.1031
	R(OH)	0.9694	0.9669	0.9691	0.9684	-0.0006	0.9662
	A(HgOH)	103.86	103.99	103.86	103.75	-0.11	103.88

Species	Rotational Constants (cm^{-1})		
OH	18.9016		
HOHg	20.5065	0.2395	0.2367

Table S2. Absolute Energies (Hartree) and zero-point energy (ZPE, kcal/mol) of OH, Hg and HOHg at CCSD(T)/AVQZ+ ΔCV geometries.

Level of theory/Basis Set	HgOH	Hg	OH
CCSD(T,full)/AcwVTZ	-229.0311101	-153.3103858	-75.7028212
CCSD(T,full)/AcwVQZ	-229.1220877	-153.3776988	-75.7253279
CCSD(T,full)/AcwV5Z	-229.1583990	-153.4066457	-75.7322037
CCSD(T,full)/CBS ^a	-229.1795636	-153.4235391	-75.7361871
CCSD(T)/VTZ	-228.6195091	-152.9666018	-75.6377222
CCSDT/VTZ	-228.6185704	-152.9651402	-75.6380173
CCSDT/VDZ	-228.4423767	-152.8719825	-75.5594626
CCSDT(Q)/VDZ	-228.4439567	-152.8728023	-75.5597117
ZPE CCSD(T)/AVTZ (kcal/mol)	7.11	0	5.31
SF-RASSI/CASPT2	-19679.99314	-19604.27270	-75.69673
SO-RASSI/CASPT2	-19679.99333	-19604.27271	-75.69707

a) see Equation (5) in the text of the paper

Input File 1: Input file for program *thermo* for computing Kc for OH + Hg = HOHg•.

```

KCAL  MCC
9
200. 220. 240. 260. 280. 298.15 300. 320. 340.

3
reac  Hg      15.42
Hg
1  1  1
0.0  1
0  'HAR'  'CM-1'

reac  OH      8.90
OH
1  1  2
0.0  2
139.7  2
2  'HAR'  'CM-1'
1  vib    3718.      -75.40      1
2  qro    18.9016    1.0        2

prod  HOHg_10.5      13.30
HOHg
1  1  1
0.0  2
4  'HAR'  'CM-1'
1  vib    401.      -5.91      1
2  vib    824.      -3.47      1
3  vib    3749.     -78.33     1
4  top    0.2381    20.50651  1  ! SQRT(0.2395×0.2367)  20.5065

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Table S3: Literature enthalpies (kcal mole⁻¹) for OH and Hg, calculated enthalpies for HOHg•, and calculated entropies (cal mole⁻¹ K⁻¹) and free energies (kcal mole⁻¹) for all three species from the program *thermo*. Entropies in parentheses are from JPL Data Evaluation #18.^a Standard state is 1 bar partial pressure.

Species	$\Delta_f H^\circ$ (0 K)	$\Delta_f H^\circ$ (298.15 K)	S° (298.15 K)	$\Delta_f G^\circ$ (298.15 K)
OH ^b	8.90	8.96	43.86 (43.91)	7.93
Hg ^a	15.42	14.67	41.82 (41.81)	7.62
HOHg	13.30	11.64	64.52	9.78

a) J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, D. M. Wilmouth, and P. H. Wine "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18," JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015
<http://jpldataeval.jpl.nasa.gov>.

b) Active Thermochemical Tables version 1.22c. <https://atct.anl.gov>.

Table S4. Cartesian coordinates (Å), unscaled harmonic vibrational frequencies (cm⁻¹) and rotational constants (GHz) for all species at PBE0/AVTZ.

<p>CH₃OO• C 1.08387500 -0.17975500 0.00002000 H 1.13923100 -0.79795000 -0.89521900 H 1.86351300 0.57900300 -0.00163700 H 1.14115300 -0.79618200 0.89630700 O -0.15795900 0.53737200 0.00005700 O -1.17293400 -0.27566400 -0.00000300</p>	<p>Frequencies: 135.19, 499.83, 953.36, 1129.88, 1184.91, 1253.47, 1440.09, 1467.09, 1478.31, 3063.10, 3158.63, 3173.04</p>
<p>HOHg• O 0.01050700 1.90746000 0.00000000 H -0.92465100 2.14652800 0.00000000 Hg 0.01050700 -0.21757800 0.00000000</p>	<p>Frequencies: 366.40, 812.34, 3813.72</p>
<p>HOHgCH₂CH₂• Hg -0.20991000 -0.07257600 -0.00001800 C 1.85215200 -0.52123000 -0.00172800 H 2.01172300 -1.13133000 0.88726500 H 2.01120800 -1.12566200 -0.89468900 C 2.59894700 0.72236800 0.00196400 H 2.82179800 1.24007900 -0.92150100 H 2.82234100 1.23423500 0.92855200 O -2.10869100 0.56984000 -0.00344900 H -2.71135000 -0.17680000 0.02796900</p>	<p>Frequencies: 37.77, 93.61, 140.12, 227.56, 322.55, 466.58, 557.76, 612.20, 721.96, 853.78, 950.10, 1054.68, 1122.01, 1244.22, 1445.89, 1484.60, 3076.42, 3137.64, 3162.98, 3263.13</p>
<p>TS for HOHg•g + CH₂=CH₂ Hg -0.26950400 -0.14869400 -0.00000100 C 2.34486700 -0.39014500 0.00000700 H 2.30742000 -0.96201700 0.91967100 H 2.30742700 -0.96203400 -0.91964700 C 2.73534000 0.90167200 -0.00000300 H 2.87573200 1.44976400 -0.92345700 H 2.87572400 1.44978100 0.92344200 O -2.06432100 0.94480700 0.00000500 H -2.77268100 0.29241000 -0.00001100</p>	<p>Frequencies: 133.90i, 32.00, 44.86, 153.52, 194.56, 341.53, 410.02, 811.23, 814.34, 899.20, 935.37, 1017.22, 1233.18, 1313.42, 1460.59, 1591.45, 3149.51, 3160.67, 3229.54, 3257.21, 3841.98</p>
<p>HOHgNO O 2.15154700 -0.35930400 -0.00005300 H 2.64857100 0.46357600 0.00093100 Hg 0.18414500 0.04060500 -0.00001200 N -1.93867800 0.44733700 -0.00005000 O -2.62772200 -0.49611300 0.00009800</p>	<p>Frequencies: 102.53, 108.87, 116.87, 247.95, 518.94, 573.92, 860.93, 1730.87, 3861.73</p>
<p>HOHgNO₂ O -0.11231300 2.29827400 0.00000000 H 0.77341300 2.67239400 0.00000000 Hg 0.00000000 0.34390500 0.00000000 N 0.00483200 -1.72660100 0.00000000</p>	<p>Frequencies: 104.96, 109.10, 155.74, 272.36, 294.20, 539.10, 608.50, 856.73, 945.96, 1424.91, 1627.40, 3861.00</p>

O 1.08102500 -2.27876200 0.00000000 O -1.06961600 -2.28183300 0.00000000	
HOHgONO_anti O 2.33037900 -0.36030700 0.12108500 H 2.65654100 -0.62237100 -0.74434700 Hg 0.42929700 0.04956000 -0.00296500 O -1.48539200 0.58291400 -0.01296500 N -2.31675900 -0.51296700 0.00875600 O -3.44286100 -0.19156900 0.00690700	Frequencies: 92.77, 112.61, 126.43, 193.41, 222.32, 407.90, 627.06, 790.40, 950.81, 968.07, 1745.97, 3864.42
HOHgONO syn-cis O -2.22911000 -0.41144200 -0.00058200 H -2.29566300 -1.37067800 0.00117200 Hg -0.33002400 0.08486200 0.00007800 O 1.56176300 0.89534100 -0.00014200 N 2.47732500 -0.01600900 -0.00020700 O 2.08688900 -1.14717300 -0.00001700	Frequencies: 95.79, 127.07, 145.29, 159.91, 388.67, 401.89, 616.55, 901.14, 958.09, 1095.91, 1599.67, 3861.88 12.7058231 1.6792417 1.4832153 GHz
HOHgONO syn-trans 8 -2.160242 0.617805 -0.000000 1 -2.781737 -0.115509 -0.000000 80 -0.328923 -0.086716 -0.000000 8 1.563315 -0.899394 0.000000 7 2.472319 0.019228 0.000000 8 2.070590 1.146367 0.000000	Frequencies: 94.0251, 119.9597, 140.4335, 158.2994, 388.7822, 406.4456, 612.4727, 901.6904, 950.6004, 1093.3436, 1601.9141, 3864.6126 12.1627080 1.7010833 1.4923608 GHz
HOHgOO• O 2.11318800 0.30541100 -0.11959200 H 2.43569600 0.58765300 0.74123800 Hg 0.18934100 -0.05340600 0.00317400 O -1.79370300 -0.45949100 0.01236100 O -2.51735900 0.61468400 -0.01716200	Frequencies: 9.85, 124.12, 154.80, 272.56, 529.63, 623.08, 948.39, 1210.90, 3856.72
HOHgOOH O 2.10997400 -0.39531200 -0.11045200 H 2.47761500 -0.44437600 0.77579400 Hg 0.21140500 0.06014100 0.00308600 O -1.69785700 0.56823400 -0.01468600 H -2.96205000 -0.59823000 0.73051600 O -2.46561700 -0.64400300 -0.09401500	Frequencies: 117.28, 141.60, 166.04, 247.73, 275.30, 563.26, 636.41, 953.90, 969.87, 1374.20, 3814.37
HOHgOBr O -1.210006 0.222304 2.448117 H -1.118086 -0.065304 3.360519 Hg 0 0.498846 0.002806 1.532879 O 2.154774 -0.271331 0.489574 Br 3.261446 1.177288 0.517167	Frequencies: 82.3287, 100.4642, 173.1336, 176.7552, 513.2004, 625.5346, 722.0277, 966.1473, 3865.2590 17.26172 0.72400 0.69635 GHz
HOO• O 0.05511600 -0.60142000 0.00000000 H -0.88185800 -0.86402100 0.00000000 O 0.05511600 0.70942300 0.00000000	Frequencies: 1217.99, 1458.48, 3647.41

NO N 0.00000000 0.00000000 -0.60818500 O 0.00000000 0.00000000 0.53216200	Frequency: 2022.61
NO₂ N 0.00000000 0.00000000 0.31610400 O 0.00000000 1.09253500 -0.13829600 O 0.00000000 -1.09253500 -0.13829600	Frequencies: 780.43, 1435.84, 1776.38
O₂ O 0.00000000 0.00000000 0.59693600 O 0.00000000 0.00000000 -0.59693600	Frequency: 1704.60
CH₂=CH₂ C 0.00000000 0.00000000 0.66173400 H 0.00000000 0.92272200 1.23063300 H 0.00000000 -0.92272200 1.23063300 C 0.00000000 0.00000000 -0.66173400 H 0.00000000 -0.92272200 -1.23063300 H 0.00000000 0.92272200 -1.23063300	Frequencies: 824.37, 979.62, 985.82, 1063.67 1237.78, 1378.90, 1466.22, 1700.22, 3141.96, 3158.10, 3218.10
TS [HOHgNO₂ → anti-HOHgONO] Hg 0.36291000 0.00830000 0.00000000 O -1.64885500 1.03472200 -0.00000000 N -1.87194200 -0.23726900 0.00000000 O -2.98689000 -0.63402500 -0.00000000 O 2.30061100 -0.33983100 -0.00000000 H 2.75185200 0.50992500 0.00000000	Frequencies: 307.58i, 110.97, 120.42, 162.12, 232.50, 312.84, 598.90, 784.90, 979.37, 1230.64, 1679.45, 3852.48 19.0988135 1.4294076 1.3298760 GHz
TS [anti-HOHgONO-->syn-HOHgONO] Hg 0.39934400 -0.06230000 -0.01543500 O -1.45080100 -0.74460800 -0.17316900 N -2.45937700 -0.03154300 0.48118500 O -2.96406700 0.77566500 -0.19444000 O 2.23751200 0.58948000 0.00362300 H 2.68697800 0.24053800 0.77843000	Frequencies: 224.05i, 98.88, 116.57, 155.43, 186.48, 516.74, 631.49, 720.91, 858.29, 971.00, 1739.44, 3862.65 16.9404489, 1.3206041, 1.2553045 GHz
TS [cis-trans] syn-HOHgONO 8 2.191253 0.533108 -0.111050 1 2.578641 0.532119 0.768719 80 0.332563 -0.086265 0.001208 8 -1.555719 -0.892553 -0.003517 7 -2.484694 0.011572 0.001360 8 -2.109386 1.145457 0.005203	Frequencies: 89.6158i, 120.8916, 136.6857, 164.1415, 380.6952, 412.8314, 612.5693, 900.2156, 947.3333, 1073.6658, 1612.7089, 3864.1433 12.3995991 1.6707267 1.4790194 GHz
HOHgOOCH₃ H 2.764289 0.256176 0.706042 Hg 0.451305 -0.072863 -0.026777 O -1.365741 -0.837678 -0.191041 O -2.238793 -0.066395 0.639194 C -3.032927 0.710621 -0.216165 H -3.601223 0.083227 -0.90789	Frequencies: 44.8170, 113.8309, 129.3393, 166.0633, 217.9223, 275.7847, 442.9395, 585.8291, 644.6935, 907.5841, 953.2643, 1079.3058, 1174.1647, 1214.2159, 1440.9058, 1454.3649, 1499.6806, 3001.5221, 3078.7218, 3124.9196, 3867.7840

H -3.717848 1.252909 0.438834	
H -2.427556 1.427759 -0.784712	
HOHgH	Frequencies: 598.47, 605.80, 620.13, 875.29
H -0.000018734 0.00000 0.0000	2189.33 3888.08
Hg 0.000063362 0.00000 0.0000	
O -0.000032451 0.00000 0.0000	684.0818399 7.6429827 7.5585341 GHz
H -0.000012177 0.00000 0.0000	

Table S5. Absolute energies (in Hartree), zero-point vibrational energies (ZPE, in kcal/mole), and value of the T_1 diagnostic at PBE0/AVTZ geometries for HOHg• chemistry.

Species	PBE0/AVTZ	ZPE	CCSD(T)/AVTZ	T_1
HOHg•	-229.2097675	7.14	-228.6431202	0.0222
NO ₂	-204.9465629	5.71	-204.8164244	0.0239
HOO	-150.8139351	9.04	-150.72615	0.0290
CH ₃ OO (conformer?)	-190.0847754	27.07	-189.96061	0.0281
NO	-129.8023078	2.89	-129.72574	0.0231
O ₂	-150.2301511	2.43	-150.14049	0.0172
BrO	-491.891995	1.09	-490.71793	0.0324
HHgO	-229.1499778	5.64	-228.580582	0.0255
CH ₂ =CH ₂	-78.5120167	32.02	--	--
HOHgH	-229.8363131	12.54	--	--
syn-HOHgONO	-434.2214999	14.79	-433.53477	0.0239
anti-HOHgONO	-434.2114166	14.44	-433.52589	0.0222
HOHgNO ₂	-434.2166795	15.39	-433.524166	0.0234
HOHgOOH	-380.0893637	18.76	-379.44362	0.0203
HOHgOOCH ₃	-419.3585639	36.31	-418.6774353	0.0198
HOHgNO	-359.0325453	11.6	-358.38887	0.0292
HOHgOO	-379.4560835	11.10	-378.80090	0.0294
HOHgOBr	-721.1878517	10.32	-719.45479	
HOHgO•	-304.3302811	9.18	-303.72133	0.0215
HOHgCH ₂ CH ₂ •	-307.7322529	39.89	--	0.0292
TS (HOHg + CH ₂ =CH ₂ → HOHgCH ₂ CH ₂ •)	-307.7218942	39.85	--	--
HOHg-- CH ₂ =CH ₂ (van der Waals complex)	-307.724828	39.94	--	--
TS (HOHgNO ₂ → anti- HOHgONO)	-434.1849917	14.38	-433.49771	0.0214
TS (anti → syn HOHgONO)	-434.1986904	14.09	-433.51397	0.0215
TS syn-HOHgONO (cis → trans)	-434.2208763	14.61	-433.53424	0.0237

NOTES

a) The “O₂, NO” over an arrow represents two reactions: First, O₂ adds to a carbon centered radical to form a peroxy radical (ROO); second, the peroxy radical reacts with NO to make an alkoxy radical (RO) + NO₂.

b) “isom.” stands for isomerization, that is, a 1,5 H-shift reaction

c) “decomp.” stands for β C-C scission to form a C-centered radical and an aldehyde or ketone.

ASSUME branching ratio for RONO₂ formation is 0.15, so ROO + NO makes 85% RO + NO₂. So the product of each reaction arrow with “O₂, NO” over it is only formed in 85% yield.

ASSUME we can neglect ROO + NO₂ → ROONO₂ as a loss process for ROO (because the ROONO₂ will dissociate in ~1 sec).

Branching Fractions:

Note: cyclohexoxy makes cyclohexanone (via reaction R6 of the mechanism paper) in competition with scission (R5). Scission occurs to a significant extent as a chemically activated reaction when RO is produced from ROO + NO. As a result, the ratio of O₂ reaction to scission at high [NO] (as in Sommar et al and this cyclohexane mechanism paper) is ~0.7. This means that the fraction of cyclohexoxy reacting with O₂ is 0.4 and the fraction undergoing scission (propagating the organic radical chemistry) is 0.6.

Note that the 4th generation carbon-centered radical reacts with O₂ mostly makes an aldehyde (90%) versus making RC(O•)OH (10%).

Let f equal the ratio of molecules of NO₂ produced per molecule of cyclohexane (CH) reacted. f decreases as we proceed from the first to the second, etc. generation of ROO•.

For the 1st generation, f=0.85

For the 2nd generation, $f = 0.85 \times 0.6 \times 0.85 = 0.43$

For the 3rd generation, $f = 0.85 \times 0.6 \times 0.85 \times 0.85 = 0.37$

For the 4th generation, $f = 0.85 \times 0.6 \times 0.85 \times 0.85 \times 0.1 = 0.04$

Approximate f for each of the next two as 0.04, also. So $\Sigma f = 1.8$ and

So the [NO₂] produced from ROO + NO (not including R=H) = $1.8 \times [\text{CH}]_{\text{reacted}}$

At t=5 minutes (300 sec), we can see from Figure 2 of Sommar et al. that $\ln([\text{CH}]_0/[\text{CH}]_t) = 0.44$. This means $[\text{CH}]_t/[\text{CH}]_0 = 0.64$, meaning $[\text{CH}]_{\text{reacted}} = 0.36 \times (5.2 \times 10^{14}) = 1.9 \times 10^{14}$ molecule cm⁻³.

So the [NO₂] produced from ROO + NO (not including R=H) is (from 2.a.) 1.8 times $[\text{CH}]_{\text{reacted}}$
[NO₂] produced from ROO + NO = 3.3×10^{14} molecule cm⁻³

2. NO₂ produced in HOO + NO → OH + NO₂

Consider, next, that HOO is produced in cyclohexane oxidation, and this HOO is source of NO₂, via the reaction $\text{HOO} + \text{NO} \rightarrow \text{OH} + \text{NO}_2$.

We will get at the extent of this NO₂ production by considering the OH produced in the same reaction. Every OH produced corresponds to a molecule of NO₂ produced. All of the OH produced in the first 5 minutes has reacted, mostly with cyclohexane or CH₃ONO (for the moment, we neglect $\text{OH} + \text{NO}_2 \rightarrow \text{HONO}_2$). ASSUME a negligible fraction of OH has reacted with Hg due to its low concentration and the low OH + Hg rate constant. ASSUME that the fraction of loss of OH with oxidation products of cyclohexane is low at 5 minutes (not a good assumption at longer times).

Then the extent of OH reacted with CH equals $[\text{CH}]_{\text{reacted}} = 1.9 \times 10^{14} \text{ molecule cm}^{-3}$. But we also need to compute the extent of the reaction $\text{OH} + \text{CH}_3\text{ONO}$, which is trickier:

Consider $\text{OH} + \text{CH}_3\text{ONO} \rightarrow \text{CH}_2\text{ONO}^* \rightarrow \text{HCHO} + \text{NO}_2$. If the pseudo-first order rate constant, k' , for loss of OH via reaction with CH₃ONO and CH were the same, then OH reacted with CH₃ONO would equal $[\text{CH}]_{\text{reacted}}$. However, this is not the case:

a) k for $\text{OH} + \text{CH}_3\text{ONO}$ is $2.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (NIST) but k for $\text{OH} + \text{CH}$ is $7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

b) The initial $[\text{CH}_3\text{ONO}]$ is much greater than the initial $[\text{CH}]$. I am going to ASSUME that the concentration ratio $[\text{CH}_3\text{ONO}]/[\text{CH}]$ stays constant (at 5.8).

The ratio of OH lost in reaction with CH₃ONO to that lost in reaction with CH is $k'_{\text{loss via CH}_3\text{ONO}}/k'_{\text{loss via CH}}$. Using the information in (a) and (b), one gets:

$$\begin{aligned} [\text{OH}]_{\text{reacted with CH}_3\text{ONO}} &= 5.8 (2.6 \times 10^{-13}) / (7.2 \times 10^{-12}) [\text{CH}]_{\text{reacted}} \\ &= 0.4 \times 10^{14} \text{ molecule cm}^{-3} \end{aligned}$$

$[\text{OH}]_{\text{produced}} = [\text{OH}]_{\text{reacted}} = (1.9 + 0.4) \times 10^{14} \text{ molecule cm}^{-3} = 2.3 \times 10^{14} \text{ molecule cm}^{-3}$. Recall that these mechanistic and kinetic gymnastics were carried out with the goal of computing the NO₂ produced in $\text{HOO} + \text{NO} \rightarrow \text{OH} + \text{NO}_2$. The NO₂ produced in this reaction equals the OH produced in this reaction, which equals the OH lost in all reaction (what we just calculated, above).

So the **[NO₂] produced in HOO + NO = 2.3 × 10¹⁴ molecule cm⁻³**

The TOTAL [NO₂] produced (from HOO + NO AND ROO + NO)=

$$3.4 \times 10^{14} \text{ molecule cm}^{-3} + 2.3 \times 10^{14} \text{ molecule cm}^{-3} = \mathbf{5.7 \times 10^{14} \text{ molecule cm}^{-3}}$$

3. Competition between HOHg dissociation and reaction with NO₂

Above, we determined that the gross (total) production of NO₂ amounted to $5.7 \times 10^{14} \text{ molecule cm}^{-3}$. Of course, NO₂ will also be lost by various processes, so the [NO₂] above does not correspond to the actual value of [NO₂] at $t=5$ minutes. Here I assume that only ~40% of this

NO₂ is available for reaction with HOHg when I estimate k' for loss of HOHg by reaction with NO₂: [NO₂] ≈ 2.0 × 10¹⁴ molecule cm⁻³

ASSUME: k_{HOHg + NO₂} ≈ k_{BrHg + NO₂}

$$\approx 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \text{ at 1 atm and 295 K from Jiao, Y.};$$

Dibble, T. S. First Kinetic Study of the Atmospherically Important Reactions BrHg + NO₂ and BrHg + HOO. *Phys. Chem. Chem. Phys.* **2017**, *19* (3).

The pseudo-first order rate constant, k'_{HOHg + NO₂}, or loss of HOHg by reaction with NO₂ equals:

$$\begin{aligned} k'_{\text{HOHg} + \text{NO}_2} &= k_{\text{HOHg} + \text{NO}_2}[\text{NO}_2] \\ &= 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} [2.0 \times 10^{14} \text{ molecule cm}^{-3}] \\ &= 1.4 \times 10^4 \text{ sec}^{-1} \end{aligned}$$

By contrast, the rate constant for HOHg dissociation, k_{dissoc}, as listed in Eqn 13 of the paper, is k_{-1,0(T)} = 1.22 × 10⁻⁹ e^{-5720/T} cm³ molecule⁻¹ sec⁻¹, where the rate of dissociation equals

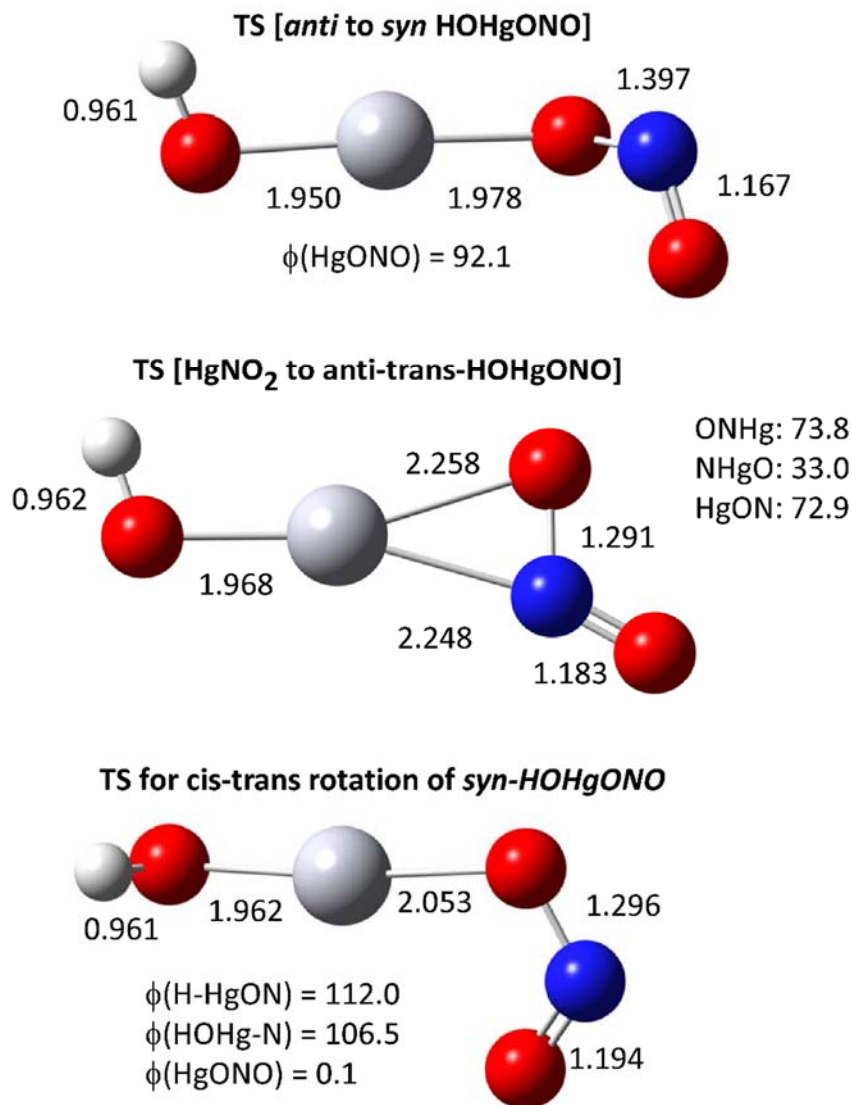
$$k_{-1,0}(T)[\text{HOHg}\cdot][\text{M}]$$

so the pseudo-first rate constant for HOHg dissociation, k'_{dissoc}:

$$\begin{aligned} k'_{\text{dissoc}} &= k_{-1,0}(T)[\text{M}] \\ &= 4.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} [2.5 \times 10^{19} \text{ molecule cm}^{-3}] \\ &= 110 \text{ sec}^{-1} \end{aligned}$$

Because k'_{dissoc} is ~100× smaller than k'_{HOHg + NO₂}, it is reasonable to equate the observed (net) rate of loss of Hg(0) with the rate of reaction of Hg(0) with OH radical.

Figure S1. Structures of transition states connecting isomers and conformers of the products of HOHg• + NO₂.



Substitution of OH for Br adds a degree of conformational freedom, but only one of these isomers possesses more than one conformer (See Figure 2 in the text). In HOHgNO₂, all atoms lie in the same plane; a structure with the hydrogen atom *perp* to the NO₂ group corresponds to a transition state connecting two indistinguishable planar HOHgNO₂ structures. For *anti*-HOHgONO, only one conformer was found; in this structure of C₁ symmetry, the hydrogen atom sticks out of the roughly planar arrangement of the other atoms. *Syn*-HOHgONO possesses two conformers of C_s symmetry; one in which the hydrogen atom is *cis* to the -ON=O group and one *trans*. The *cis* structure is more stable by 0.07 kcal/mole. These two are connected by a transition state in which the hydrogen atom is *perp* to the -ON=O group. This transition state lies only 0.15 kcal/mole above the *cis* conformer.

Figure S2. Annually averaged [Br]:[OH] ratio. (Left) spatial variation at ground level for the entire globe. (Right) variation with altitude and latitude averaged over longitude.

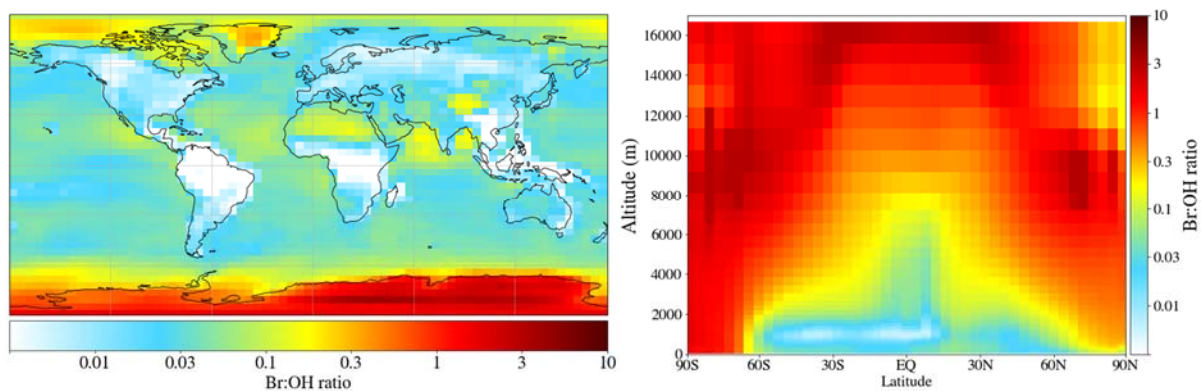


Figure S3. Annually averaged fraction of Hg(I) as HgOH. (Left) spatial variation at ground level for the entire globe. (Right) variation with altitude and latitude averaged over longitude.

