Supplementary Materials

for

Thermodynamics of reactions of ClHg• and BrHg• radicals

with atmospherically abundant free radicals

T. S. Dibble, M. J. Zelie, and H. Mao

{Chemistry Department, State University of New York-Environmental Science and Forestry, Syracuse, NY, USA}

Correspondence to: T. S. Dibble (tsdibble@esf.edu)

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Table S1 Absolute Energies (Hartree), zero point energies (ZPE, in kJ/mol at B3LYP/aVTZ), and values of the T_1 diagnostic for all neutral species. See manuscript for definition of aVTZ basis set. 1 Hartree = 2625.5 kJ/mol.

Species	B3LYP	B3LYP ZPE	CCSD	CCSD(T)	T1 Diag
BrHg•	-570.47347	0.9	-568.98573	-569.02146	0.019
Br	-416.87989	0.0	-415.74309	-415.75140	0.004
NO	-129.94325	11.8	-129.70673	-129.72598	0.025
NO_2	-205.16046	23.0	-204.77953	-204.81699	0.031
O_2 (^3S_g)	-150.38462	9.7	-150.12201	-150.14094	0.018
OOH	-150.97335	37.0	-150.70799	-150.72659	0.030
ClO	-535.37180	5.1	-534.72945	-534.74826	0.036
BrO	-492.06934	4.4	-490.79932	-490.82055	0.0284
Br-Hg-Br	-987.46115	3.7	-984.84532	-984.89380	0.012
Br-Hg-NO	-700.43233	16.5	-698.70088	-698.76761	0.024
Br-Hg-ONO	-775.67761	26.3	-773.82564	-773.90050	0.018
Br-Hg-NO_2	-775.68039	30.4	-773.82067	-773.89764	0.020
Br-Hg-OO•	-720.86581	13.4	-719.11403	-719.17410	0.025
Br-Hg-OOH	-721.50155	44.7	-719.75748	-719.81827	0.017
ClHg	-613.77696	1.5	-612.91753	-612.95128	0.023
Cl	-460.17533	0.0	-459.67005	-459.67622	0.007
Cl-Hg-Cl	-1074.07376	5.4	-1072.71282	-1072.75733	0.016
Cl-Hg-NO	-743.73873	17.2	-742.63520	-742.69947	0.028
Cl-Hg-ONO	-818.98408	27.3	-817.75929	-817.83217	0.021
Cl-Hg-NO_2	-818.98666	31.5	-817.75439	-817.82935	0.023
Cl-Hg-OO•	-764.17173	14.4	-763.04816	-763.10599	0.029
Cl-Hg-OOH	-764.80831	45.7	-763.69164	-763.75037	0.020
Hg	-153.56632	0.0	-153.21769	-153.24311	0.014
BrHgOBr	-1062.6146	10.0	-1059.86961	-1059.93238	0.015
BrHgOCl	-1105.9149	11.2	-1103.79559	-1103.85576	0.016
ClHgOBr	-1105.9210	11.1	-1103.80334	-1103.86409	0.016
ClHgOCl	-1149.2213	12.2	-1147.72928	-1147.78742	0.019
HgOBr	-645.6378	5.0	-644.01581	-644.06474	0.024
HgOCl	-688.9396	5.8	-687.94528	-687.99134	0.026
$HgONO_2$	-433.91187	37.5	-433.04961	-433.12401	0.030
NO_3	-280.33633	27.3	-279.81145	-279.86909	0.023

Table S2. Absolute Energies (Hartree), zero point energies (ZPE, in kJ/mol at B3LYP/aVTZ), and values of the T_1 diagnostic for all anionic species. See manuscript for definition of aVTZ basis set. 1 Hartree = 2625.5 kJ/mol.

Species	SCF	ZPE	CCSD	CCSD(T)	T_1
Br-Hg-Br$^-$	-987.53609	1.5	-984.90310	-984.95260	0.016
Br-Hg-NO$^-$	-700.53459	13.0	-698.80093	-698.86040	0.016
Br-Hg-ONO$^-$	-775.76137	23.5	-773.89065	-773.96595	0.023
Br-Hg-NO$_2^-$	-775.76939	24.2	-773.88860	-773.96588	0.027
Br-Hg-OO$^-$	-720.93793	11.2	-719.16581	-719.24058	0.022
Br-Hg-OOH$^-$	-721.56845	40.3	-719.80169	-719.86383	0.025
Br-Hg$^-$	-570.58640	0.4	-569.09488	-569.13287	0.013
Hg-NO$^-$	-283.50239	10.2	-282.90082	-282.95603	0.053
Hg-ONO$^-$	-358.81860	21.8	-358.09087	-358.15473	0.022
Hg-NO$_2^-$	-358.81819	22.3	-358.08937	-358.15325	0.022
Hg-OO$^-$	-303.98962	7.9	-303.36931	-303.41840	0.024
Hg-OOH$^-$	-304.60278	37.4	-303.98408	-304.03478	0.022
Br$^-$	-417.00817	0.0	-415.86314	-415.87443	0.004
NO$^-$ (triplet)	-129.95523	8.4	-129.70606	-129.72569	0.032
NO$_2^-$	-205.24209	20.4	-204.86124	-204.89858	0.025
O$_2^-$	-150.40429	7.0	-150.13180	-150.15394	0.025
HO$_2^-$	-151.01030	34.1	-150.73969	-150.76337	0.023
Cl-Hg-Cl-	-1074.14502	2.3	-1072.76169	-1072.81458	0.019
Cl-Hg-NO$^-$	-743.83945	12.4	-742.73355	-742.79137	0.019
Cl-Hg-ONO$^-$	-819.06598	22.1	-817.82397	-817.89711	0.027
Cl-Hg-NO$_2^-$	-819.07401	22.6	-817.82124	-817.89661	0.032
Cl-Hg-OO*$^-$	-764.24290	10.8	-763.09909	-763.17196	0.028
Cl-Hg-OOH$^-$	-764.87261	40.4	-763.73345	-763.79380	0.025
Cl-Hg$^-$	-613.89099	0.7	-613.02804	-613.06423	0.017
Cl$^-$	-460.31052	0.0	-459.79555	-459.80504	0.006
Hg-	-153.55647	0.0	-153.21769	-153.24311	0.014

Table S3. Cartesian coordinates (Ångstroms) of all Hg-containing species at B3LYP/aVTZ (integers refer to the atomic number of the atom). See manuscript for definition of aVTZ basis set.

Neutrals

$HgBr_2$

80	0.000000	0.000000	0.000000
35	0.000000	0.000000	2.424902
35	0.000000	0.000000	-2.424902

$HgCl_2$

80	0.000000	0.000000	0.000000
17	0.000000	0.000000	2.286253
17	0.000000	0.000000	-2.286253

BrHgNO

80	0.000000	0.378806	0.000000
35	-0.313829	-2.113207	0.000000
7	0.160879	2.678926	0.000000
8	1.232231	3.113156	0.000000

$BrHgNO_2$

80	0.000000	0.000000	0.194133
35	0.000000	0.000000	-2.231132
7	0.000000	0.000000	2.337214
8	0.000000	1.082255	2.887403
8	0.000000	-1.082255	2.887403

BrHgONO

80	0.121880	-0.141817	-0.000038
35	-2.254227	0.213371	0.000044
8	2.113946	-0.523065	0.000179
7	2.870124	0.663345	-0.000039
8	4.018144	0.427311	0.000049

BrHgOO•

80	0.000000	0.367496	0.000000
8	0.395760	2.432719	0.000000
8	1.656335	2.728721	0.000000

35 -0.469050 -2.019749 0.000000

BrHgOOH
80 -0.330678 -0.129999 0.003467
35 2.064815 0.170645 -0.001557
8 -2.329062 -0.432290 -0.021349
8 -2.968392 0.873654 -0.099881
1 -3.434662 0.896491 0.746929

ClHgNO
80 0.000000 0.056359 0.000000
17 -2.297427 -0.562127 0.000000
7 2.172275 0.777265 0.000000
8 2.981292 -0.049177 0.000000

$ClHgNO_2$
80 0.000000 0.000000 0.155787
17 0.000000 0.000000 2.451900
7 0.000000 0.000000 -1.971810
8 0.000000 1.082412 -2.521410
8 0.000000 -1.082412 -2.521410

ClHgONO
80 -0.236973 -0.097108 -0.000022
8 1.726195 -0.556717 0.000010
7 2.539164 0.597914 -0.000329
8 3.672801 0.306801 0.000308
17 -2.471076 0.328385 0.000089

ClHgOO•
80 0.000000 0.083202 0.000000
17 -2.269878 -0.284381 0.000000
8 2.054827 0.428072 0.000000
8 2.768664 -0.655780 0.000000

Anions

$ClHgOOH^-$
80 0.017844 -0.101759 0.003087
17 2.267697 0.297264 -0.002278
8 -1.953879 -0.493495 -0.020178
8 -2.651815 0.782642 -0.098413
1 -3.132848 0.774047 0.740471

$HgBr_2^-$

80	0.000000	0.000000	0.273257
35	0.000000	2.742626	-0.312293
35	0.000000	-2.742626	-0.312293

$HgCl_2^-$

80	0.000000	0.000000	0.234238
17	0.000000	2.524427	-0.551148
17	0.000000	-2.524427	-0.551148

$BrHgNO^-$

80	0.422377	-0.004599	-0.000330
35	-2.594336	-0.005256	0.000400
7	3.431752	0.536282	0.000749
8	4.123670	-0.400267	0.000894

$BrHgNO_2^-$

80	0.200604	-0.000045	-0.000045
35	-2.650860	0.000050	0.000054
7	2.933483	0.000062	0.000061
8	3.512384	-1.077724	0.000080
8	3.512288	1.077900	0.000080

$BrHgONO^-$

80	-0.157736	-0.172038	-0.047136
35	2.597543	0.198863	0.073256
8	-2.430603	0.686036	-0.239167
7	-3.309876	-0.130080	0.249823
8	-4.460149	0.278141	0.171441

$BrHgOO^-$

80	0.000000	0.415477	0.000000
8	0.029064	2.734578	0.000000
8	1.161719	3.378851	0.000000
35	-0.272179	-2.347016	0.000000

$BrHgOOH^-$

80	0.422170	-0.410357	-0.036752
35	-2.350636	0.445809	0.032454
8	2.676888	0.377067	0.504087
8	3.059960	1.497592	-0.296317
1	2.603919	2.227978	0.142097

$ClHgNO^-$

80	0.019902	-0.011073	-0.000326
17	2.850151	0.005094	0.000840
7	-2.962431	0.549946	0.000636
8	-3.663467	-0.381299	0.000921

$ClHgNO_2^-$

80	0.000000	0.220813	0.000000
17	-0.000009	2.917327	0.000000
7	0.000006	-2.522264	0.000000
8	-1.077827	-3.100234	0.000000
8	1.077840	-3.100231	0.000000

$ClHgONO^-$

80	0.262059	-0.195713	-0.000034
8	-1.971878	0.743817	-0.000270
7	-2.908992	-0.151837	0.000255
8	-4.038210	0.317165	0.000130
17	2.792878	0.484240	0.000123

$ClHgOO^-$

80	0.012750	-0.028912	-0.000001
17	-2.605692	0.106521	0.000002
8	2.271594	-0.457687	0.000003
8	3.137998	0.520454	0.000001

$ClHgOOH^-$

80	0.017364	-0.135157	-0.006392
17	2.733051	0.277437	0.016401
8	-2.230703	0.860382	0.013091
8	-3.321220	-0.056754	-0.087837
1	-3.435647	-0.332875	0.830517

Table S4. Harmonic vibrational frequencies (cm^{-1}) and mode assignments for all species at B3LYP/aVTZ. See manuscript for definition of aVTZ basis set.

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Compound	Frequency (cm^{-1})	Mode Description
Cl-Hg-NO_2	70	Cl-Hg-NO2 bend in plane
	77	Cl-Hg-NO2 bend out of plane
	248	NO2 rotation in plane
	253	Symmetric Cl-Hg-NO2 stretch
	360	Antisymmetric Cl-Hg-NO2 stretch
	508	Nitrogen wagging
	828	NO bend
	1357	Symmetric O=N=O stretch
	1566	Antisymmetric O=N=O stretch
$HgCl_2$	91	Cl-Hg-Cl bend1
	91	Cl-Hg-Cl bend2
	332	Symmetric stretch
	386	Antisymmetric stretch
Cl-Hg-NO	60	Cl-Hg-N Bend (in plane)
	71	Cl-Hg-N Bend (out of plane)
	190	Symmetric Cl-Hg-NO stretch
	308	Antisymmetric Cl-Hg-NO stretch
	501	Hg-N=O bend/Hg-N stretch
	1753	N=O stretch
Cl-Hg-OO	79	Cl-Hg-OO bend (in plane)
	97	Cl-Hg-OO bend (out of plane)
	227	Symmetric Cl-Hg-OO stretch
	352	Antisymmetric Cl-Hg-OO stretch
	497	Hg-O-O bend/Hg-O stretch
	1149	O-O stretch
Cl-Hg-OOH	89	Cl-Hg-OOH bend (in plane)
	103	Cl-Hg-OOH bend (out of plane)
	232	Symmetric Cl-Hg-OOH stretch
	286	H-atom rock
	362	Antisymmetric Cl-Hg-OOH stretch
	557	Hg-O stretch
	911	O-O stretch
	1349	H-atom wag
	3749	O-H stretch

Cl-Hg-ONO	74	Cl-Hg-ONO bend (in plane)
	88	Cl-Hg-ONO bend (out of plane)
	162	Hg-ON=O bend
	192	Hg-O-NO bend
	353	Symmetric Cl-Hg-ONO stretch
	408	Antisymmetric Cl-Hg-ONO stretch
	690	Antisymmetric Hg-O-NO stretch
	890	O-N=O bend
	1715	N=O stretch
Br-Hg-NO_2	57	Br-Hg-NO2 bend (in plane)
	62	Br-Hg-NO2 bend (out of plane)
	210	Symmetric Br-Hg-NO2 stretch
	238	Hg-NO2 rock
	284	Antisymmetric Br-Hg-NO2 stretch
	495	HgNO2 pyramidal
	825	NO bend
	1355	Symmetric O=N=O stretch/Hg-N stretch
	1564	Antisymmetric O=N=O stretch
$HgBr_2$	66	Br-Hg-Br bend1
	66	Br-Hg-Br bend2
	206	Symmetric Br-Hg-Br stretch
	274	Antisymmetric Br-Hg-Br stretch
Br-Hg-NO	50	Br-Hg-NO bend (in plane)
	56	Br-Hg-NO bend (out of plane)
	173	Symmetric Br-Hg-NO stretch
	236	Antisymmetric Br-Hg-NO stretch
	489	Hg-N=O bend/Hg-N stretch
	1756	N=O stretch
Br-Hg-OO	63	Br-Hg-OO bend (in plane)
	86	Br-Hg-OO bend (out of plane)
	191	Symmetric Br-Hg-OO stretch
	261	Antisymmetric Br-Hg-OO stretch
	480	Hg-O-O bend/Hg-O stretch
	1153	O-O stretch
Br-Hg-OOH	78	Br-Hg-OOH bend (in plane)
	79	Br-Hg-OOH bend (out of plane)
	214	Symmetric Br-Hg-OOH stretch

	257	Antisymmetric Br-Hg-OOH stretch
	296	H-atom rock
	547	Hg-O stretch
	909	O-O stretch
	1347	H-atom wag
	3750	O-H stretch
Br-Hg-ONO	58	Br-Hg-ONO bend (in plane)
	65	Br-Hg-ONO bend (out of plane)
	156	Hg-ON=O bend (out of plane)
	185	Hg-O-NO bend
	246	Symmetric Br-Hg-ONO stretch
	392	Antisymmetric Br-Hg-ONO stretch
	695	Antisymmetric Hg-O-N stretch
	893	O-N=O bend
	1708	N=O stretch
$HgBr_2^-$	14	Br-Hg-Br in plane bend
	112	Symmetric Br-Hg-Br stretch
	131	Asymmetric Br-Hg-Br stretch
BrHgNO-	11	Br-Hg-NO bend, in plane
	21	Br-Hg-NO bend, out of plane
	58	Symmetric Br-Hg-NO stretch
	92	Asymmetric Br-Hg-NO stretch
	223	Hg-N=O bend
	1770	N=O stretch
$BrHgNO_2^-$	15	Br-Hg-NO2 bend out of plane
	17	Br-Hg-NO2 bend in plane
	88	Symmetric Br-Hg-NO2 stretch
	114	Asymmetric Br-Hg-NO2 stretch
	121	Hg-N-O bend in plane
	158	N pyramidal stretch
	772	Symmetric Hg-N-O stretch
	1292	Asymmetric Hg-N-O stretch
	1474	Asymmetric O-N-O stretch
BrHgONO-	10	Br, NO wag
	26	wag
	103	NO2 rock

	120	NO2 twist
	129	Asymmetric Br-Hg-ONO stretch
	196	Hg-O-NO in plane bend
	780	ONO in plane bend
	1096	N-O stretch/Asymmetric O=N-O stretch
	1471	Asymmetric O-N=O stretch (mostly N=O stretch)
BrHgOO-	40	Br-Hg-OO in plane bend
	66	Br-Hg-OO out of plane bend
	99	Symmetric Br-Hg-OO stretch
	166	Asymmetric Br-Hg-OO stretch
	370	Hg-O-O bend
	1132	O-O stretch
BrHgOOH-	16	Br, OH wag
	44	HO2 rock
	88	HO2-Hg-Br symmetric stretch
	118	HO2-Hg-Br Asymmetric stretch
	223	HO2 twist
	333	H wag
	869	OO stretch
	1314	OOH bend
	3724	OH stretch
$HgCl_2^-$	30	In-plane bend
	179	Symmetric stretch
	183	Asymmetric stretch
ClHgNO-	20	Cl-Hg-NO bend in plane
	26	Cl-Hg-NO bend out of plane
	60	Symmetric Cl-Hg-NO stretch
	135	Asymmetric Cl-Hg-NO stretch
	230	Hg-N=O bend
	1767	N=O stretch
$ClHgNO_2^-$	24	Cl-Hg-NO2 bend, out of plane
	27	Cl-Hg-NO2 bend, in plane
	92	Symmetric Cl-Hg-NO2 stretch
	122	Hg-N-O bend, in plane
	149	N pryamidal stretch

	166	Asymmetric Cl-Hg-NO2 stretch
	772	Hg-N-O stretch/Hg-N stretch
	1293	Asymmetric Hg-N-O stretch
	1476	Asymmetric O-N-O stretch
ClHgONO-	18	Cl, NO2 rock
	29	Cl-Hg-ONO bend, in plane
	107	Hg-O-N bend
	117	NO2 twist
	190	Cl-Hg stretch
	200	Hg-O stretch
	782	O-N=O bend
	1095	Asymmetric O-N=O stretch (mostly O-N stretch)
	1473	Asymmetric O-N=O stretch (mostly N=O stretch)
ClHgOO-	23	Cl-Hg-OO bend in plane
	55	Cl-Hg-OO bend out of plane
	115	Symmetric Cl-Hg-OO stretch
	203	Asymmetric Cl-Hg-OO stretch
	372	Hg-O-O bend
	1117	O-O stretch
ClHgOOH-	10	Cl, OH wag
	16	Cl, HO2 wag
	99	HO2-Hg-Cl symmetric stretch
	153	HO2-Hg-Cl Asymmetric stretch
	224	HO2 twist
	320	H wag
	871	OO stretch
	1313	OOH bend
	3727	OH stretch

Table S5. Inputs for thermodynamic analysis of BrHg• molecule (cited errors are 1 s.d.)

D_e = 5525 ± 100 cm^{-1} [a] (bond dissociation energy at the minimum of the potential well)
ω_e ($^{79}Br^{200}Hg$) = 188.7 ± 0.26 cm^{-1} [e] (harmonic vibrational frequency)
$\omega_e x_e$ = 1.04 ± 0.1 cm^{-1} [a] (anharmonic term)
R(Br-Hg)=2.494 Å [b] (Br-Hg internuclear bond distance in HgBr•)
g_e (Br) = 2 [c] (electronic state degeneracy of Br)
g_e (BrHg•) = 4 [c] (electronic state degeneracy of HgBr•)

a) Tellinghuisen and Ashmore (1983)

b) Shepler et al (2007). Note that Goodsite et al. (2004) cited R(Br-Hg)=2.62 Å from Lipson et al (1992), who were citing Tellinghuisen and Ashmore, (1982), who in turn were citing an value from Cheung and Cool (1979), who were citing a conference presentation by Wadt and Hay (1978). Later, Wadt (1979) published a value of 2.61 A.
c) Chase, et al., 1998

The value of ω_e was calculated separately for each isotopologue using the force constant calculated from ω_e of $^{79}Br^{200}Hg$. Then, for each isotopologue, D_0 was calculated as D_e -1/2 ω_e + 1/4 $\omega_e x_e$.

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