Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for first kinetic study of the atmospherically important reactions BrHg• + NO_2 and BrHg• + HOO

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Table of Content

Table S11. Lennard-Jones parameters used in the current study.

Table S12. Collision frequency (in molecule^{-1} cm^3 s^{-1}) for BrHg + NO2 and BrHg + HOO estimated using L-J parameters.

Table S13. Pressure- and temperature-dependent rate constants at CASPT2//PBE0 and RCCSDT//PBE0 levels.

Table S14. Equilibrium constant for $BrHg\bullet + NO_2 \rightarrow Hg + BrNO_2$ using literature reaction enthalpy (-7.9 kcal/mol) and PBE0/AVTZ vibrational frequencies and rotational constants.

Figure S1. Structures for all transition states.

References

Table S1. Cartesian coordinate (in Å), vibrational frequencies (in cm^{-1}), and (on the last line of data for each molecule) rotational constants (in cm^{-1}) of all stationary points at the PBE0/AVTZ level.

BrHg							
Hg	0.000000	0.000000	0.773862				
Br	0.000000	0.000000	-1.768828				
	177.26						
	0.04595						
NO_2				HOO			
N	0.000000	0.000000	0.316090	H	-0.881888	0.864047	0.000000
O	0.000000	1.092545	-0.138290	O	0.055118	0.601389	0.000000
O	0.000000	-1.092545	-0.138290	O	0.055118	-0.709394	0.000000
	780.6866, 1435.3189,1775.0439			1218.7923 1459.3304 3646.1403			
	8.3833, 0.44147, 0.41939			1.00317 0.05535 0.05246			
$BrHgNO_2$				BrHgOOH			
Hg	0.000000	0.000000	0.191154	Hg	-0.326304	-0.128626	0.002101
N	0.000000	0.000000	2.302531	Br	2.038202	0.168677	-0.000148
O	0.000000	1.075682	2.850050	O	-2.301951	-0.425237	-0.013188
O	0.000000	-1.075682	2.850050	O	-2.928049	0.861315	-0.100121
Br	0.000000	0.000000	-2.200309	H	-3.392778	0.897741	0.743554
	61.1443 68.7713 226.6662 243.3904						
	301.1193 514.1836 846.3580			74.8359 117.3231 221.9169 268.1089 293.5889			
	1409.7026 1637.6791			570.4866 965.1554 1375.2899 3807.7731			
	0.455427 0.023312 0.022177			0.77755 0.028893 0.027921			
anti-$BrHgNO_2$				Hg-BrOOH vdW			
Hg	0.120844	-0.141137	0.000000	Hg	-1.441043	0.049070	-0.000955
Br	-2.224435	0.212448	0.000000	Br	1.486233	-0.213821	0.004940
O	2.092319	-0.523049	0.000000	O	3.370995	-0.453622	0.011968
N	2.816391	0.649719	0.000000	O	4.021393	0.766144	-0.123167
O	3.966797	0.436457	0.000000	H	4.126156	1.057916	0.793125
	60.1906 93.9136 169.7068 187.2132						
	260.5935 411.9575 770.6671 943.7050			53.3428 63.5540 78.9719 294.4710 423.2864			
	1750.0474			559.2139 962.5017 1425.9192 3752.8042			
	0.80902 0.020419 0.019916			0.90315 0.01615 0.015890			
syn-$BrHgNO_2$				BrOOH			
Hg	0.000000	-0.271690	0.000000	Br	1.522015	-0.220497	0.004768
Br	1.146683	1.825019	0.000000	O	3.368272	-0.446083	0.011198
O	-0.742400	-2.242912	0.000000	O	4.016509	0.782308	-0.122660
N	-2.020674	-2.198516	0.000000	H	4.125792	1.065779	0.795598
O	-2.506249	-1.100944	0.000000				
	66.6430 81.6545 138.8908 242.8589						
	380.3460 394.7665 909.6703			319.6141 421.0324 617.1238 951.2963 1431.5701			
	1134.8736 1578.0497			3748.9269			
	0.35895 0.025230 0.023572			1.64130 0.13788 0.12880			
$BrNO_2$				O2			

Br	0.000000	0.000000	0.930817	O	0.000000	0.000000	0.596845
O	0.000000	1.079194	-1.563678	O	0.000000	0.000000	-0.596845
N	0.000000	0.000000	-1.079962	1691.789			
O	0.000000	-1.079194	-1.563678	1.479320			
	316.8932 365.6068 656.2225 825.4295						
	1383.5281 1798.9260						
	0.45247 0.10382 0.08444						
Hg-$BrNO_2$ vdW				BrHgH			
Hg	0.000000	0.000000	1.652015	Hg	0.000000	0.000000	0.715255
N	0.000000	0.000000	-3.386653	Br	0.000000	0.000000	-1.701272
O	0.000000	1.079359	-3.875430	H	0.000000	0.000000	2.324123
O	0.000000	-1.079359	-3.875430	248.9175 525.9320 525.9320 2115.8728			
Br	0.000000	0.000000	-1.327078				
	45.8095 48.1013 55.8411 272.8055						
	342.9858 621.6873 820.2194						
	1383.5274 1783.5813						
	0.45233 0.012760 0.012410			0.05008			
TS1				TS4			
Hg	0.000000	0.184153	0.000000	Hg	-1.372470	0.055916	-0.001633
Br	-0.484860	-2.148984	0.000000	Br	1.211470	-0.213818	0.006895
O	-0.347346	2.421871	0.000000	O	3.625882	-0.456701	0.014354
N	0.931289	2.241423	0.000000	O	4.255224	0.701884	-0.125323
O	1.653730	3.177162	0.000000	H	4.347346	1.048873	0.777069
	-272.1429 65.6308 68.9120 225.9982						
	239.6359 324.8132 784.3766			-105.6997 44.7746 60.8317 131.0150 226.5144			
	1219.6278 1685.4246			378.2261 1120.4974 1450.5977 3677.5068			
	0.62656 0.022599 0.021812			0.97368 0.01673 0.01647			
TS2				TS5			
Hg	-0.143465	0.177578	0.022537	Hg	0.000000	0.251199	0.000000
Br	2.185696	-0.268610	-0.027912	Br	-0.642431	-2.151590	0.000000
O	-2.083365	0.637109	0.101612	O	1.994151	3.408060	0.000000
N	-2.992053	-0.237425	-0.502633	O	0.753671	3.229389	0.000000
O	-3.426363	-1.029975	0.234938	H	0.502501	2.110129	0.000000
	-221.7141 61.1604 98.4375 154.0220						
	262.3660 510.3132 711.4285 846.3702			-1421.2703 33.3385 44.9978 149.9196 209.5967			
	1740.6038			320.7553 667.3083 1319.8048 1447.0947			
	0.41193 0.021951 0.021088			1.2559 0.02039 0.02006			
TS3							
Hg	0.047596	-0.009045	0.000000				
Br	-0.119950	-2.541387	0.000000				
O	-0.119950	3.919027	1.092397				
N	0.329974	3.852531	0.000000				
O	-0.119950	3.919027	-1.092397				
	-115.8120 5.2722 5.4168 17.2336						

	27.4033 178.5735 778.3596 1431.0364 1773.2269 0.40963 0.013922 0.013529			
TSX				
Hg	0.000000	0.000000	0.230648	
Br	0.000000	0.000000	-2.173040	
O	0.000000	1.039020	2.303285	
N	0.000000	0.000000	2.964566	
O	0.000000	-1.039020	2.303285	
	-97.3654 65.2174 118.1207 223.9521 293.4425 431.2387 932.6985 1361.3079 1423.1541 0.48813 0.02494 0.02373			

Table S2. Single point energies (in Hartree) at the PBE0/AVTZ level and the CCSD(T)//PBE0/AVTZ level, vibrational zero-point energies (kcal/mol) at the PBE0/AVTZ level, and T1 diagnostic values.

Species	PBE0	ZPE	CCSD(T)	T1 diag
HgBr	-570.316325	0.25	-568.657280	0.020
NO_2	-204.946563	5.71	-204.816425	0.024
$BrHgNO_2$	-775.315463	7.59	-773.529373	0.020
anti-BrHgONO	-775.310356	6.64	-773.532047	0.022
syn-BrHgONO	-775.322619	7.04	-773.542524	0.024
TS2	-775.298286	6.27	-773.520500	0.021
TS1	-775.288440	6.60	-773.506958	0.033
TS3	-775.263039	6.03	-773.474875	0.025
TSX	-775.320508	6.93	-773.540417	0.026
Hg	-153.501083	0.00	-152.979161	0.016
$BrNO_2$	-621.775027	7.64	-620.514339	0.022
Hg-$BrNO_2$ vdW	-775.280910	7.68	-773.496432	0.021
HOO	-150.813935	9.04	-150.726155	0.029
BrHgOOH	-721.188916	11.00	-719.449959	0.020
HHgBr	-570.936052	4.88	-569.277431	0.016
O2	-150.230151	2.44	-150.140496	0.017
TS5	-721.127348	5.99	-719.370630	0.030
BrOOH	-567.635154	10.71	-566.422829	0.017
Hg-BrOOH vdW	-721.141654	10.88	-719.404971	0.017
TS4	-721.130410	10.14	-719.382293	0.033

Table S3. Absolute and relative energies (not including vibrational ZPE) for BrHg• + $NO_2 \rightarrow$ BrHg-NO_2 intermediate at various points along the minimum energy path at PBE0/AVTZ geometries.

r(Hg-N)	PBE0/AVTZ	Relative E	CASPT2(16,13)/AVTZ	Relative E	RCCSDT/AVDZ	Relative E
Å	Hartree	kcal/mol	Hartree	kcal/mol	Hartree	kcal/mol
2.1	-775.315463	-32.99	-773.497358	-31.89	-773.216552	-37.47
2.4	-775.305072	-26.47	-773.494463	-30.08	-773.206599	-31.22
2.7	-775.286477	-14.80	-773.477491	-19.43	-773.190308	-21.00
3.0	-775.273284	-6.52	-773.465064	-11.63	-773.177794	-13.15
3.1	-775.270901	-5.03	-773.461925	-9.66	-773.174566	-11.12
3.2	-775.269098	-3.90	-773.459255	-7.98	-773.171784	-9.38
3.3	-775.267718	-3.03	-773.457000	-6.57	-773.169408	-7.89
3.4	-775.266653	-2.36	-773.455119	-5.39	-773.167394	-6.62
3.5	-775.265830	-1.85	-773.453559	-4.41	-773.165694	-5.56
3.6	-775.265188	-1.44	-773.452286	-3.61	-773.164266	-4.66
3.7	-775.264684	-1.13	-773.451246	-2.96	-773.163067	-3.91
3.8	-775.264289	-0.88	-773.450401	-2.43	-773.162064	-3.28
3.9	-775.263978	-0.68	-773.449716	-2.00	-773.161222	-2.75
4.0	-775.263736	-0.53	-773.449156	-1.65	-773.160513	-2.31
4.1	-775.263535	-0.41	-773.448729	-1.38	-773.159917	-1.93
4.2	-775.263379	-0.31	-773.448378	-1.16	-773.159415	-1.62
4.3	-775.263256	-0.23	-773.448082	-0.97	-773.158989	-1.35
4.4	-775.263158	-0.17	-773.447834	-0.82	-773.158627	-1.12
4.5	-775.263079	-0.12	-773.447624	-0.69	-773.158319	-0.93
4.6	-775.263015	-0.08	-773.447456	-0.58	-773.158056	-0.76
4.7	-775.262964	-0.05	-773.447314	-0.49	-773.157830	-0.62
4.8	-775.262925	-0.02	-773.447190	-0.41	-773.157635	-0.50
4.9	-775.262894	0.00	-773.447088	-0.35		
5.0	-775.262868	0.01	-773.447000	-0.29	Morse potential	
					De	β
10.0			-773.446530		37.47	1.8417

Table S4. Absolute and relative energies (not including vibrational ZPE) for BrHg• + $NO_2 \rightarrow$ *syn*-BrHg-ONO intermediate at PBE0/AVTZ geometries; parameters used for the Morse potential extrapolation of the RCCSDT energies to infinite separation.

r(Hg-N)	PBE0/AVTZ	PBE0/AVTZ	CASPT2(16, 13)/AVTZ	CASPT2(16, 13)/AVDZ	CASPT2(18, 16)/AVDZ	CASPT2 relative E	RCCSDT/AVDZ	RCCSDT Relative E
Å	Hartree	kcal/mol	Hartree	Hartree	Hartree	kcal/mol	Hartree	kcal/mol
2.73	-775.32051	-36.16	-773.50413	-773.20106	-773.20580	-43.40	-773.23024	-46.85
2.80	-775.31979	-35.71	-773.51076	-773.20640	-773.20499	-43.70	-773.22983	-46.59
2.90	-775.31613	-33.41	-773.50646	-773.20286	-773.20099	-40.72	-773.22635	-44.41

3.00	-775.31051	-29.88	-773.50019	-773.19707	-773.19478	-36.51	-773.22055	-40.77
3.10	-775.30380	-25.67	-773.49306	-773.19023	-773.18740	-31.70	-773.21343	-36.30
3.20	-775.29663	-21.17	-773.48590	-773.18325	-773.17980	-26.82	-773.20582	-31.52
3.30	-775.28941	-16.64	-773.47927	-773.17672	-773.17263	-22.26	-773.19831	-26.82
3.40	-775.28239	-12.24	-773.47344	-773.17095	-773.16636	-18.29	-773.19132	-22.43
3.50	-775.27658	-8.59	-773.46935	-773.16677	-773.16175	-15.45	-773.18469	-18.27
3.60	-775.27309	-6.40	-773.46547	-773.16282	-773.15739	-12.76	-773.17912	-14.77
3.70	-775.27078	-4.95	-773.46210	-773.15942	-773.15383	-10.54	-773.17485	-12.09
3.80	-775.26912	-3.91	-773.45932	-773.15662	-773.15058	-8.52	-773.17153	-10.01
3.90	-775.26787	-3.13	-773.45704	-773.15433	-773.14834	-7.12	-773.16889	-8.36
4.00	-775.26691	-2.53	-773.45518	-773.15247	-773.14582	-5.54	-773.16677	-7.02
4.10	-775.26616	-2.05	-773.45366	-773.15094	-773.14433	-4.61	-773.16504	-5.94
4.20	-775.26556	-1.68	-773.45242	-773.14969	-773.14307	-3.83	-773.16363	-5.05
4.30	-775.26508	-1.37	-773.45142	-773.14868	-773.14203	-3.18	-773.16246	-4.32
4.40	-775.26469	-1.13	-773.45060	-773.14784	-773.14115	-2.63	-773.16150	-3.72
4.50	-775.26438	-0.94	-773.44993	-773.14716	-773.14044	-2.20	-773.16071	-3.22
4.60	-775.26412	-0.78	-773.44938	-773.14660	-773.13988	-1.85	-773.16005	-2.80
4.70	-775.26392	-0.65	-773.44894	-773.14614	-773.13939	-1.56	-773.15950	-2.46
4.80	-775.26375	-0.54	-773.44857	-773.14576	-773.13906	-1.36	-773.15904	-2.17
4.90	-775.26361	-0.45	-773.44827	-773.14544	-773.13872	-1.15	-773.15866	-1.93
5.00	-775.26350	-0.38	-773.44802	-773.14518	-773.13844	-0.99	-773.15834	-1.73
5.10	-775.26341	-0.28	-773.44781	-773.14497	-773.13821	-0.84	-773.15808	-1.57
5.20	-775.26333	-0.23	-773.44763	-773.14478	-773.13802	-0.73	-773.15785	-1.43
5.30	-775.26326	-0.20	-773.44749	-773.14463	-773.13786	-0.63	-773.15766	-1.31
5.40	-775.26321	-0.18	-773.44736	-773.14450	-773.13772	-0.55	-773.15750	-1.21
							Morse parameter	
							De	β
10.0			-773.44659	-773.14360	-773.13671		46.85	1.94340875

Table S5. Absolute and relative energies (not including vibrational ZPE) for BrHg• + $NO_2 \rightarrow$ Hg-$BrNO_2$ intermediate at PBE0/AVTZ geometries.

r(Br-N)	UPBE0/AVTZ	Relative E	RCCSDT/AVDZ	Relative E
Å	Hartree	kcal/mol	Hartree	kcal/mol
2.0	-775.28041	-11.00	-773.18725	-17.99
2.1	-775.28074	-11.20	-773.18729	-18.01
2.2	-775.27894	-10.07	-773.18530	-16.76
2.3	-775.27569	-8.03	-773.18241	-14.95
2.4	-775.27174	-5.56	-773.17910	-12.88
2.5	-775.26919	-3.96	-773.17585	-10.84

2.6	-775.26775	-3.05	-773.17309	-9.10
2.7	-775.26686	-2.49	-773.17075	-7.63
2.8	-775.26626	-2.12	-773.16874	-6.38
2.9	-775.26581	-1.83	-773.16704	-5.31
3.0	-775.26545	-1.61	-773.16557	-4.39
3.1	-775.26515	-1.42	-773.16431	-3.60
3.2	-775.26488	-1.25	-773.16323	-2.92
3.3	-775.26465	-1.11	-773.16230	-2.34
3.4	-775.26444	-0.98	-773.16151	-1.84
3.5	-775.26426	-0.86	-773.16085	-1.42
3.6	-775.26410	-0.76	-773.16025	-1.05
3.7	-775.26396	-0.67	-773.15976	-0.74
3.8	-775.26384	-0.59	-773.15933	-0.47
4.0	-775.26362	-0.46	-773.15866	-0.86
4.1	-775.26355	-0.41	-773.15839	-0.69
4.2	-775.26349	-0.37	-773.15816	-0.55
4.3	-775.26342	-0.33	-773.15796	-0.42
4.4	-775.26336	-0.30	-773.15779	-0.32
4.5	-775.26331	-0.27	-773.15763	-0.22
			Morse potential	
			De	β
			18.19	2.2325

Table S6. Absolute and relative energies (not including vibrational ZPE) for BrHg• + HOO → BrHg-OOH intermediate at PBE0/AVTZ geometries.

r(Hg-O)	UPBE0/AVTZ	Relative E	CASPT2(14,12)/AVTZ	Relative E	RCCSDT/AVDZ	Relative E
Å	Hartree	kcal/mol	Hartree	kcal/mol	Hartree	kcal/mol
2.0	-721.18892	-36.81	-719.42248	-43.27	-719.17677	-42.19
2.1	-721.18610	-35.04	-719.42303	-43.61	-719.17527	-41.25
2.2	-721.17977	-31.07	-719.41623	-39.34	-719.16960	-37.70
2.3	-721.17164	-25.96	-719.40764	-33.95	-719.16198	-32.92
2.4	-721.16292	-20.49	-719.39867	-28.33	-719.15388	-27.83
2.5	-721.15450	-15.21	-719.39026	-23.05	-719.14606	-22.93
2.6	-721.14830	-11.32	-719.38281	-18.37	-719.13909	-18.55

2.7	-721.14397	-8.60	-719.37685	-14.63	-719.13336	-14.96
2.8	-721.14084	-6.64	-719.37218	-11.70	-719.12877	-12.08
2.9	-721.13854	-5.20	-719.36854	-9.42	-719.12511	-9.78
3.0	-721.13684	-4.13	-719.36567	-7.62	-719.12222	-7.97
3.1	-721.13558	-3.34	-719.36342	-6.20	-719.11992	-6.52
3.2	-721.13461	-2.73	-719.36164	-5.09	-719.11808	-5.37
3.3	-721.13386	-2.26	-719.36023	-4.21	-719.11661	-4.44
3.4	-721.13329	-1.90	-719.35911	-3.50	-719.11542	-3.70
3.5	-721.13284	-1.62	-719.35820	-2.93	-719.11445	-3.09
3.6	-721.13248	-1.39	-719.35745	-2.46	-719.11362	-2.57
3.65	-721.13233	-1.30	-719.35715	-2.28	-719.11319	-2.30
4.0			-719.35588	-1.48	-719.11212	-1.63
					De	β
					42.194	2.257
10.0			-719.35353	0		

Table S7. Cartesian geometries (in Å), projected vibrational frequencies (in cm^{-1}), and rotational constants (in cm^{-1}) at PBE0/AVTZ along the path for BrHg + NO_2 → BrHg-NO_2.

r(Hg-N)	3.5		
Hg	0.00000	0.00000	-0.00354
Br	0.00000	0.00000	2.52059
N	0.00000	0.00000	-3.50354
O	0.00000	-1.09071	-3.96330
O	0.00000	1.09071	-3.96330
17.0149 18.0270 72.5649 155.0542 178.0747 513.3614 1248.6049 1770.9823			
0.44292 0.01436 0.01391			
r(Hg-N)	3.6		
Hg	0.00000	0.00000	0.01202
Br	0.00000	0.00000	2.53979
N	0.00000	0.00000	-3.58798
O	0.00000	1.09120	-4.04616
O	0.00000	-1.09120	-4.04616
14.7797 15.5937 62.9539 136.2014 176.7735 515.4443 1251.0291 1772.2684			
0.44254 0.01392 0.01349			
r(Hg-N)	3.7		
Hg	0.00000	0.00000	0.02782
Br	0.00000	0.00000	2.55845
N	0.00000	0.00000	-3.67218
O	0.00000	1.09159	-4.12916
O	0.00000	-1.09159	-4.12916
12.9923 13.6707 54.4782 119.9156 175.7828 518.7964 1249.9978 1773.1983			
0.44225 0.01349 0.01310			

r(Hg-N)	3.8		
Hg	0.00000	0.00000	0.04382
Br	0.00000	0.00000	2.57669
N	0.00000	0.00000	-3.75618
O	0.00000	1.09188	-4.21230
O	0.00000	-1.09188	-4.21230
11.4892 11.9706 47.2776 105.8679 174.9971 520.6885 1258.8221 1773.7175			
0.44201 0.01309 0.01272			
r(Hg-N)	3.9		
Hg	0.00000	0.00000	0.05997
Br	0.00000	0.00000	2.59461
N	0.00000	0.00000	-3.84003
O	0.00000	1.09210	-4.29552
O	0.00000	-1.09210	-4.29552
10.0731 10.4267 40.8222 93.5082 174.4080 522.6606 1261.2420 1774.1373			
0.44184 0.01271 0.01235			
r(Hg-N)	4.0		
Hg	0.00000	0.00000	0.07622
Br	0.00000	0.00000	2.61226
N	0.00000	0.00000	-3.92378
O	0.00000	1.09224	-4.37879
O	0.00000	-1.09224	-4.37879
8.8945 9.2162 34.9974 82.5372 173.9822 520.7699 1255.0442 1774.5060			
0.44171 0.01234 0.01200			
r(Hg-N)	4.1		
O	0.00000	1.09226	-4.46211
N	0.00000	0.00000	-4.00711
O	0.00000	-1.09226	-4.46211
Hg	0.00000	0.00000	0.09289
Br	0.00000	0.00000	2.62893
7.9305 8.2128 29.9397 73.1155 173.6134 521.6515 1254.3898 1774.6897			
0.44161 0.01198 0.01166			
r(Hg-N)	4.2		
O	0.00000	1.09241	-4.54516
N	0.00000	0.00000	-4.09049
O	0.00000	-1.09241	-4.54516
Hg	0.00000	0.00000	0.10952
Br	0.00000	0.00000	2.64556
7.0586 7.2553 25.5322 64.8301 173.3494 522.1686 1253.7045 1774.8072			
0.44153 0.01164 0.01134			
r(Hg-N)	4.3		
O	0.00000000	1.09249600	-4.62840400

N	0.00000000	0.00000000	-4.17395500
O	0.00000000	-1.09249600	-4.62840400
Hg	0.00000000	0.00000000	0.12604500
Br	0.00000000	0.00000000	2.66253000
6.3177 6.4244 21.6802 57.7916 173.1426 522.6901 1254.0018 1774.8885			
0.441475	0.011313	0.011030	
r(Hg-N)	4.4		
O	0.00000000	1.09256200	-4.71172600
N	0.00000000	0.00000000	-4.25745200
O	0.00000000	-1.09256200	-4.71172600
Hg	0.00000000	0.00000000	0.14254800
Br	0.00000000	0.00000000	2.67959800
5.6274 5.7943 17.8159 51.4606 172.9022 522.7090 1237.7576 1774.9799			
0.441437	0.010997	0.010730	
r(Hg-N)	4.5		
O	0.00000000	1.09261300	-4.79508300
N	0.00000000	0.00000000	-4.34093600
O	0.00000000	-1.09261300	-4.79508300
Hg	0.00000000	0.00000000	0.15906400
Br	0.00000000	0.00000000	2.69665000
5.0239 5.2526 14.3403 45.9301 172.7973 524.3206 1240.8167 1774.9671			
0.441405 0.010694 0.010441			

Table S8. Cartesian geometries (in Å), projected vibrational frequencies (in cm^{-1}), and rotational constants (in cm^{-1}) along the path for BrHg + NO_2 → *syn*-BrHgONO at the PBE0/AVTZ level.

r(Hg-N)	4.0		
Hg	0.00000	0.00000	0.02887
Br	0.00000	0.00000	-2.49592
O	0.00000	1.08622	3.55283
N	0.00000	0.00000	4.02887
O	0.00000	-1.08622	3.55283
19.8066 20.4000 175.7292 193.8201 492.4143 1244.5188 1745.7609			
0.44664	0.01503	0.01454	
r(Hg-N)	4.1		
Hg	0.00000	0.00000	0.01266
Br	0.00000	0.00000	-2.51631
O	0.00000	1.08768	3.64187
N	0.00000	0.00000	4.11266
O	0.00000	-1.08768	3.64187
17.2118 17.7538 172.4394 174.9269 500.7147 1247.8520 1753.4262			

0.44544	0.01454	0.01408	
r(Hg-N)	4.2		
Hg	0.00000	0.00000	0.00366
Br	0.00000	0.00000	2.53578
O	0.00000	1.08876	-3.72939
N	0.00000	0.00000	-4.19634
O	0.00000	-1.08876	-3.72939
15.1850 15.5840 154.1564 174.2927 506.8598 1250.5215 1758.8627			
0.44456	0.01408	0.01365	
r(Hg-N)	4.3		
Hg	0.00000	0.00000	0.02005
Br	0.00000	0.00000	2.55459
O	0.00000	1.08959	-3.81591
N	0.00000	0.00000	-4.27996
O	0.00000	-1.08959	-3.81591
13.2742 13.4411 137.8867 173.7919 511.4852 1252.5335 1762.8712			
0.44388	0.01364	0.01324	
r(Hg-N)	4.4		
Hg	0.00000	0.00000	0.03649
Br	0.00000	0.00000	2.57292
O	0.00000	1.09022	-3.90166
N	0.00000	0.00000	-4.36351
O	0.00000	-1.09022	-3.90166
11.6863 11.7004 123.6075 173.3840 515.1231 1254.0615 1765.8327			
0.44336	0.01323	0.01284	
r(Hg-N)	4.5		
Hg	0.00000	0.00000	0.05297
Br	0.00000	0.00000	2.59087
O	0.00000	1.09070	-3.98681
N	0.00000	0.00000	-4.44703
O	0.00000	-1.09070	-3.98681
10.4017 10.5787 111.4184 173.0514 517.8301 1255.2584 1768.0057			
0.44297	0.01283	0.01247	
r(Hg-N)	4.6		
Hg	0.00000	0.00000	0.06949
Br	0.00000	0.00000	2.60854
O	0.00000	1.09107	-4.07152
N	0.00000	0.00000	-4.53051
O	0.00000	-1.09107	-4.07152
9.2272 9.6021 100.7718 172.8587 520.2928 1257.0623 1769.6108			
0.44267	0.01245	0.01211	
r(Hg-N)	4.7		

Hg	0.00000	0.00000	0.08605
Br	0.00000	0.00000	2.62596
O	0.00000	1.09135	-4.15592
N	0.00000	0.00000	-4.61395
O	0.00000	-1.09135	-4.15592
8.0777 8.3913 91.1718 172.6625 521.3425 1259.2723 1770.8200			
0.44244 0.01209 0.01177			
r(Hg-N)	4.8		
Hg	0.00000	0.00000	0.10263
Br	0.00000	0.00000	2.64323
O	0.00000	1.09158	-4.24009
N	0.00000	0.00000	-4.69737
O	0.00000	-1.09158	-4.24009
7.0777 7.3454 82.6755 172.4595 521.4475 1262.3067 1771.7731			
0.44226 0.01175 0.01144			
r(Hg-N)	4.9		
Hg	0.00000	0.00000	0.11922
Br	0.00000	0.00000	2.66038
O	0.00000	1.09175	-4.32408
N	0.00000	0.00000	-4.78078
O	0.00000	-1.09175	-4.32408
6.2171 6.5569 75.3114 172.2526 520.7063 1266.3674 1772.5289			
0.44212 0.01141 0.01113			
r(Hg-N)	5		
Hg	0.00000	0.00000	0.13583
Br	0.00000	0.00000	2.67741
O	0.00000	1.09189	-4.40791
N	0.00000	0.00000	-4.86417
O	0.00000	-1.09189	-4.40791
5.5627 5.8509 68.8825 172.0810 519.2881 1271.1654 1773.0882			
0.44200 0.01109 0.01082			
r(Hg-N)	5.1		
Hg	0.00000	0.00000	0.15246
Br	0.00000	0.00000	2.69435
O	0.00000	1.09200	-4.49161
N	0.00000	0.00000	-4.94755
O	0.00000	-1.09200	-4.49161
5.0878 5.3108 63.3200 172.3405 525.5300 1259.1231 1773.4391			
0.44192 0.01079 0.01053			

Table S9. Cartesian geometries (in Å), projected vibrational frequencies (in cm^{-1}), and rotational constants (in cm^{-1}) along the path for BrHg + NO_2 → Hg-$BrNO_2$ vdW at the PBE0/AVTZ level.

r(Br-N)	3		
Hg	0.00000	0.00000	1.62826
N	0.00000	0.00000	-3.93046
O	0.00000	1.09079	-4.38634
O	0.00000	-1.09079	-4.38634
Br	0.00000	0.00000	-0.93046
19.6498 21.0913 93.0334 143.9572 173.9329 554.4275 1266.6776 1783.7428			
0.44294 0.01183 0.01153			
r(Br-N)	3.1		
O	0.00000	1.09110	-4.46648
N	0.00000	0.00000	-4.01069
O	0.00000	-1.09110	-4.46648
Br	0.00000	0.00000	-0.91069
Hg	0.00000	0.00000	1.64266
17.2021 18.2141 79.9173 146.3922 149.1732 557.3337 1270.1758 1781.7601			
0.44265	0.01153	0.01123	
r(Br-N)	3.2		
O	0.00000	1.09138	-4.54758
N	0.00000	0.00000	-4.09203
O	0.00000	-1.09138	-4.54758
Br	0.00000	0.00000	-0.89203
Hg	0.00000	0.00000	1.65783
14.9975 15.5150 69.4561 128.4388 148.1705 560.3175 1274.3957 1780.2376			
0.44242	0.01122	0.01094	
r(Br-N)	3.3		
O	0.00000	1.09159	-4.62932
N	0.00000	0.00000	-4.17396
O	0.00000	-1.09159	-4.62932
Br	0.00000	0.00000	-0.87396
Hg	0.00000	0.00000	1.67344
12.7552 13.0799 59.9029 110.5534 149.2731 560.8801 1270.0519 1779.1612			
0.44225 0.01092 0.01066			
r(Br-N)	3.4		
O	0.00000	1.09175	-4.71157
N	0.00000	0.00000	-4.25632
O	0.00000	-1.09175	-4.71157
Br	0.00000	0.00000	-0.85632
Hg	0.00000	0.00000	1.68938
10.8767 11.1336 50.8276 95.3737 150.1123 562.3975 1270.8652 1778.2665			

0.44212 0.01063 0.01038			
r(Br-N)	3.5		
Hg	0.00000	0.00000	1.70556
N	0.00000	0.00000	-4.33900
O	0.00000	1.09186	-4.79419
O	0.00000	-1.09186	-4.79419
Br	0.00000	0.00000	-0.83900
9.2549 9.2760 43.7365 82.8854 151.0866 565.0067 1272.8728 1777.5429 0.44203 0.01035 0.01011			
r(Br-N)	3.6		
O	0.00000	1.09196	-4.87696
N	0.00000	0.00000	-4.42184
O	0.00000	-1.09196	-4.87696
Br	0.00000	0.00000	-0.82184
Hg	0.00000	0.00000	1.72186
7.1237 7.3036 39.3340 72.3874 151.0888 564.7612 1272.0432 1777.0392 0.44195 0.01007 0.00985			
r(Br-N)	3.7		
O	0.00000	1.09204	-4.95992
N	0.00000	0.00000	-4.50484
O	0.00000	-1.09204	-4.95992
Br	0.00000	0.00000	-0.80484
Hg	0.00000	0.00000	1.73827
4.8904 5.0814 36.2165 63.0619 151.5002 567.3581 1274.8883 1776.6375 0.44189 0.00981 0.00959			
r(Br-N)	3.8		
O	0.00000	1.09210	-5.04297
N	0.00000	0.00000	-4.58794
O	0.00000	-1.09210	-5.04297
Br	0.00000	0.00000	-0.78794
Hg	0.00000	0.00000	1.75476
1.5748 3.0216 31.9855 54.1347 151.7144 568.1001 1275.3864 1776.3256 0.44184 0.00955 0.00935			

Table S10. Cartesian geometries (in Å), projected vibrational frequencies (in cm^{-1}), and rotational constants (in cm^{-1}) along the path for BrHg + HOO → BrHgOOH at the PBE0/AVTZ level.

r(Hg-O)	3.0		
Hg	-0.23115	-0.09189	0.011937
Br	2.279652	0.138049	-0.01445
O	-3.20938	-0.44995	-0.03225
O	-3.92894	0.656365	-0.12256
H	-4.18924	0.867895	0.789285

27.6462 45.2863 120.4766 183.9682 306.9534 1100.3209 1441.2214 3671.5346			
1.12266	0.01982	0.01952	
r(Hg-O)	3.1		
Hg	-0.21983	-0.0863	0.019317
Br	2.29916	0.131761	-0.02388
O	-3.29651	-0.45657	-0.06392
O	-4.02569	0.641276	-0.12361
H	-4.30663	0.814699	0.790659
23.1682 38.1569 105.3316 180.9041 271.9401 1114.2709 1443.4361 3664.4244			
1.16954	0.01918	0.01891	
r(Hg-O)	3.2		
Hg	-0.20779	-0.08341	0.025979
Br	2.316594	0.128906	-0.03261
O	-3.38355	-0.45821	-0.09252
O	-4.12057	0.63249	-0.12343
H	-4.42461	0.766487	0.790453
19.5554 32.1390 91.7922 178.6696 239.3671 1124.9043 1444.7899 3659.0773			
1.18682	0.01859	0.01835	
r(Hg-O)	3.3		
Hg	-0.19537	-0.07811	0.031672
Br	2.333437	0.122728	-0.04034
O	-3.46955	-0.46347	-0.11415
O	-4.21721	0.618089	-0.12429
H	-4.54654	0.716002	0.785674
16.3730 27.1841 79.7621 176.7659 209.2997 1132.5547 1445.3883 3655.1811			
1.22048	0.01802	0.01780	
r(Hg-O)	3.4		
Hg	-0.18255	-0.07516	0.039548
Br	2.348985	0.119556	-0.05103
O	-3.55519	-0.46337	-0.1464
O	-4.3118	0.610097	-0.12314
H	-4.67476	0.654761	0.778375
13.4155 22.8458 69.0594 172.8137 184.1348 1138.0774 1445.2829 3652.3011			
1.22733	0.01748	0.01729	
r(Hg-O)	3.5		
Hg	-0.16891	-0.08585	0.06034
Br	2.360403	0.134696	-0.07828
O	-3.63764	-0.42714	-0.25822
O	-4.39722	0.631314	-0.09886

H	-4.82235	0.520478	0.76931
10.8447 20.3346 59.2728 153.1640 177.1555 1142.3696 1444.4604 3650.1876			
1.09087	0.01700	0.01684	
r(Hg-O)	3.6		
Hg	-0.15372	-0.13437	0.0717
Br	2.363182	0.200913	-0.0901
O	-3.71145	-0.25405	-0.46519
O	-4.46659	0.687117	0.049208
H	-4.98957	0.252702	0.74544
7.6622 18.0778 50.0470 129.2272 176.0710 1146.9122 1442.6588 3648.6042			
0.79844	0.01662	0.01646	
r(Hg-O)	3.65		
Hg	0.148611	-0.07906	-0.10208
Br	-2.37655	0.124965	0.134682
O	3.743531	-0.37557	0.455709
O	4.533525	0.59275	0.057981
H	5.073867	0.213702	-0.65714
5.9970 16.8634 44.9391 114.8628 175.8669 1151.0839 1440.2522 3647.8493			
0.50173	0.01667	0.01637	

Table S11. Lennard-Jones parameters used in the current study.

	σ/Å	ε/k_B	Reference
N_2	3.74	82	Hippler et al.[1]
BrHg	4.24	750	Estimated from additive volume[b] and boiling point of $HgBr_2$[2]
NO_2	4.68	146	Troe[3]
$BrHgNO_2$[a]	4.95	750	Estimated from additive volume[b] and boiling point of $HgBr_2$
HOO	3.699	289.3	Estimated from additive volume[b] and Troe[4]
BrHgOOH	5.03	750	Estimated from additive volume and boiling point of $HgBr_2$

a. The same value is used for *anti*- and *syn*-BrHgONO as for $BrHgNO_2$. b. from Refs. 5 and 6.

Table S12. Collision frequency (in $molecule^{-1}$ cm^3 s^{-1}) for BrHg + NO_2 and BrHg + HOO estimated using Lennard-Jones parameters.[7]

T/K	BrHg + NO_2	BrHg + HOO
200	4.25E-10	4.60E-10
220	4.24E-10	4.61E-10
240	4.23E-10	4.62E-10
260	4.22E-10	4.62E-10
280	4.21E-10	4.62E-10

300	4.20E-10	4.61E-10
320	4.19E-10	4.60E-10
340	4.19E-10	4.60E-10
360	4.19E-10	4.59E-10
380	4.19E-10	4.58E-10
400	4.19E-10	4.57E-10

Table S13. Pressure- and temperature-dependent rate constants at CASPT2//PBE0 and RCCSDT//PBE0 levels.

		CASPT2//PBE0				
T/K	p/atm	BrHg + NO_2 -->$BrHgNO_2$	BrHg + NO_2 -->anti	BrHg + NO_2 -->syn	NO_2 oxidation total	HOO oxidation
220	0.01	4.81E-13	1.24E-12	4.14E-11	4.31E-11	1.69E-11
220	0.1	1.45E-12	3.74E-12	1.09E-10	1.14E-10	6.07E-11
220	1	2.75E-12	7.55E-12	1.71E-10	1.82E-10	1.12E-10
220	10	4.09E-12	1.27E-11	1.94E-10	2.11E-10	1.37E-10
220	100	6.49E-12	2.14E-11	1.90E-10	2.18E-10	1.43E-10
260	0.01	2.37E-13	8.31E-13	2.03E-11	2.14E-11	7.93E-12
260	0.1	7.94E-13	2.42E-12	6.01E-11	6.33E-11	3.21E-11
260	1	1.65E-12	4.73E-12	1.04E-10	1.10E-10	6.50E-11
260	10	2.57E-12	7.95E-12	1.24E-10	1.35E-10	8.32E-11
260	100	3.96E-12	1.34E-11	1.24E-10	1.41E-10	8.77E-11
280	0.01	1.72E-13	7.88E-13	1.47E-11	1.56E-11	5.53E-12
280	0.1	6.21E-13	2.26E-12	4.69E-11	4.97E-11	2.35E-11
280	1	1.39E-12	4.31E-12	8.80E-11	9.37E-11	5.07E-11
280	10	2.29E-12	7.17E-12	1.12E-10	1.21E-10	6.84E-11
280	100	3.55E-12	1.22E-11	1.13E-10	1.29E-10	7.35E-11
298	0.01	1.31E-13	7.88E-13	1.10E-11	1.19E-11	4.17E-12
298	0.1	5.00E-13	2.26E-12	3.75E-11	4.03E-11	1.88E-11
298	1	1.20E-12	4.16E-12	7.60E-11	8.14E-11	4.38E-11
298	10	2.09E-12	6.68E-12	1.02E-10	1.11E-10	6.25E-11
298	100	3.27E-12	1.13E-11	1.06E-10	1.21E-10	6.87E-11
320	0.01	9.50E-14	8.11E-13	7.80E-12	8.70E-12	2.97E-12
320	0.1	3.89E-13	2.37E-12	2.88E-11	3.15E-11	1.42E-11
320	1	1.02E-12	4.23E-12	6.38E-11	6.90E-11	3.55E-11
320	10	1.88E-12	6.35E-12	9.22E-11	1.00E-10	5.40E-11
320	100	3.00E-12	1.05E-11	9.94E-11	1.13E-10	6.13E-11

		RCCSDT//PBE0						
T/K	p/atm	BrHg + NO_2 -->$BrHgNO_2$	BrHg + NO_2 -->anti	BrHg + NO_2 -->syn	NO2 oxidation total	HOO oxidation	NO_2 reduction[a]	NO_2 reduction[b]
220	0.01	7.07E-01	1.83E+00	6.08E+01	6.34E-11	1.80E-11	2.25E-11	5.14E-11

220	0.1	2.67E+00	6.89E+00	2.01E+02	2.11E-10	6.94E-11	2.29E-11	5.13E-11
220	1	5.58E+00	1.53E+01	3.48E+02	3.69E-10	1.33E-10	2.30E-11	5.13E-11
220	10	8.55E+00	2.66E+01	4.07E+02	4.42E-10	1.65E-10	2.35E-11	5.14E-11
220	100	1.42E+01	4.50E+01	3.99E+02	4.59E-10	1.73E-10	2.85E-11	5.20E-11
260	0.01	3.13E-01	1.10E+00	2.70E+01	2.84E-11	8.70E-12	1.67E-11	4.01E-11
260	0.1	1.41E+00	4.30E+00	1.07E+02	1.13E-10	4.03E-11	1.70E-11	4.00E-11
260	1	3.52E+00	1.01E+01	2.24E+02	2.37E-10	8.90E-11	1.69E-11	4.02E-11
260	10	6.00E+00	1.85E+01	2.94E+02	3.18E-10	1.18E-10	1.71E-11	4.01E-11
260	100	9.50E+00	3.20E+01	3.01E+02	3.43E-10	1.25E-10	2.02E-11	4.05E-11
280	0.01	2.24E-01	1.03E+00	1.91E+01	2.04E-11	6.09E-12	1.33E-11	3.41E-11
280	0.1	1.07E+00	3.93E+00	8.16E+01	8.66E-11	2.98E-11	1.30E-11	3.40E-11
280	1	2.87E+00	8.88E+00	1.82E+02	1.94E-10	7.10E-11	1.32E-11	3.40E-11
280	10	5.11E+00	1.59E+01	2.52E+02	2.73E-10	9.95E-11	1.36E-11	3.39E-11
280	100	8.14E+00	2.76E+01	2.64E+02	2.99E-10	1.08E-10	1.58E-11	3.43E-11
298	0.01	1.66E-01	1.01E+00	1.40E+01	1.52E-11	4.51E-12	1.10E-11	3.00E-11
298	0.1	8.39E-01	3.81E+00	6.33E+01	6.79E-11	2.30E-11	1.08E-11	3.00E-11
298	1	2.39E+00	8.29E+00	1.52E+02	1.63E-10	5.83E-11	1.09E-11	3.03E-11
298	10	4.51E+00	1.44E+01	2.23E+02	2.42E-10	8.62E-11	1.12E-11	3.02E-11
298	100	7.30E+00	2.49E+01	2.40E+02	2.72E-10	9.57E-11	1.29E-11	3.05E-11
320	0.01	1.31E-01	1.11E+00	1.07E+01	1.20E-11	3.20E-12	1.08E-11	2.93E-11
320	0.1	7.01E-01	4.23E+00	5.19E+01	5.68E-11	1.71E-11	1.05E-11	2.92E-11
320	1	2.12E+00	8.78E+00	1.33E+02	1.44E-10	4.66E-11	1.07E-11	2.91E-11
320	10	4.18E+00	1.41E+01	2.05E+02	2.24E-10	7.34E-11	1.09E-11	2.91E-11
320	100	6.91E+00	2.37E+01	2.26E+02	2.56E-10	8.43E-11	1.25E-11	2.95E-11

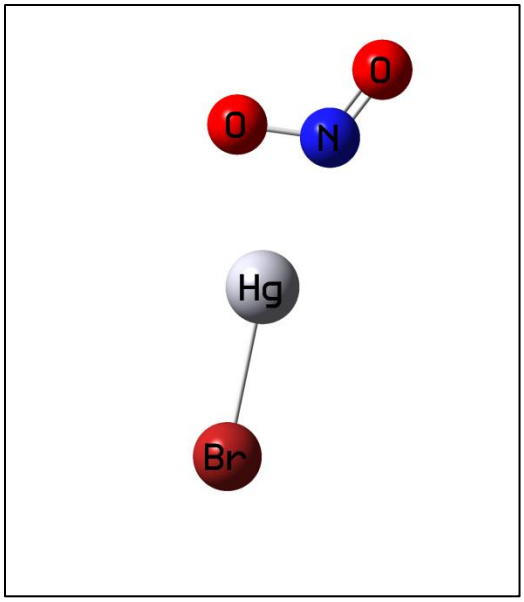
a. by assuming that k_{-12}(T) is one tenth of k_{11}(T). b. by assuming that k_{-12}(T) is equal to k_{11}(T).

Table S14 Equilibrium constant for BrHg• + NO_2 → Hg + $BrNO_2$ using literature reaction enthalpy (-7.9 kcal/mol[8,9]) and PBE0/AVTZ vibrational frequencies and rotational constants.

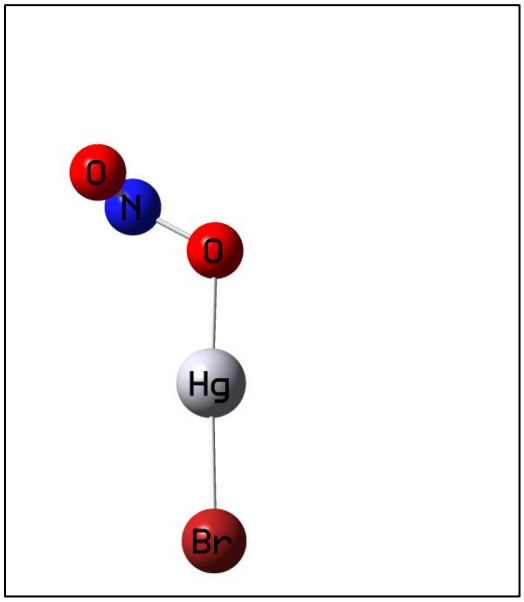
T/K	K_{eq}
200.0	3.66×10^{6}
220.0	5.10×10^{5}
240.0	9.85×10^{4}
260.0	2.44×10^{4}
280.0	7.41×10^{3}
300.0	2.63×10^{3}
320.0	1.06×10^{3}
340.0	4.80×10^{2}
360.0	2.36×10^{2}
380.0	1.25×10^{2}
400.0	7.10×10^{1}

Figure S1. Structures for all transition states.

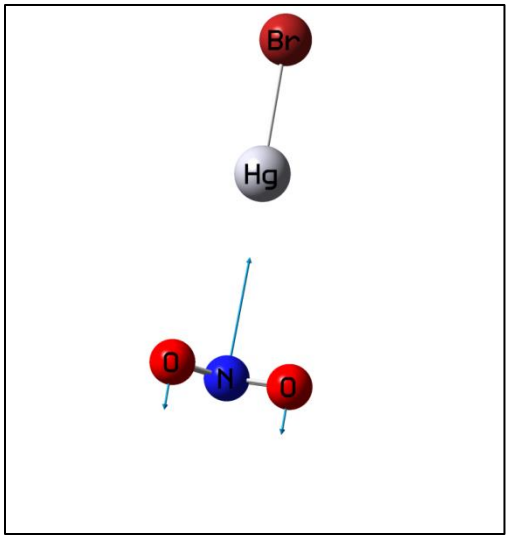
TS1



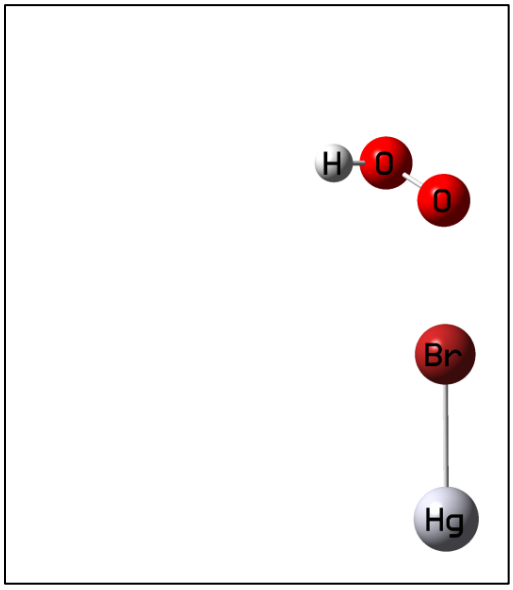
TS2



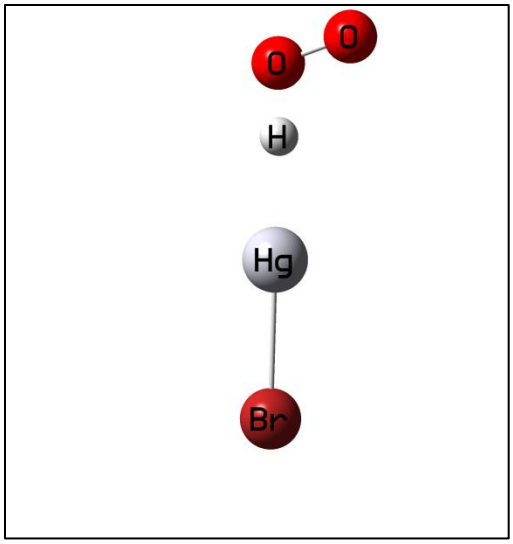
TS3



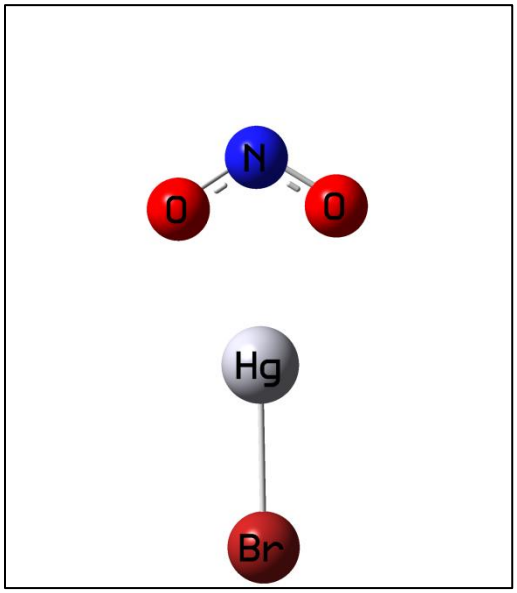
TS4



TS5



TSX



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