

Computational Study on the Mechanisms and Kinetics of the CH₂BrO₂ + ClO Reaction in the Atmosphere

Yunju Zhang,^{1*} Yizhen Tang,² Bing He,³

¹Key Laboratory of Photoinduced Functional Materials, Mianyang Normal University,

Mianyang 621000, PR China

²School of Environmental and municipal engineering, Qingdao University of

Technology, Fushun Road 11. Qingdao, Shandong, 266033 P.R. China.

³College of Chemistry and Life Science, Institute of functional molecules, Chengdu

Normal University, Chengdu, Sichuan 611130, PR China

Table S1. The Zero-point energy correction (ZPE), relative energies (ΔE), reactions enthalpies (ΔH) and reaction Gibbs free energies (ΔG) of all the species for the reaction channels involved in the CH_2BrO_2 with ClO reaction (energies in kcal/mol).

Species	ZPE ^a	T_1^b	ΔE^b	ΔH^b	ΔG^b
$\text{CH}_2\text{BrO}_2 + \text{ClO}$	22.3	0.021 0.034	0.0	0.0	0.0
IM1 (CH_2BrOOCl)	23.9	0.016	-17.1	-12.0	-6.4
IM2 ($\text{CH}_2\text{BrOOCIO}$)	23.6	0.022	2.2	7.5	12.8
IM3 ($\text{CH}_2\text{BrOCIO}_2$)	23.9	0.022	-8.0	-3.0	3.0
TS1	23.5	0.020	11.1	16.0	21.7
TS2	21.8	0.022	18.5	23.7	28.6
TS3	21.2	0.024	-5.0	-0.1	6.2
TS4	21.0	0.024	6.9	11.9	17.7
TS5	21.7	0.034	12.1	17.1	23.1
TS6	21.3	0.057	52.6	58.1	63.3
TS7	21.8	0.037	56.6	62.1	66.7
TS8	21.9	0.030	19.8	25.1	30.6
TS9	21.7	0.036	17.4	22.7	28.4
TS10	22.0	0.031	47.8	53.1	58.1
TS11	21.9	0.022	-0.8	3.9	10.8
TS12	22.7	0.024	15.8	21.0	26.5
TS13	21.6	0.083	61.5	67.0	71.7
TS14	20.7	0.048	58.1	64.1	67.8
T-TS1	19.4	0.027	28.0	34.6	34.3
T-TS2	21.0	0.046	45.0	50.6	53.5
T-TS3	20.9	0.036	26.4	32.4	34.8
T-TS4	21.4	0.142	72.0	77.7	80.8
T-h-TS1	18.8	0.023	13.9	19.3	23.2
P1 ($\text{CHBrO} + \text{HO}_2 + \text{Cl}$)	20.4	0.014 0.028	-39.5	-32.9	-47.5
P2 ($\text{HOOC} + \text{CHBrO}$)	22.2	0.014 0.016	-66.2	-60.6	-66.7
P3 ($\text{CHBrO}_2 + \text{HOCl}$)	21.8	0.032 0.010	-22.0	-16.4	-21.8
P4 ($\text{CH}_2\text{BrOCl} + \text{O}_2(^1\Delta)$)	22.4	0.010 0.014	-15.3	-9.5	-13.7
P5 ($\text{CH}_2\text{BrCl} + \text{O}_3$)	22.5	0.008 0.026	-10.5	-5.1	-10.7
P6 ($\text{CH}_2\text{O} + \text{BrClO}_2$)	21.2	0.015	-8.1	-2.2	-7.6
P7 ($\text{CH}_2\text{O} + \text{BrOClO}$)	20.1	0.015 0.024	-9.2	-3.0	-9.1

P8 (CHBrO + HOClO)	21.6	0.014 0.028	-52.1	-46.3	-52.6
P9 (CH ₂ BrClO + O ₂ (¹ Δ))	21.4	0.016 0.014	32.7	38.7	33.9
P10 (CH ₂ BrClO + O ₂ (³ Σ))	21.4	0.016 0.015	2.5	8.5	3.1
P11 (CH ₂ BrO + OClO)	20.2	0.017 0.027	8.6	14.1	7.8
P12 (CH ₂ BrOCl + O ₂ (³ Σ))	22.4	0.010 0.015	-45.4	-39.6	-44.5
P13 (CH ₂ BrOOCl + O(³ P))	22.1	0.013 0.005	25.9	31.7	28.5

^aAt the B3LYP/6-311++G(d,p) level

^bThe relative energies are calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311++G(d,p) + ZPE level

Table S2. The Cartesian coordinates of all the species in the CH₂BrO₂ + ClO reaction.

Species		Coordinates(Atom, X, Y, Z)		
CH ₂ BrO ₂	C	-0.01627	0.77538	0.25882
	H	0.1943	1.76345	-0.14101
	H	-0.23212	0.7703	1.32353
	O	-1.16527	0.30985	-0.45693
	O	-1.81031	-0.63735	0.20177
	Br	1.5026	-0.33774	-0.06068
ClO	O	-1.84698	0.42469	0.68901
	Cl	-2.92846	-0.52679	-0.13943
IM1	C	0.83834	1.0425	0.25915
	H	1.37233	1.98289	0.14608
	O	-0.11451	0.97571	-0.80282
	O	-1.36647	0.81627	-0.33662
	O	-2.14433	-0.72009	-0.30746
	Cl	-3.52247	-0.0658	0.37933
	H	0.33175	0.9482	1.21477
	Br	2.14647	-0.3839	0.0682
IM2	C	-1.73547	0.85511	-0.01572
	H	-2.42771	1.29272	-0.73136
	O	-0.46957	1.25278	-0.45147
	O	0.46827	1.03359	0.57316
	O	2.81847	-0.17054	-0.53037
	Cl	1.5205	-0.49654	0.23907
	H	-1.92022	1.17426	1.0071
	Br	-1.99023	-1.03732	-0.05953
IM3	C	0.62389	1.04187	0.27858
	O	-0.49262	0.40458	0.50703
	O	-2.47376	-1.05605	0.96138
	O	-3.51396	0.83795	-0.34563
	Cl	-2.51394	-0.26978	-0.29294
	H	0.62438	1.74025	-0.56874
	H	0.98223	1.55621	1.18415
	Br	2.3116	-0.11847	-0.1491
TS1	C	2.13649	-0.40662	-0.37339
	H	2.9543	-1.11362	-0.23242
	O	1.21891	-0.6835	0.68269
	O	0.01533	-0.16129	0.43102
	O	-1.88547	1.10588	0.28867
	Cl	-2.10069	-0.34364	-0.30768
	H	1.62102	-0.49959	-1.32953
	Br	2.80397	1.37364	-0.19106

TS2	C	1.56494	0.75389	0.45046
	O	0.36207	0.32603	0.19761
	O	-1.31038	-0.98335	0.7842
	O	-2.84956	0.88299	-0.09546
	Cl	-1.94515	-0.28346	-0.38564
	H	1.74037	1.77493	0.0634
	H	1.7915	0.76347	1.53101
	Br	2.9723	-0.23813	-0.28425
TS3	C	-0.99427	-0.11405	0.69549
	H	-0.84943	-0.89667	1.45582
	O	-0.75086	1.07876	0.96047
	O	0.73157	1.45769	-0.47854
	O	0.9357	0.31199	-0.82665
	Cl	2.44754	-0.68467	0.15904
	H	-0.10042	-0.41801	-0.10717
	Br	-2.5254	-0.55352	-0.35837
TS4	C	1.63198	0.68574	0.41725
	O	1.05275	1.27392	-0.53501
	O	-0.53007	-0.05993	-0.08281
	O	-1.53303	-0.68723	-0.43542
	Cl	-3.21068	0.00404	0.18708
	H	2.00223	1.28922	1.26276
	H	0.81078	-0.01706	0.91129
	Br	2.98295	-0.60536	0.02223
TS5	C	-1.24355	0.21513	0.75549
	H	-1.98409	0.28212	1.54677
	O	-1.29391	1.39643	0.02567
	O	-0.43624	1.41762	-0.94606
	O	1.3352	0.62659	0.75397
	Cl	2.17912	-0.44079	-0.17248
	H	-0.12166	0.22795	1.07566
	Br	-1.44506	-1.40107	-0.24222
TS6	C	-1.00306	-0.78922	0.80367
	H	-0.93493	-0.29544	1.75879
	O	0.13144	1.53443	0.71103
	O	0.13743	1.39929	-0.51828
	O	0.75481	-0.30198	-0.78513
	Cl	2.18096	-0.52123	0.07929
	H	-0.49953	-1.71599	0.58548
	Br	-2.40623	-0.25051	-0.37488

TS7	C	1.14778	-0.11837	0.91344
	H	0.9795	-1.06338	1.40035
	O	-0.50387	-1.6927	0.10361
	O	-1.56831	-1.17889	-0.47903
	O	-2.13596	-0.26693	0.18958
	Cl	-0.79754	1.61519	-0.07831
	H	0.8989	0.81801	1.38302
	Br	2.42777	-0.07664	-0.50359
TS8	C	-1.76894	1.10717	-0.13198
	H	-2.5173	1.01784	-0.93212
	O	-0.6784	1.61372	-0.43829
	O	0.81345	0.86346	0.90245
	O	2.42992	-0.21579	-0.76043
	Cl	1.29065	-0.3849	0.19996
	H	-2.14959	1.12493	0.8947
	Br	-1.59884	-1.1961	-0.01176
TS9	C	-1.67681	0.99874	0.29243
	O	-0.91054	1.70866	-0.36481
	O	1.09674	1.23977	0.38684
	O	1.19792	-1.34204	0.36425
	Cl	1.64552	-0.03357	-0.2583
	H	-1.57777	0.891	1.37824
	H	-2.69729	0.83097	-0.11051
	Br	-1.45359	-1.17617	-0.10126
TS10	C	-0.98854	-0.22582	0.78155
	H	-0.8717	0.62125	1.44331
	O	0.05162	1.2251	-0.43509
	O	0.94957	1.79668	0.18105
	O	0.5988	-0.76551	-0.58391
	Cl	2.10704	-0.66381	0.08958
	H	-0.6465	-1.1913	1.11609
	Br	-2.60347	-0.2922	-0.23615
TS11	C	1.0427	-0.48462	0.60412
	O	0.23538	-1.15329	-0.13329
	O	-2.6156	-0.57489	0.21691
	O	-0.85144	1.27389	0.4654
	Cl	-1.5139	0.21683	-0.41158
	H	0.48514	0.49607	0.94247
	H	1.35924	-0.96217	1.54239
	Br	2.60889	0.21818	-0.23328

TS12	C	-1.26475	1.43075	-0.26618
	O	-0.06918	1.52994	0.1031
	O	2.28227	0.123	0.8043
	O	0.45658	-1.29374	-0.27855
	Cl	1.42635	-0.16535	-0.37359
	H	-1.52715	1.28215	-1.31797
	H	-2.01866	1.91726	0.35952
	Br	-2.0277	-0.69686	0.22798
TS13	C	0.64167	-0.16652	0.10755
	H	0.36299	-0.72472	-0.78122
	O	2.33869	-0.24671	-0.48719
	O	3.05143	-1.06039	0.11781
	O	-1.22687	-0.97419	0.46809
	Cl	-2.59172	-0.31065	-0.20888
	H	0.83443	-0.64117	1.05759
	Br	0.3013	1.71291	0.10828
TS14	C	0.5662	-0.5904	0.10439
	H	0.49049	-1.21347	-0.77081
	O	2.76548	-0.16229	-0.51004
	O	3.55013	-0.44362	0.38524
	Cl	-2.37385	-0.78539	-0.04253
	O	-2.2514	0.85045	0.11828
	H	0.76818	-1.05627	1.04623
	Br	0.12786	1.26411	-0.02502
T-TS1	C	-0.21334	0.59167	0.04853
	O	-2.36056	1.92211	0.04306
	O	-3.34371	1.21778	-0.04144
	O	3.9344	1.0899	-0.14334
	Cl	2.76432	-0.00397	0.07976
	H	-0.03513	1.02365	1.02051
	H	0.02167	1.0763	-0.88428
	Br	-0.90117	-1.12631	-0.01856
T-TS2	C	-2.23392	-0.16927	0.51816
	H	-1.78363	0.29263	1.40315
	O	-1.35354	-0.91036	-0.19047
	O	0.06925	0.09319	-0.34695
	O	3.00636	0.63845	0.23657
	Cl	1.7511	-0.27257	-0.04967
	H	-3.03839	-0.86603	0.80356
	Br	-3.02966	1.231	-0.50855

T-TS3	C	0.59519	-0.51215	-0.00001
	O	2.5181	-0.96598	-0.00005
	O	3.27774	0.00742	0.00007
	O	-1.6531	-1.11364	-0.00001
	Cl	-2.77736	0.08877	0.00002
	H	0.43185	-1.00447	0.94363
	H	0.43179	-1.00451	-0.94359
	Br	0.56344	1.39759	-0.00003
T-TS4	C	-1.5194	-0.58413	0.44098
	H	-2.48328	-0.10933	0.63022
	O	-0.57238	0.4243	0.3636
	O	-1.41535	1.96213	-0.24983
	O	0.92085	-0.40746	0.77664
	Cl	2.10374	0.03956	-0.29195
	H	-1.23661	-1.27766	1.23624
	Br	-1.6298	-1.56184	-1.19609
T-h-TS1	C	0.99567	-0.0072	0.74159
	H	1.22689	0.11646	1.79753
	O	1.82878	-1.02618	0.23452
	O	1.40919	-1.52083	-0.92696
	O	-1.40266	-0.80563	0.77068
	Cl	-2.3395	0.1072	-0.29936
	H	-0.30601	-0.44015	0.70168
	Br	1.07734	1.63477	-0.2307
CH ₂ BrOCl	C	-0.50596	0.59021	1.04727
	H	-0.95149	1.58079	1.09525
	O	0.7824	0.80678	0.59066
	O	1.56919	-0.37776	0.94224
	Cl	2.63985	-0.71799	-0.35865
	H	-0.51965	0.07399	2.0044
	Br	-1.66714	-0.47636	-0.16892
CH ₂ BrOCl	C	-0.75923	-0.00001	0.
	H	-1.3027	-0.25564	0.80264
	O	0.53884	-1.2399	0.
	Cl	-0.00137	-2.8608	0.
	H	-1.3027	-0.25564	-0.80264
	Br	0.08042	1.6849	0.
CH ₂ BrClO	C	-0.04539	0.84321	0.
	O	-3.25168	0.2962	0.
	Cl	-1.81555	-0.42965	0.
	H	-0.19626	1.38998	-0.92256
	H	-0.19626	1.38998	0.92256
	Br	1.64397	-0.08315	0.

CH ₂ BrCl	C	-0.88827	0.47798	0.
	H	-1.42504	0.69939	-0.90402
	Cl	0.25368	1.98395	0.
	H	-1.42504	0.69939	0.90402
	Br	0.106	-1.08757	0.
BrOClO	O	2.18459	0.90775	0.47736
	O	0.79317	-1.30083	0.32372
	Cl	1.97684	-0.41233	-0.24417
	Br	-1.38276	-0.60339	-0.03688
CH ₂ BrO	C	-0.49356	1.20166	0.
	H	-1.12412	1.29146	-0.89865
	O	0.45858	2.08883	0.
	H	-1.12412	1.29146	0.89865
	Br	0.04435	-0.75751	0.
HOClO	O	-2.65351	-0.61971	0.2854
	O	-0.78711	1.40305	0.56891
	Cl	-1.6476	0.26438	-0.47992
	H	-0.34526	0.8452	1.22632
CHBrO ₂	C	-0.86083	1.06189	0.73505
	H	-1.21827	1.26838	1.72222
	O	-0.14811	1.90728	0.13429
	O	0.29284	1.65255	-1.08352
	Br	-1.30456	-0.58982	-0.11525
CHBrO	C	-0.43593	1.2302	0.
	O	0.36762	2.08473	0.
	H	-1.52898	1.33441	0.
	Br	0.03439	-0.72553	0.
HOCl	O	-1.7909	-0.16184	0.17055
	O	-2.94944	0.20414	0.84356
	Cl	-4.32062	0.13275	-0.27935
	H	-1.49756	0.6851	-0.21538
CHBrO	C	-0.4425	-1.2284	0.
	O	0.37295	-2.07133	0.
	H	-1.52947	-1.34106	0.
	Br	0.03431	0.72234	0.
BrClO ₂	O	1.38624	0.74376	1.03702
	O	2.25609	-0.64306	-0.88041
	Cl	1.29638	-0.52204	0.25803
	Br	-1.17772	-0.64921	0.00754
CH ₂ O	C	0.	0.	-0.53126
	H	0.94543	0.	-1.10164
	O	0.	0.	0.67592
	H	-0.94543	0.	-1.10164

OCIO	O	-1.68274	0.47267	0.58164
	O	-4.08123	0.24692	-0.39703
	Cl	-2.76002	-0.41583	-0.02726
HOCl	H	1.31415	-0.30068	0.93031
	O	1.76298	0.2081	0.23343
	Cl	3.28586	-0.45143	-0.01996
HO ₂	O	0.243	1.58861	-0.1652
	O	0.6068	0.53885	-0.78251
	H	0.00183	-0.22065	-0.55046
O ₂ (³ Σ)	O	-1.64401	2.04671	0.00049
	O	-2.59351	1.30427	-0.00047
O ₂ (¹ Δ)	O	-1.64401	2.04671	0.00049
	O	-2.59351	1.30427	-0.00047
O ₃	O	0.	-1.07923	-0.21417
	O	0.	0.	0.4284
	O	0.	1.07923	-0.21417

Table S3. The harmonic vibrational frequencies (imaginary frequency is suffixed with *i*) and the moment of inertia (I_a , I_b and I_c) of all the species in the $\text{CH}_2\text{BrO}_2 + \text{ClO}$ reaction at the B3LYP/6-311++G(d,p) level.

Species	Frequencies (cm^{-1})	I_a, I_b, I_c (amu bohr ²)
IM1	29, 85, 123, 263, 298, 452, 511, 591, 601, 656, 885, 935, 1034, 1258, 1295, 1443, 3092, 3174	417.94133, 2541.96118, 2795.51661
IM2	59, 63, 102, 220, 232, 313, 434, 509, 595, 840, 917, 934, 1023, 1257, 1296, 1449, 3107, 3196	488.82053, 2092.47058, 2467.55741
IM3	40, 66, 208, 229, 355, 382, 427, 486, 571, 869, 953, 1089, 1105, 1200, 1264, 1432, 2999, 3091	325.08365, 2393.24135, 2502.38443
TS1	141 <i>i</i> , 32, 92, 106, 219, 303, 493, 524, 611, 846, 893, 964, 1037, 1263, 1298, 1449, 3110, 3203,	362.53098, 3200.17764, 3419.15068
TS2	140 <i>i</i> , 21, 60, 109, 205, 325, 341, 440, 528, 674, 866, 1043, 1072, 1102, 1258, 1339, 2917, 2953	262.44427, 3661.82386, 3737.88436
TS3	468, 85, 97, 122, 273, 315, 424, 521, 566, 594, 806, 954, 1140, 1244, 1396, 1444, 1806, 3001	498.12133, 2696.46034, 2876.23991
TS4	249 <i>i</i> , 50, 95, 124, 241, 292, 399, 519, 563, 572, 708, 969, 1129, 1228, 1292, 1374, 2147, 2982	279.73662, 4019.77453, 4202.62594
TS5	468 <i>i</i> , 52, 75, 184, 185, 247, 404, 568, 661, 736, 902, 973, 1115, 1193, 1332, 1347, 2032, 3178	783.36783, 1641.27083, 2166.48013
TS6	378 <i>i</i> , 71, 88, 108, 149, 235, 314, 388, 476, 536, 718, 751, 815, 954, 1337, 1415, 3191, 3347	478.43013, 2156.75330, 2370.38280
TS7	461 <i>i</i> , 40, 47, 99, 163, 219, 324, 381, 520, 715, 744, 904, 949, 1003, 1139, 1429, 3198, 3349	676.97653, 2029.10569, 2522.44289
TS8	209 <i>i</i> , 67, 95, 106, 182, 215, 308, 422, 449, 612, 82, 989, 1019, 1153, 1390, 1483, 2974, 3079	639.58709, 1796.28437, 2248.64893
TS9	228 <i>i</i> , 83, 90, 137, 163, 231, 336, 420, 449, 650, 783, 954, 985, 1133, 1366, 1443, 2901, 3056	690.85400, 1505.06242, 2108.78814
TS10	517 <i>i</i> , 30, 89, 136, 156, 202, 369, 411, 443, 696, 745, 827, 954, 1077, 1402, 1431, 3154, 3295	454.35434, 2348.75974, 2653.67789
TS11	309 <i>i</i> , 73, 114, 165, 302, 374, 443, 489, 570, 801, 865, 1036, 1103, 1170, 1271, 1361, 2211, 3009	291.40957, 2634.19462, 2779.01083
TS12	261 <i>i</i> , 36, 113, 135, 203, 220, 295, 452, 460, 736, 913, 1059, 1100, 1194, 1347, 1504, 3017, 3103	492.27827, 1915.38624, 2256.13553
TS13	699 <i>i</i> , 58, 84, 92, 161, 199, 213, 306, 452, 680, 737, 901, 1022, 1152, 1327, 1362, 3103, 3279	842.86432, 1873.37706, 2625.30290
TS14	237 <i>i</i> , 48, 72, 85, 112, 141, 185, 279, 297, 666, 733, 769, 816, 960, 1414, 1427, 3181, 3335	560.31698, 2082.33153, 2564.22175
T-TS1	163 <i>i</i> , 27, 44, 44, 51, 72, 95, 108, 266, 450, 580, 710, 807, 940, 1392, 1509, 3173, 3333	724.37033, 2991.18471, 3702.54658
T-TS2	837 <i>i</i> , 29, 44, 65, 96, 215, 289, 320, 466, 572, 783, 827, 1071, 1172, 1243, 1395, 3020, 3106	330.56714, 3526.64117, 3760.05338
T-TS3	837 <i>i</i> , 29, 44, 65, 96, 215, 289, 320, 466, 572, 783, 827, 1071, 1172, 1243, 1395, 3020, 3106	330.56714, 3526.64117, 3760.05338

T-TS4	644 <i>i</i> , 19, 60, 87, 121, 231, 311, 353, 360, 591, 755, 876, 990, 1225, 1273, 1417, 3091, 3171	740.18184, 2140.79054, 2586.76730
T-h-TS1	1601 <i>i</i> , 40, 59, 89, 122, 233, 292, 443, 521, 701, 743, 921, 1015, 1056, 1079, 1292, 1396, 3150	915.50259, 1674.59292, 2295.56320