Photo-oxidation reaction of *tert*-butyl chloride with OH radicals and Cl atoms in the troposphere and its implications

Fredy Joy[a] and Balla Rajakumar[a,b]*

[a]Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India

[b]Centre for Atmospheric and Climate Sciences, Indian Institute of Technology Madras, Chennai-600036, India

*Corresponding Email: rajakumar@iitm.ac.in

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Table S1: <S2> values for all stationary points optimized at the M062-X/6-31+G(d,p) level for the reaction of TBC with OH radicals.

Species	Before Annihilation	After Annihilation
TBC	0.0	0.0
OH	0.7528	0.7500
RCg	0.7530	0.7500
RCa	0.7531	0.7500
TSg	0.7590	0.7500
TSa	0.7590	0.7500
PCg	0.7565	0.7500
PCa	0.7562	0.7500
P1	0.7564	0.7500
H_2O	0.0	0.0

Table S2: <S2> values for all stationary points optimized at the MP2/6-311+G(d,p) level for the reaction of TBC with Cl atoms.

Species	Before Annihilation	After Annihilation
TBC	0.0	0.0
Cl	0.7552	0.7500
RCg	0.7563	0.7500
RCa	0.7555	0.7500
TSg	0.7825	0.7505
TSa	0.7844	0.7506
PCg	0.7656	0.7502
PCa	0.7650	0.7502
P1	0.7652	0.7502
HCl	0.0	0.0

Table S3: T1-diagnostic values for all the stationary points involved in the reaction of TBC with OH radicals evaluated at the CCSD(T)/aug-cc-pVTZ//M062-X/6-31+G(d,p) level.

Species	T1-diagnostic

TBC	0.009
OH	0.007
RCg	0.010
RCa	0.009
TSg	0.017
TSa	0.017
PCg	0.012
PCa	0.012
P1	0.012
H_2O	0.010

Table S4: T1-diagnostic values for all the stationary points involved in the reaction of TBC with Cl atoms evaluated at the CCSD(T)/cc-pVDZ//MP2/6-311+G(d,p) level.

Species	**T1-diagnostic**
TBC	0.008
Cl	0.004
RCg	0.009
RCa	0.015
TSg	0.011
TSa	0.012
PCg	0.009
PCa	0.010
P1	0.010
HCl	0.004

Table S5: Values of k_d obtained from 268 – 363 K.

Temperature (K)	**k_d (s^{-1})**
268	144.3
283	97.7
298	164.9
323	183.0

343	330.6
363	273.3

Table S6: Pseudo-1st-order rate coefficients for the reaction of TBC with OH radicals measured from 268 – 363 K at various concentrations of TBC.

268 K		**283 K**		**298 K**	
[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})	[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})	[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})
0	(82.2 ± 13.0)	0	(95.6 ± 9.4)	0	(177.7 ± 8.1)
3.78	(372.5 ± 13.2)	3.84	(275.9 ± 12.0)	3.76	(353.5 ± 14.2)
7.54	(533.4 ± 31.8)	7.50	(485.1 ± 31.6)	7.49	(557.3 ± 12.9)
11.28	(708.9 ± 40.0)	11.44	(649.8 ± 53.8)	11.20	(743.3 ± 27.6)
14.99	(838.5 ± 64.6)	15.21	(856.9 ± 38.0)	14.90	(940.3 ± 32.6)
18.68	(1015.5 ± 98.4)	18.68	(1018.1 ± 98.8)	18.96	(1175.2 ± 56.6)
323 K		**343 K**		**363 K**	
[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})	[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})	[TBC] × 10^{14} (molecule cm^{-3})	k' (s^{-1})
0	(178.4 ± 15.6)	0	(323.4 ± 9.8)	0	(272.8 ± 21.0)
3.74	(381.6 ± 21.4)	4.24	(649.9 ± 13.1)	4.18	(472.0 ± 19.4)
7.60	(609.6 ± 25.0)	8.67	(733.1 ± 14.5)	8.34	(765.6 ± 34.8)
11.61	(807.9 ± 21.2)	12.97	(968.2 ± 44.5)	12.47	(991.0 ± 46.4)
15.12	(956.4 ± 59.4)	17.24	(1237.4 ± 48.0)	16.62	(1131.4 ± 91.4)
18.84	(1208.7 ± 97.0)	21.07	(1529.3 ± 29.3)	20.66	(1420.8 ± 122.2)

Table S7: Optimized geometries in Cartesian Coordinates for the reactants, reactant complexes, transition states, product complexes, and products of the reaction of TBC with OH radicals computed at the M06-2X/6-31+G(d,p) level of theory.

TBC				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.811023000	1.274834000	-0.699260000
2	6	0.355567000	-0.000006000	-0.000003000
3	6	0.810642000	-1.243215000	-0.754268000
4	6	0.810363000	-0.031835000	1.453819000
5	1	0.446403000	2.159929000	-0.172068000
6	1	0.446440000	1.306180000	-1.729021000
7	1	1.906304000	1.304159000	-0.715303000
8	1	0.446041000	-1.229302000	-1.784389000
9	1	0.445694000	-2.150427000	-0.266365000
10	1	1.905904000	-1.272212000	-0.771587000
11	1	0.445476000	-0.930885000	1.956650000
12	1	0.445481000	0.844301000	1.995617000
13	1	1.905622000	-0.032592000	1.487729000
14	17	-1.477584000	0.000128000	-0.000176000

OH				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	8	0.000000000	0.000000000	0.108401000
2	1	0.000000000	0.000000000	-0.867207000

RCg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.120189000	-1.046723000	-1.189419000
2	6	-0.664895000	-0.269995000	0.001612000
3	6	-2.161575000	-0.020445000	-0.127241000
4	6	-0.314815000	-0.943239000	1.321494000
5	1	0.958025000	-1.211407000	-1.100072000

6	1	-0.320777000	-0.520878000	-2.126032000
7	1	-0.611351000	-2.025365000	-1.225831000
8	1	-2.393143000	0.499780000	-1.059890000
9	1	-2.531850000	0.576513000	0.709753000
10	1	-2.682793000	-0.983930000	-0.126111000
11	1	-0.667628000	-0.349585000	2.168460000
12	1	0.764337000	-1.091212000	1.412577000
13	1	-0.802904000	-1.923565000	1.355951000
14	17	0.146534000	1.388798000	-0.003623000
15	8	2.868052000	-0.418351000	-0.008148000
16	1	2.421433000	0.449294000	0.079295000

RCa				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.576953000	-0.058248000	-1.167721000
2	6	0.340535000	0.303298000	-0.006136000
3	6	0.979433000	1.671295000	-0.209337000
4	6	-0.390020000	0.219148000	1.327106000
5	1	-0.996677000	-1.058604000	-1.024961000
6	1	-0.035508000	-0.038814000	-2.117155000
7	1	-1.393962000	0.671996000	-1.213100000
8	1	1.530324000	1.709782000	-1.152527000
9	1	1.667681000	1.903225000	0.607161000
10	1	0.193323000	2.434178000	-0.230663000
11	1	0.287980000	0.443999000	2.154370000
12	1	-0.815693000	-0.775810000	1.477752000
13	1	-1.211611000	0.943567000	1.332809000
14	17	1.693199000	-0.933636000	0.023068000
15	8	-3.313884000	-0.303927000	0.103128000
16	1	-3.617147000	-0.743244000	-0.714342000

TSg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.446600000	-0.964269000	-0.951376000
2	6	-0.543846000	-0.324997000	0.000012000
3	6	-1.974806000	-0.509584000	-0.497539000
4	6	-0.369285000	-0.836971000	1.423831000
5	1	1.557169000	-0.761247000	-0.560351000
6	1	0.401170000	-0.557651000	-1.963358000
7	1	0.355773000	-2.054813000	-0.952729000
8	1	-2.096736000	-0.099420000	-1.502760000
9	1	-2.680095000	-0.012522000	0.173394000
10	1	-2.210047000	-1.578897000	-0.522630000
11	1	-1.057029000	-0.328576000	2.103632000
12	1	0.656465000	-0.685360000	1.767459000
13	1	-0.587746000	-1.910341000	1.443748000
14	17	-0.204172000	1.480388000	0.011141000
15	8	2.674679000	-0.254714000	-0.009489000
16	1	2.382595000	0.674870000	0.050543000

TSa				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.616820000	-1.117513000	0.038021000
2	6	-0.215462000	0.148723000	-0.003387000
3	6	0.018829000	1.006019000	1.232508000
4	6	0.026335000	0.930174000	-1.287148000
5	1	0.491437000	-1.742609000	-0.848431000
6	1	0.479957000	-1.691900000	0.956500000
7	1	1.724008000	-0.733113000	0.038640000
8	1	-0.199821000	0.444249000	2.144119000

9	1	-0.614469000	1.896053000	1.209157000
10	1	1.069423000	1.314502000	1.252246000
11	1	-0.606614000	1.820143000	-1.320549000
12	1	-0.188106000	0.314834000	-2.164588000
13	1	1.077277000	1.236199000	-1.319182000
14	17	-1.969810000	-0.392728000	0.007432000
15	8	3.004372000	-0.130614000	0.013491000
16	1	3.539564000	-0.941480000	-0.062143000

PCg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.133693000	-0.927719000	1.279517000
2	6	0.707232000	-0.352415000	0.054111000
3	6	2.216199000	-0.171947000	0.125481000
4	6	0.259956000	-1.077413000	-1.206835000
5	1	-2.244997000	0.458872000	0.049022000
6	1	0.608576000	-0.735085000	2.234768000
7	1	-0.860404000	-1.359178000	1.255200000
8	1	2.500592000	0.403758000	1.009349000
9	1	2.588041000	0.341220000	-0.764299000
10	1	2.684547000	-1.160324000	0.184022000
11	1	0.614202000	-0.554975000	-2.098764000
12	1	-0.828768000	-1.161331000	-1.241253000
13	1	0.689642000	-2.085221000	-1.195901000
14	17	0.000438000	1.417315000	-0.081649000
15	8	-2.748571000	-0.367183000	0.061924000
16	1	-3.672791000	-0.127663000	-0.053144000

PCa				
Centre number	Atomic number	Coordinates		
		X	Y	Z

1	6	-0.265691000	0.000282000	1.366432000
2	6	0.234904000	-0.000002000	-0.025696000
3	6	-0.144145000	-1.262854000	-0.786387000
4	6	-0.144109000	1.262561000	-0.786884000
5	1	-0.296778000	0.932239000	1.921017000
6	1	-0.297038000	-0.931490000	1.921312000
7	1	-2.713813000	0.000474000	0.892223000
8	1	0.168039000	-2.155947000	-0.238970000
9	1	0.333035000	-1.271827000	-1.769209000
10	1	-1.231354000	-1.277472000	-0.915117000
11	1	0.333116000	1.271159000	-1.769687000
12	1	0.168051000	2.155865000	-0.239798000
13	1	-1.231312000	1.277126000	-0.915670000
14	17	2.104627000	0.000010000	0.128453000
15	8	-3.127235000	-0.000062000	0.020012000
16	1	-4.078468000	0.000270000	0.165308000

P1				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.727103000	0.000000000	1.505146000
2	6	0.407165000	0.000000000	0.065288000
3	6	0.883360000	1.263900000	-0.638591000
4	6	0.883360000	-1.263900000	-0.638591000
5	1	0.727976000	-0.932219000	2.057677000
6	1	0.727976000	0.932219000	2.057677000
7	1	0.490281000	2.155805000	-0.145055000
8	1	0.559352000	1.269602000	-1.681900000
9	1	1.977667000	1.297806000	-0.607536000
10	1	0.559352000	-1.269602000	-1.681900000
11	1	0.490281000	-2.155805000	-0.145055000

12	1	1.977667000	-1.297806000	-0.607536000
13	17	-1.465675000	0.000000000	-0.059170000

H_2O				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	1	0.000000000	0.768653000	-0.462418000
2	8	0.000000000	0.000000000	0.115605000
3	1	0.000000000	-0.768653000	-0.462418000

Table S8: Vibrational frequencies of the reactants, reactant complexes, transition states, product complexes, and products of the reaction of TBC with OH radicals computed at the M06-2X/6-31+G(d,p) level of theory. i denotes imaginary frequency and frequencies treated as hindered rotors are shown in bold.

TBC	**OH**	**RCg**	**RCa**	**TSg**	**TSa**	**PCg**	**PCa**	**P1**	**H_2O**
236.1	3781.5	57.5	35.2	1110.5i	774.0i	62.2	77.7	241.3	1598.5
296.1		78.6	73.1	**86.8**	60.1	94.9	93.2	265.1	3882.5
297.5		119.8	94.6	117.5	**80.5**	107.7	124.4	281.6	4007.2
306.3		229.5	106.2	**248.8**	83.9	134.4	134.6	295.1	
306.5		274.6	224.3	277.4	**251.5**	246.8	150.7	302.2	
379.3		285.5	248.3	**288.7**	272.1	258.2	199.4	360.7	
412.4		297.2	297.9	294.8	**298.3**	282.1	277.4	407.3	
412.6		303.5	304.9	309.9	301.1	293.1	295.0	412.8	
594.5		309.4	310.9	362.9	367.4	296.5	306.1	519.9	
842.5		318.5	324.0	376.2	379.9	314.1	310.2	629.5	
947.7		379.5	380.7	412.1	408.8	350.6	335.1	829.8	
947.8		410.7	414.1	431.0	417.0	358.5	371.4	937.2	
974.6		418.1	415.4	583.5	580.6	406.7	408.1	968.5	
1056.5		577.7	591.9	768.4	707.7	424.2	413.6	1017.2	
1056.9		837.3	843.0	843.6	840.0	476.2	535.0	1044.5	
1191.2		947.1	946.8	917.7	948.7	664.8	686.9	1126.0	

1277.2		948.2	951.6	947.0	966.2	823.2	828.1	1281.2	
1277.5		976.6	976.2	959.4	976.0	944.3	941.7	1306.8	
1410.2		1056.8	1056.9	992.8	1024.7	978.0	973.9	1410.1	
1410.5		1058.5	1060.5	1052.8	1057.6	1024.1	1020.5	1424.4	
1436.6		1184.8	1191.5	1088.0	1144.5	1046.9	1053.8	1473.2	
1476.0		1278.0	1276.0	1200.3	1266.8	1121.9	1135.9	1484.2	
1490.3		1279.5	1278.2	1253.4	1274.0	1289.7	1283.2	1489.8	
1490.8		1412.0	1407.7	1278.8	1321.0	1314.4	1304.9	1503.2	
1504.7		1413.7	1411.7	1322.1	1329.3	1411.6	1412.9	1514.0	
1504.8		1439.2	1436.8	1408.3	1371.6	1426.9	1427.8	3070.3	
1523.1		1475.1	1475.1	1423.6	1413.4	1477.4	1469.4	3074.1	
3066.8		1485.1	1488.2	1435.9	1429.2	1486.4	1487.7	3151.0	
3066.9		1491.4	1489.8	1458.8	1472.6	1491.4	1496.4	3154.2	
3073.2		1504.8	1502.1	1488.2	1488.6	1504.9	1511.8	3170.5	
3146.0		1505.7	1509.1	1490.6	1490.4	1518.2	1516.5	3172.5	
3146.1		1520.7	1521.4	1504.1	1507.3	1605.1	1590.4	3187.5	
3151.8		3064.6	3057.7	1513.7	1517.6	3068.7	3072.7	3299.5	
3165.7		3068.4	3067.8	3069.6	3071.7	3073.5	3076.1		
3168.5		3073.6	3074.0	3073.2	3075.1	3149.0	3159.0		
3168.7		3141.3	3133.0	3102.9	3116.7	3153.6	3161.8		
		3147.9	3147.3	3150.1	3154.8	3172.3	3166.3		
		3152.5	3153.2	3153.9	3157.8	3176.4	3168.8		
		3162.9	3157.1	3169.4	3167.1	3184.0	3173.2		
		3168.4	3166.5	3176.8	3169.6	3301.1	3284.3		
		3169.9	3169.7	3186.6	3193.6	3823.5	3846.1		
		3715.6	3769.8	3763.7	3792.9	3977.6	3982.5		

Table S9: Optimized geometries in Cartesian Coordinates for the reactants, reactant complexes, transition states, product complexes, and products of the reaction of TBC with Cl atoms computed at the MP2/6-311+G(d,p) level of theory.

TBC		
Centre	Atomic	Coordinates

number	number	X	Y	Z
1	6	-0.805613000	-1.266398000	0.710750000
2	6	-0.345224000	0.000000000	0.000001000
3	6	-0.805617000	0.017670000	-1.452106000
4	6	-0.805616000	1.248726000	0.741357000
5	1	-0.439595000	-1.287290000	1.740725000
6	1	-0.439605000	-2.156467000	0.192032000
7	1	-1.901208000	-1.294424000	0.726486000
8	1	-0.439617000	-0.863880000	-1.985179000
9	1	-0.439593000	0.911916000	-1.963579000
10	1	-1.901212000	0.018076000	-1.484242000
11	1	-0.439606000	2.151155000	0.244454000
12	1	-0.439602000	1.244547000	1.771536000
13	1	-1.901211000	1.276361000	0.757766000
14	17	1.465510000	0.000001000	-0.000001000

RCg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.857151000	-1.020296000	-1.258051000
2	6	-1.150704000	-0.213892000	0.000010000
3	6	-2.578394000	0.317043000	-0.000021000
4	6	-0.857157000	-1.020270000	1.258080000
5	1	0.177222000	-1.372301000	-1.263226000
6	1	-1.027714000	-0.417640000	-2.154011000
7	1	-1.523426000	-1.889863000	-1.288083000
8	1	-2.766359000	0.925774000	-0.888314000
9	1	-2.766423000	0.925739000	0.888285000
10	1	-3.274840000	-0.529012000	-0.000057000
11	1	-1.027559000	-0.417577000	2.154046000
12	1	0.177204000	-1.372325000	1.263156000
13	1	-1.523439000	-1.889826000	1.288196000

14	17	-0.044781000	1.227776000	0.000001000
15	17	2.763356000	-0.188863000	-0.000007000

RCa				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.364305000	-1.249764000	-0.704892000
2	6	-0.852524000	-0.000203000	0.016915000
3	6	-0.447146000	-0.017598000	1.485305000
4	6	-0.364278000	1.266088000	-0.675118000
5	1	-0.686229000	-1.243763000	-1.749687000
6	1	-0.754790000	-2.151068000	-0.224969000
7	1	0.729998000	-1.280461000	-0.671627000
8	1	-0.832303000	-0.911567000	1.982923000
9	1	-0.832316000	0.864322000	2.003964000
10	1	0.646080000	-0.018432000	1.555928000
11	1	-0.754672000	2.155794000	-0.173956000
12	1	-0.686263000	1.284860000	-1.719743000
13	1	0.730027000	1.295926000	-0.641228000
14	17	-2.663042000	0.000634000	-0.052316000
15	17	3.522452000	0.000146000	-0.012088000

TSg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.147017000	-0.776739000	-0.984963000
2	6	-0.902835000	-0.340765000	-0.000186000
3	6	-2.271172000	-0.838134000	-0.480447000
4	6	-0.606323000	-0.830949000	1.412802000
5	1	1.373313000	-0.337861000	-0.505351000
6	1	0.132908000	-0.284977000	-1.956918000
7	1	0.328741000	-1.852281000	-1.015305000

8	1	-2.493409000	-0.464338000	-1.482881000
9	1	-3.047654000	-0.486513000	0.204760000
10	1	-2.280901000	-1.933159000	-0.494347000
11	1	-1.405171000	-0.519406000	2.090159000
12	1	0.341523000	-0.428556000	1.774920000
13	1	-0.549883000	-1.925276000	1.413087000
14	17	-0.946976000	1.460572000	0.018138000
15	17	2.676412000	0.007186000	-0.001159000

TSa				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.198355000	-1.065419000	-0.000075000
2	6	-0.645942000	0.177339000	0.000001000
3	6	-0.455903000	1.006346000	1.261873000
4	6	-0.455936000	1.006475000	-1.261790000
5	1	0.184170000	-1.652755000	-0.918087000
6	1	0.184154000	-1.652878000	0.917856000
7	1	1.497367000	-0.616470000	-0.000031000
8	1	-0.622113000	0.398774000	2.155207000
9	1	-1.159025000	1.842676000	1.271014000
10	1	0.564738000	1.401185000	1.285243000
11	1	-1.158981000	1.842872000	-1.270774000
12	1	-0.622278000	0.399024000	-2.155181000
13	1	0.564740000	1.401224000	-1.285201000
14	17	-2.351823000	-0.463993000	-0.000005000
15	17	2.864987000	-0.130836000	-0.000001000

PCg				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.714846000	-0.917898000	-1.318722000

2	6	-1.211864000	-0.323045000	-0.056914000
3	6	-2.715634000	-0.083143000	-0.084014000
4	6	-0.782074000	-1.121165000	1.167055000
5	1	1.895264000	0.563298000	0.003927000
6	1	-1.168675000	-0.634419000	-2.261155000
7	1	0.228302000	-1.451313000	-1.331546000
8	1	-2.995279000	0.530817000	-0.943705000
9	1	-3.040496000	0.421503000	0.829361000
10	1	-3.227851000	-1.048348000	-0.157658000
11	1	-1.088249000	-0.612273000	2.084459000
12	1	0.301048000	-1.261750000	1.184992000
13	1	-1.260895000	-2.105615000	1.131588000
14	17	-0.428566000	1.351465000	0.093465000
15	17	2.952292000	-0.159135000	-0.021976000

PCa				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	-0.082160000	0.001599000	-1.230106000
2	6	-0.767466000	-0.000143000	0.088414000
3	6	-0.480773000	-1.263497000	0.890035000
4	6	-0.480657000	1.261019000	0.893438000
5	1	-0.000194000	0.933554000	-1.780832000
6	1	-0.000235000	-0.928889000	-1.783314000
7	1	2.084138000	0.000854000	-0.660919000
8	1	-0.721183000	-2.155877000	0.306603000
9	1	-1.076662000	-1.273502000	1.805995000
10	1	0.579847000	-1.290280000	1.160993000
11	1	-1.076567000	1.268621000	1.809407000
12	1	-0.720961000	2.154992000	0.312404000
13	1	0.579959000	1.286962000	1.164492000
14	17	-2.562474000	0.000464000	-0.297366000

15	17	3.222368000	0.000106000	-0.066488000

P1				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	6	0.713290000	0.000000000	1.510301000
2	6	0.389063000	0.000000000	0.063645000
3	6	0.879745000	1.261882000	-0.635028000
4	6	0.879745000	-1.261882000	-0.635028000
5	1	0.694660000	-0.932009000	2.063475000
6	1	0.694660000	0.932009000	2.063475000
7	1	0.481665000	2.154359000	-0.145699000
8	1	0.564736000	1.266623000	-1.681618000
9	1	1.973873000	1.293624000	-0.593034000
10	1	0.564736000	-1.266623000	-1.681618000
11	1	0.481665000	-2.154359000	-0.145699000
12	1	1.973873000	-1.293624000	-0.593034000
13	17	-1.447113000	0.000000000	-0.065270000

HCl				
Centre number	Atomic number	Coordinates		
		X	Y	Z
1	1	0.000000000	0.000000000	-1.202131000
2	17	0.000000000	0.000000000	0.070714000

Table S10: Vibrational frequencies of the reactants, reactant complexes, transition states, product complexes, and products of the reaction of TBC with Cl atoms computed at the MP2/6-311+G(d,p) level of theory. i denotes imaginary frequency and frequencies treated as hindered rotors are shown in bold.

TBC	**RCg**	**RCa**	**TSg**	**TSa**	**PCg**	**PCa**	**P1**	**HCl**
235.7	33.6	18.9	1121.2i	1069.2i	34.6	36.7	222.9	3089.2

301.2	57.6	26.1	56.4	66.1	52.7	51.4	269.3	
301.2	69.8	48.3	94.2	96.2	82.6	72.4	280.7	
310.1	227.5	229.6	**243.7**	233.4	218.9	225.3	307.1	
310.1	290.7	268.1	272.0	**246.1**	264.9	266.9	307.8	
380.3	297.4	296.9	**295.1**	**291.2**	283.5	289.6	365.0	
409.8	309.4	307.3	308.0	303.2	291.4	300.0	405.6	
409.8	310.6	307.5	361.5	360.7	306.5	303.5	411.4	
620.9	379.7	379.8	386.9	399.3	306.9	341.2	582.7	
858.6	408.8	404.5	**403.4**	403.6	352.1	348.8	641.9	
955.6	411.4	409.4	420.0	**437.2**	366.8	372.2	847.5	
955.6	613.2	619.1	526.5	528.0	405.2	405.3	946.2	
980.5	854.7	858.1	626.8	625.2	414.2	412.1	976.0	
1066.1	955.2	946.9	861.3	844.8	562.3	600.1	1024.6	
1066.1	955.9	954.6	886.7	880.6	633.3	734.7	1053.9	
1209.8	981.2	980.4	930.6	937.7	842.8	846.2	1146.1	
1282.5	1066.0	1051.8	963.5	970.2	947.6	946.1	1286.6	
1282.5	1066.0	1065.8	971.0	999.3	977.5	976.6	1308.8	
1414.7	1206.0	1210.2	1019.8	1031.4	1025.1	1025.3	1414.7	
1414.7	1283.4	1278.5	1061.0	1063.2	1053.9	1056.5	1430.2	
1442.1	1283.6	1282.8	1164.1	1145.8	1142.2	1148.4	1486.8	
1483.8	1415.1	1412.4	1205.5	1211.2	1289.4	1288.1	1492.3	
1493.5	1415.5	1413.2	1251.8	1294.4	1310.7	1305.2	1496.3	
1493.5	1442.8	1440.3	1281.8	1298.4	1416.5	1417.5	1510.5	
1512.6	1482.7	1449.1	1408.6	1418.6	1432.2	1433.4	1519.8	
1512.6	1493.6	1486.2	1429.3	1434.3	1489.4	1483.1	3069.6	
1524.7	1493.9	1492.2	1469.9	1474.5	1493.0	1491.9	3072.9	
3065.1	1511.7	1495.6	1490.7	1492.2	1496.1	1497.2	3161.1	
3065.1	1512.7	1509.2	1493.5	1496.6	1510.7	1512.8	3164.7	
3070.6	1525.3	1523.9	1508.9	1513.2	1520.9	1519.0	3176.9	
3154.9	3067.3	3068.3	1517.3	1519.3	2981.8	2913.0	3179.3	
3154.9	3068.0	3069.7	3069.2	3075.0	3072.0	3072.7	3191.4	
3160.9	3073.1	3074.1	3074.1	3077.9	3075.3	3075.7	3311.5	

3171.5	3157.2	3159.2	3132.1	3138.4	3163.1	3165.1		
3175.2	3157.7	3160.4	3162.2	3169.0	3166.8	3168.4		
3175.2	3163.3	3166.3	3166.5	3172.3	3179.4	3175.8		
	3175.0	3171.2	3177.6	3178.4	3184.1	3177.9		
	3178.8	3174.7	3190.7	3181.1	3194.6	3180.4		
	3180.7	3174.7	3240.7	3244.2	3316.4	3295.1		

Table S11: Kinetic branching ratios (Γ) for the reaction of TBC with OH radicals.

T(K)	**Γ_{TSg} (%)**	**Γ_{TSa} (%)**
200	38.18	61.82
225	34.25	65.75
250	31.28	68.72
275	28.78	71.22
298	27.01	72.99
300	26.83	73.17
325	25.28	74.72
350	23.96	76.04
375	22.74	77.26
400	21.90	78.10

Table S12: Kinetic branching ratios (Γ) for the reaction of TBC with Cl atoms.

T(K)	**Γ_{TSg} (%)**	**Γ_{TSa} (%)**
200	42.71	57.29
225	45.10	54.90
250	47.11	52.89
275	48.78	51.22
298	50.10	49.90
300	50.20	49.80
325	51.27	48.73
350	52.46	47.54
375	53.33	46.67

400	54.10	45.90

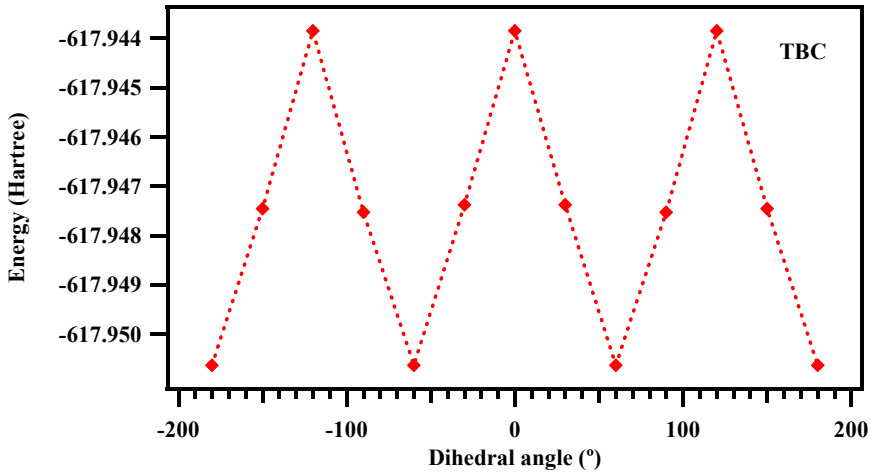


Figure S1: Tortional scan of TBC for identifying conformers.

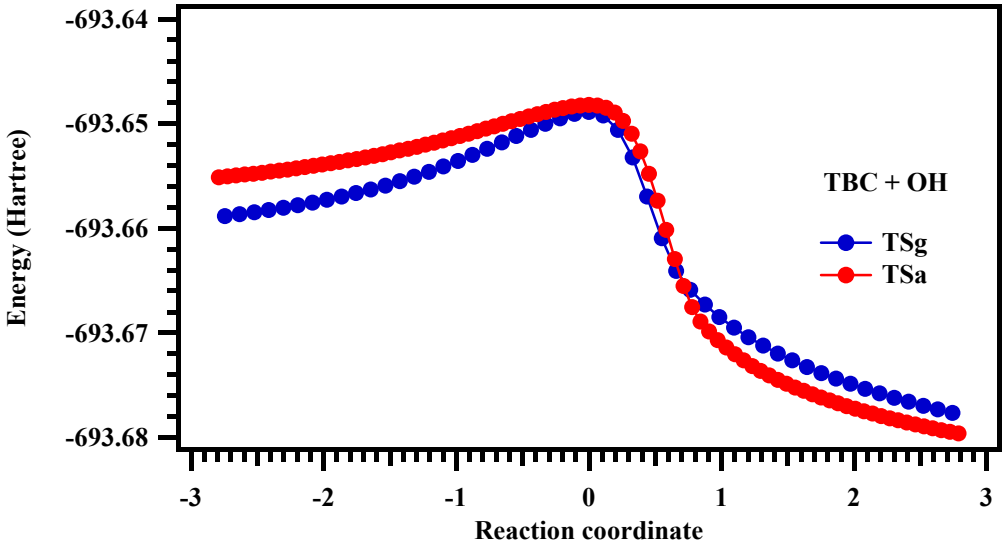


Figure S2: IRC plots for the reaction of TBC with OH radicals at the M06-2X/6-31+G(d,p) level of theory.

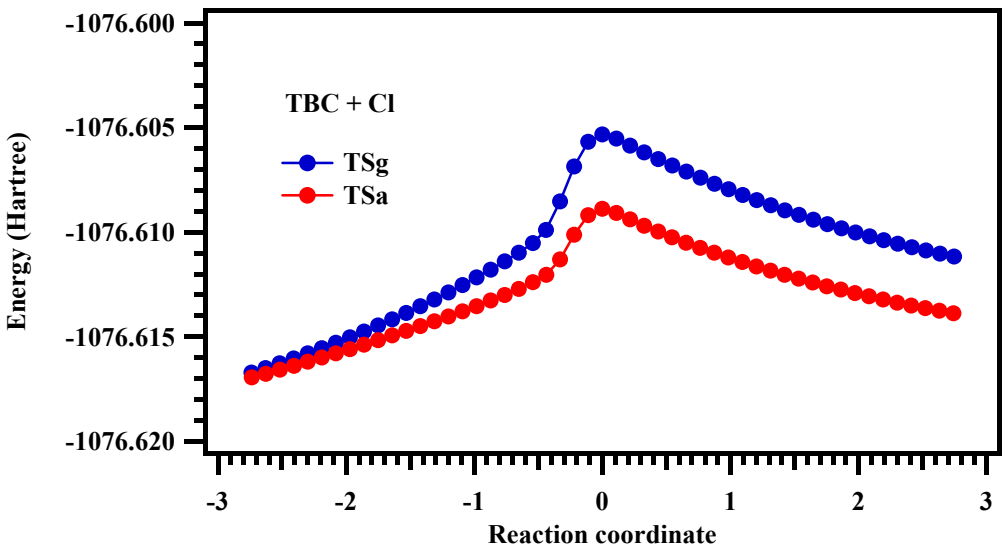
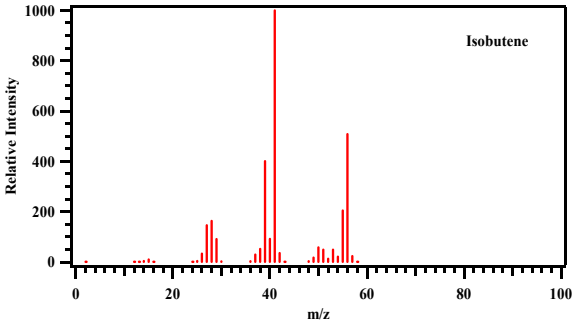
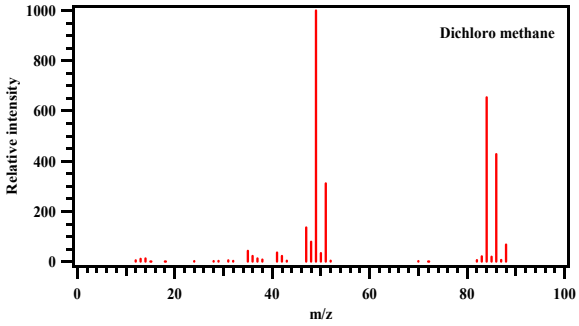
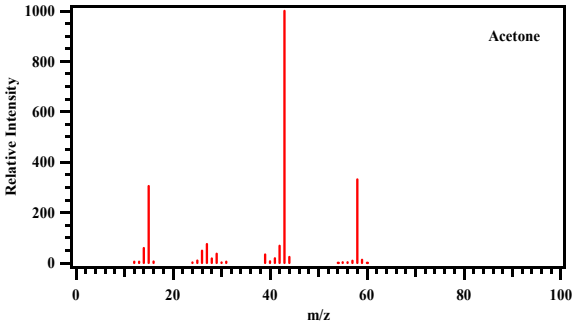
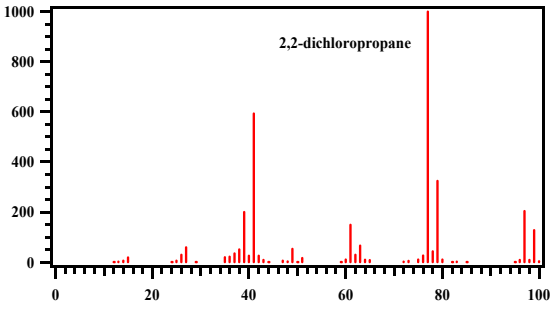


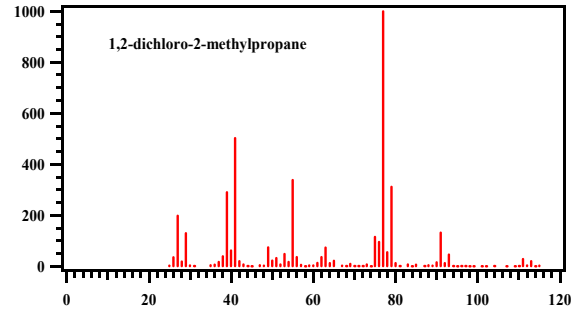
Figure S3: IRC plots for the reaction of TBC with Cl atoms at the MP2/6-311+G(d,p) level of theory.

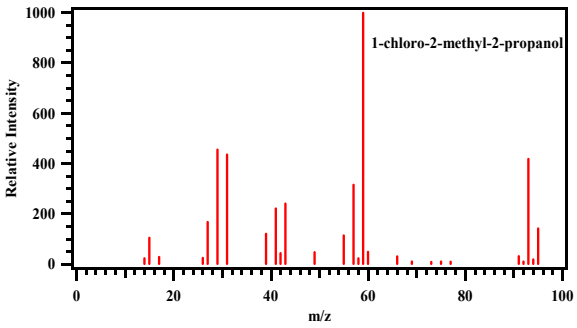

Isobutene
Relative Intensity
m/z

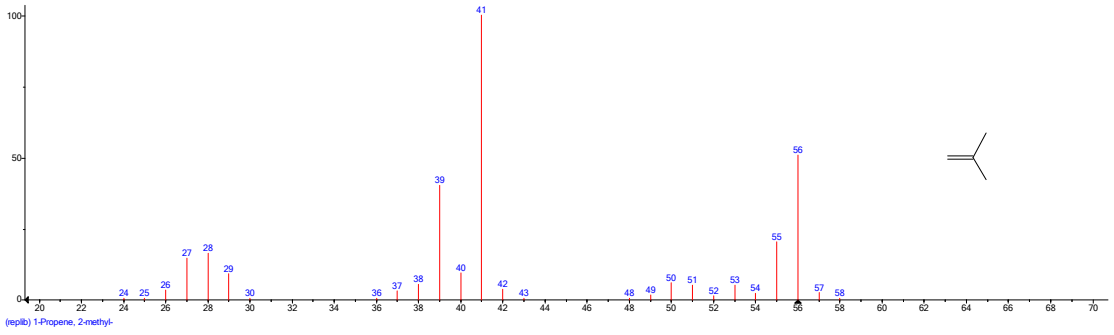

Dichloro methane
Relative intensity
m/z

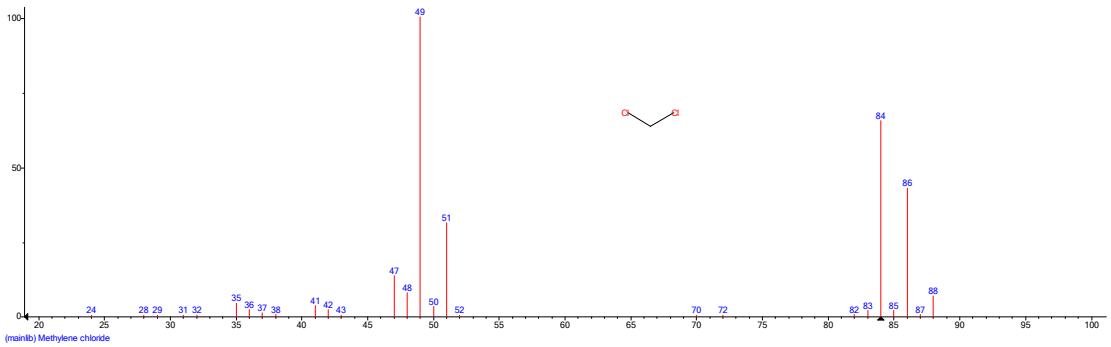

Acetone
Relative Intensity
m/z


2,2-dichloropropane


1,2-dichloro-2-methylpropane


1-chloro-2-methyl-2-propanol
Relative Intensity
m/z


(replib) 1-Propene, 2-methyl-


(mainlib) Methylene chloride

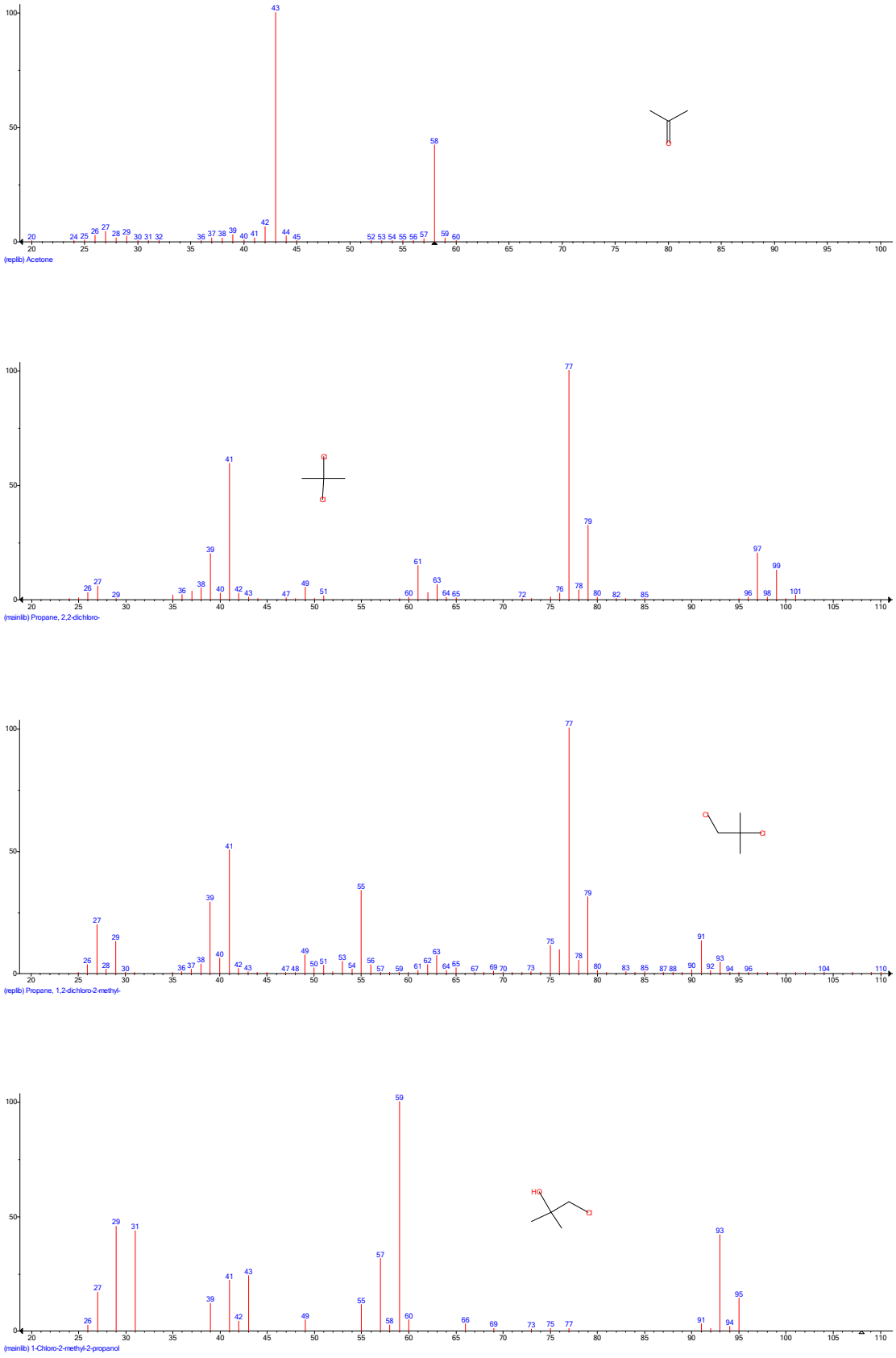


Figure S4: Mass spectra for all the detected products produced in the presence of O_2.