Supporting Information for

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

Theodore S. Dibble^{a*}, Hanna L. Tetu^a, and Yuge Jiao^a, Colin P. Thackray^b, Daniel J. Jacob^{b, c}

- a) Department of Chemistry, State University of New York, College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY, 13210
- b) Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA

c) Department of Earth & Planetary Sciences, Harvard University, Cambridge, MA, USA

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

Figure S1. Structures of transition states connecting isomers and conformers of the products of $HOHg \bullet + NO_2$.

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.

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+\DCV
OH	R(OH)		0.9706	0.9729	0.9721	-0.0007	0.9699
	R(HgO)	2.1129	2.1060	2.1116	2.1087	-0.0029	2.1031
HOHg	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 $CCSD(T)/AVQZ+\Delta CV$ 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

KCAL MCC 9 200. 220. 240. 260. 280. 298.15 300. 320. 340. 3 15.42 reac Ηq Ηq 1 1 1 0.0 1 0 'HAR ' 'CM-1' OH 8.90 reac OH 2 1 1 0.0 2 139.7 2 2 'HAR' 'CM-1' 1 -75.40vib 3718. 1 2 2 qro 18.9016 1.0 prod HOHg_10.5 13.30 HOHg 1 1 1 2 0.0 4 'HAR' 'CM-1' 1 vib 401. -5.91 1 2 vib 824. -3.471 3 vib 3749. -78.331 4 0.2381 20.50651 1 ! SQRT(0.2395×0.2367) 20.5065 top

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

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	$\Delta_{\rm f} { m H}^{\circ} \left(0 \; { m K} \right)$	Δ _f H° (298.15 K)	S° (298.15 K)	$\Delta_{\rm f} {\rm G}^{\circ} (298.15 {\rm K})$
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 1.22e. <u>https://atct.anl.gov</u>.

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

CH ₃ OO•	Frequencies: 135.19, 499.83, 953.36,
C 1.08387500 -0.17975500 0.00002000	1129.88, 1184.91, 1253.47, 1440.09, 1467.09,
H 1.13923100 -0.79795000 -0.89521900	1478.31, 3063.10, 3158.63, 3173.04
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	
HOHg•	Frequencies: 366.40, 812.34, 3813.72
O 0.01050700 1.90746000 0.00000000	
H -0.92465100 2.14652800 0.00000000	
Hg 0.01050700 -0.21757800 0.00000000	
HOHgCH ₂ CH ₂ •	Frequencies: 37.77, 93.61, 140.12, 227.56,
Hg -0.20991000 -0.07257600 -0.00001800	322.55, 466.58, 557.76, 612.20, 721.96,
C 1.85215200 -0.52123000 -0.00172800	853.78, 950.10, 1054.68, 1122.01, 1244.22,
H 2.01172300 -1.13133000 0.88726500	1445.89, 1484.60, 3076.42, 3137.64, 3162.98,
H 2.01120800 -1.12566200 -0.89468900	3263.13
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	
TS for HOH•g + CH ₂ =CH ₂	Frequencies: 133.90i, 32.00, 44.86, 153.52,
Hg -0.26950400 -0.14869400 -0.00000100	194.56, 341.53, 410.02, 811.23, 814.34,
C 2.34486700 -0.39014500 0.00000700	899.20, 935.37, 1017.22, 1233.18, 1313.42,
H 2.30742000 -0.96201700 0.91967100	1460.59, 1591.45, 3149.51, 3160.67, 3229.54,
H 2.30742700 -0.96203400 -0.91964700	3257.21, 3841.98
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	
HOHgNO	Frequencies: 102.53, 108.87, 116.87, 247.95,
O 2.15154700 -0.35930400 -0.00005300	518.94, 573.92, 860.93, 1730.87, 3861.73
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	
HOH9NO2	Frequencies: 104.96, 109.10, 155.74, 272.36
HOHgNO₂ Q -0.11231300 2.29827400 0.00000000	Frequencies: 104.96, 109.10, 155.74, 272.36, 294.20, 539.10, 608.50, 856.73, 945.96
HOHgNO₂ O -0.11231300 2.29827400 0.00000000 H 0.77341300 2.67239400 0.00000000	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
HOHgNO ₂ O -0.11231300 2.29827400 0.00000000 H 0.77341300 2.67239400 0.00000000 Hg 0.00000000 0.34390500 0.00000000	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

O 1.08102500 -2.27876200 0.00000000				
O -1.06961600 -2.28183300 0.00000000				
HOHgONO_anti	Frequencies: 92.77, 112.61, 126.43, 193.41,			
O 2.33037900 -0.36030700 0.12108500	222.32, 407.90, 627.06, 790.40, 950.81,			
H 2.65654100 -0.62237100 -0.74434700	968.07, 1745.97, 3864.42			
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				
HOHgONO syn-cis	Frequencies: 95.79, 127.07, 145.29, 159.91,			
O -2.22911000 -0.41144200 -0.00058200	388.67, 401.89, 616.55, 901.14, 958.09,			
H -2.29566300 -1.37067800 0.00117200	1095.91, 1599.67, 3861.88			
Hg -0.33002400 0.08486200 0.00007800				
O 1.56176300 0.89534100 -0.00014200	12.7058231 1.6792417 1.4832153 GHz			
N 2.47732500 -0.01600900 -0.00020700				
O 2.08688900 -1.14717300 -0.00001700				
HOHgONO syn-trans	Frequencies: 94.0251, 119.9597, 140.4335,			
8 -2.160242 0.617805 -0.00000	158.2994, 388.7822, 406.4456, 612.4727,			
1 -2.781737 -0.115509 -0.0000	901.6904, 950.6004, 1093.3436, 1601.9141,			
80 -0.328923 -0.086716 -0.0000	3864.6126			
8 1.563315 -0.899394 0.0000				
7 2.472319 0.019228 0.0000	12.1627080 1.7010833 1.4923608 GHz			
8 2.070590 1.146367 0.0000				
HOHgOO•	Frequencies: 9.85, 124.12, 154.80, 272.56,			
O 2.11318800 0.30541100 -0.11959200	529.63, 623.08, 948.39, 1210.90, 3856.72			
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				
НОНдООН	Frequencies: 117.28, 141.60, 166.04, 247.73,			
O 2.10997400 -0.39531200 -0.11045200	275.30, 563.26, 636.41, 953.90, 969.87,			
H 2.47761500 -0.44437600 0.77579400	1374.20, 3814.37			
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				
HOHgOBr	Frequencies: 82.3287, 100.4642, 173.1336,			
O -1.210006 0.222304 2.448117	176 7552 513 2004 625 5346 722 0277			
H -1.118086 -0.065304 3.360519	066 1472 3865 2500			
Hg 0 0.498846 0.002806 1.532879	900.1475, 5805.2590			
O 2.154774 -0.271331 0.489574				
Br 3.261446 1.177288 0.517167	17.26172 0.72400 0.69635 GHz			
HOO•	Frequencies: 1217.99, 1458.48, 3647.41			
O 0.05511600 -0.60142000 0.00000000	1			
H -0.88185800 -0.86402100 0.00000000				
0.0.05511600.0.70942300.0.00000000				

NO	Frequency: 2022.61		
N 0.0000000 0.0000000 -0.60818500			
O 0.0000000 0.0000000 0.53216200			
NO ₂	Frequencies: 780.43, 1435.84, 1776.38		
N 0.00000000 0.00000000 0.31610400			
O = 0.00000000 = 1.09253500 = 0.13829600			
O = 0.00000000 - 1.09253500 - 0.13829600			
0	Frequency: 1704.60		
O_{1}^{0}	requercy. 1704.00		
O = 0.00000000 = 0.00000000 = 0.59693600			
CH -CH	Engine ping: 824 27, 070 62, 085 82, 1062 67		
$C_{12} - C_{12}$	Frequencies: 824.57, 979.02, 985.82, 1005.07		
	1237.78, 1378.90, 1466.22, 1700.22, 3141.96,		
H 0.00000000 0.92272200 1.23063300	3158.10, 3218.10		
H 0.00000000 -0.92272200 1.23063300			
C = 0.0000000 = 0.0000000 = 0.001/3400			
H 0.00000000 -0.92272200 -1.23063300			
H 0.0000000 0.92272200 -1.23063300	English 207.58: 110.07, 120.42, 1(2.12)		
$1S [HOHgNO_2 \rightarrow anti-HOHgONO]$	Frequencies: 307.381, 110.97, 120.42, 162.12,		
Hg 0.36291000 0.00830000 0.00000000	232.50, 312.84, 598.90, 784.90, 979.37,		
O -1.64885500 1.03472200 -0.0000000	1230.64, 1679.45, 3852.48		
N -1.8/194200 -0.23/26900 0.00000000			
0-2.98689000-0.63402500-0.0000000	19.0988135 1.4294076 1.3298760 GHz		
0 2.30061100 -0.33983100 -0.0000000			
H 2.75185200 0.50992500 0.0000000			
TS [anti-HOHgONO>syn-HOHgONO]	Frequencies: 224.051, 98.88, 116.57, 155.43,		
Hg 0.39934400 -0.06230000 -0.01543500	186.48, 516.74, 631.49, 720.91, 858.29,		
O -1.45080100 -0.74460800 -0.17316900	971.00, 1739.44, 3862.65		
N -2.45937700 -0.03154300 0.48118500			
0-2.964067000.77566500-0.19444000	16.9404489, 1.3206041, 1.2553045 GHz		
0 2.23751200 0.58948000 0.00362300			
H 2.68697800 0.24053800 0.77843000			
TS [cis-trans] syn-HOHgONO	Frequencies: 89.6158i, 120.8916, 136.6857,		
8 2.191253 0.533108 -0.111050	164.1415, 380.6952, 412.8314, 612.5693,		
1 2.578641 0.532119 0.768719	900.2156, 947.3333, 1073.6658, 1612.7089,		
80 0.332563 -0.086265 0.001208	3864 1433		
8 -1.555719 -0.892553 -0.003517			
7 -2.484694 0.011572 0.001360	12.3995991 1.6707267 1.4790194 GHz		
8 -2.109386 1.145457 0.005203			
HOHgOOCH ₃	Frequencies: 44.8170, 113.8309, 129.3393,		
H 2.764289 0.256176 0.706042	166.0633, 217.9223, 275.7847, 442.9395,		
Hg 0.451305 -0.072863 -0.026777	585.8291, 644.6935, 907.5841, 953.2643,		
O -1.365741 -0.837678 -0.191041	1079.3058, 1174.1647, 1214.2159,		
O -2.238793 -0.066395 0.639194	1440.9058, 1454.3649, 1499.6806,		
C -3.032927 0.710621 -0.216165	3001.5221, 3078.7218, 3124.9196, 3867.7840		
Н -3.601223 0.083227 -0.90789			

Н -3.717848 1.252909 0.438834	
Н -2.427556 1.427759 -0.784712	
HOHgH	Frequencies: 598.47, 605.80, 620.13, 875.29
Н -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
Н -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
НОО	-150.8139351	9.04	-150.72615	0.0290
CH3OO (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
HOHgOOCH3	-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 \rightarrow HOHgCH ₂ CH ₂ •)	-307.7218942	39.85		
HOHg CH ₂ =CH ₂ (van der Waals complex)	-307.724828	39.94		
TS (HOHgNO ₂ \rightarrow anti- HOHgONO)	-434.1849917	14.38	-433.49771	0.0214
TS (anti \rightarrow syn HOHgONO)	-434.1986904	14.09	-433.51397	0.0215
TS syn-HOHgONO (cis \rightarrow trans)	-434.2208763	14.61	-433.53424	0.0237

Analysis of the Experiment of Sommar et al on the kinetics of OH + Hg.

The idea is to estimate the competition between HOHg dissociation and reaction with NO₂ under the conditions of the experiment of Sommar et al (Sommar, J.; Gårdfeldt, K.; Strömberg, D.; Feng, X. A Kinetic Study of the Gas-Phase Reaction between the Hydroxyl Radical and Atomic Mercury. *Atmos. Environ.* **2001**, *35* (17), 3049–3054).

We will estimate the total (gross) concentration of NO₂ produced at the time of the first data collection (5 minutes).

1. NO₂ produced by ROO + NO \rightarrow RO + NO₂ (R \neq H)

We start by using the mechanism (see Scheme below) from *J. Phys. Chem. A* **2000**, *104*, 5072-5079 to identify all reactions that convert NO to NO₂ in the OH-initiated oxidation of cyclohexane (identified in the text, below, as CH).

Revised 2019.08.18



NOTES

a) The "O2, NO" over an arrow represents two reactions: First, O_2 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 \rightarrow 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 4^{th} 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 Σ f = 1.8 and

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

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

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

2. NO₂ produced in HOO + NO \rightarrow OH + NO₂

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

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 OH + NO₂ \rightarrow HONO₂). 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 $[CH]_{reacted} = 1.9 \times 10^{14}$ molecule cm⁻³. But we also need to compute the extent of the reaction OH + CH₃ONO, which is trickier:

Consider $OH + CH_3ONO \rightarrow CH_2ONO^* \rightarrow HCHO + NO_2$. 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 [CH]_{reacted}. However, this is not the case:

a) k for OH + CH₃ONO is 2.6×10^{-13} cm³ molecule⁻¹ sec⁻¹ (NIST) but k for OH + CH is 7.2×10^{-12} cm³ molecule⁻¹ sec⁻¹

b) The initial [CH₃ONO] is much greater than the initial [CH]. I am going to ASSUME that the concentration ratio [CH₃ONO]/[CH] stays constant (at 5.8).

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

[OH] reacted with CH₃ONO = $5.8 (2.6 \times 10^{-13})/(7.2 \times 10^{-12})$ [CH]_{reacted} = 0.4×10^{14} molecule cm⁻³

[OH]produced = [OH]reacted = $(1.9 \pm 0.4) \times 10^{14}$ molecule cm⁻³ = 2.3×10^{14} molecule cm⁻³. Recall that these mechanistic and kinetic gymnastics were carried out with the goal of computing the NO₂ produced in HOO + NO \rightarrow OH + NO₂. 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 = 2.3×10^{14} molecule cm⁻³

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

 3.4×10^{14} molecule cm⁻³ + 2.3×10^{14} molecule cm⁻³ = 5.7×10^{14} molecule cm⁻³

3. Competition between HOHg dissociation and reaction with NO₂

Above, we determined that the gross (total) production of NO₂ amounted to 5.7×10^{14} 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: $[NO_2] \approx 2.0 \times 10^{14}$ molecule cm⁻³

ASSUME: $k_{HOHg + NO2} \approx k_{BrHg + NO2}$

 \approx 7 × 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹ 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:

$$k'_{HOHg+NO2} = k_{HOHg+NO2}[NO_2]$$

= 7 × 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹ [2.0 × 10¹⁴ molecule cm⁻³]
= 1.4 × 10⁴ sec⁻¹

By contrast, the rate constant for HOHg dissociation, k_{dissoc} , as listed in Eqn 13 of the paper, is $k_{-1,0}(T) = 1.22 \times 10^{-9} e^{-5720/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, where the rate of dissociation equals

$$k_{-1,0}(T)$$
[HOHg•][M]

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

k'dissoc =
$$k_{-1,0}(T)[M]$$

= 4.6 × 10⁻¹⁸ cm³ molecule⁻¹ sec⁻¹ [2.5 × 10¹⁹ molecule cm⁻³]
= 110 sec⁻¹

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 $HOHg \bullet + NO_2$.

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 C_1 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 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.

