Kinetics and mechanism of the oxidation of cyclic methylsiloxanes by hydroxyl radical in the gas phase: An experimental and theoretical study

Supporting Information

Ruiyang Xiao[†,‡,*], *Ian Zammit*[⊥], *Zongsu Wei*[#], *Wei-Ping Hu*[‖], *Matthew MacLeod*[⊥], *and* Richard *Spinney*[§,*]

[†]Institute of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha, China, 410083

[‡]Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha, China, 410083

[⊥]Department of Environmental Science and Analytical Chemistry, Stockholm University, Svante Arrhenius väg 8, SE-11418 Stockholm

[#] Department of Civil, Environmental, and Geodetic Engineering and [§] Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States

[‖]Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi 62102, Taiwan

*To whom correspondence should be addressed. R.X. Phone: +86-731-88830511; fax: +86 731-88710171; e-mail address: xiao.53@csu.edu.cn; R.S. Phone: +1 614 247 6847; fax +1 614 292 1685; e-mail address: rspinney@chemistry.ohio-state.edu

Table of Contents

Table S1	Reaction pathway degeneracies for reactions of the cyclosiloxanes and •OH	S3
Table S2	Experimentally determined k values ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}) for the reactions of D_3, D_4, and D_5 with •OH at different temperatures (°C).	S4
Table S3	Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_3 conformer	S5
Table S4	Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_4 conformer	S6
Table S5	Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_5 conformer	S7
Table S6	Cartesian coordinates for TS species at H16 on D_3 molecule	S8
Table S7	Cartesian coordinates for TS species at H18 on D_3 molecule	S8
Table S8	Cartesian coordinates for TS species at H11 on D_4 molecule	S9
Table S9	Cartesian coordinates for TS species at H23 on D_4 molecule	S9
Table S10	Cartesian coordinates for TS species at H24 on D_4 molecule	S10
Table S11	Cartesian coordinates for TS species at H40 on D_4 molecule	S10
Table S12	Cartesian coordinates for TS species at H17 on D_5 molecule	S11
Table S13	Cartesian coordinates for TS species at H30 on D_5 molecule	S11
Table S14	Cartesian coordinates for TS species at H33 on D_5 molecule	S12
Table S15	Cartesian coordinates for TS species at H45 on D_5 molecule	S12
Table S16	Imaginary frequencies (cm^{-1}) for the reactions between different cyclic methylsiloxanes and •OH at the M06–2X/6–311++G** // M06–2X/6–31+G** level of theory at 298 K in gas phase.	S13
Table S17	The temperature-dependent free energy barriers (kcal mol^{-1}) for the D chemicals.	S14
Table S18	Identification of D_3 product fragments	S15
Figure S1	Geometry of D_3 was optimized at M06-2X/6-31+G** level of theory	S16
Figure S2	Geometry of D_4 was optimized at M06-2X/6-31+G** level of theory	S17
Figure S3	Geometry of D_5 was optimized at M06-2X/6-31+G** level of theory	S18
Figure S4	Calculated zero-point corrected Born-Oppenheimer energies of reaction and barrier heights (kcal mol^{-1}) of the first step of reactions between different cyclosiloxanes (a: D_3; b: D_4, and c: D_5) and •OH at the M06-2X/6-311++G**// M06-2X/6-31+G** level of theory.	S19
Figure S5	Example of PID run show increase in m/z 193 and m/z 237.	S20

Table S1: Reaction pathway degeneracy for reactions of the cyclosiloxanes and •OH.

chemical	axial pointing outward	axial pointing inward	equatorial side ways	equatorial up or down
D_3	12	6	—	—
D_4	12	6	4	2
D_5	10	6	10	4

Table S2: Experimentally determined k values ($\times 10^{12}$ cm^3 $molecule^{-1}$ s^{-1}) for the reactions of D_3, D_4, and D_5 with •OH at different temperatures (°C).

temperature	D_3	D_5	temperature	D_4
40	1.24	2.27	40	2.04
	1.42	2.86		1.80
	1.59	2.46	50	2.63
	1.37	2.35		2.05
50	1.50	3.01		2.23
	1.40	3.09	60	2.55
	1.44	2.83		2.48
	1.27	2.86		2.49
	1.06	2.44		2.57
60	1.02	2.82		2.46
	1.17	3.05		2.92
	1.04	3.02	70	2.59
	0.99	2.82		1.91
70	0.99	2.94	80	1.78
	0.98	3.02		2.37
	0.94	2.96		2.60
	1.02	3.23		2.27
80	0.99	3.17		1.83
	0.95	3.01		2.13
	0.78	2.72		2.29
	0.81	3.06	90	2.10
				2.51
	0.71	2.58		2.14
				1.91

Table S3: Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_3 conformer within 1.2 kcal mol^{-1} of the global minima with the MMFF method.

conformer #	$\varphi_{O1\text{-}Si5\text{-}O6\text{-}Si4}$	$\varphi_{Si5\text{-}O6\text{-}Si4\text{-}O2}$	$\varphi_{O6\text{-}Si4\text{-}O2\text{-}Si3}$	$\varphi_{Si4\text{-}O2\text{-}Si3\text{-}O1}$	relative E
1	-12.4	22.3	-30.1	25.4	0

Table S4: Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_4 conformers within 1.2 kcal mol^{-1} of the global minima with the MMFF method.

conformer #[a]	$\varphi_{O1\text{-}Si5\text{-}O4\text{-}Si8}$	$\varphi_{Si5\text{-}O4\text{-}Si8\text{-}O3}$	$\varphi_{O4\text{-}Si8\text{-}O3\text{-}Si6}$	$\varphi_{Si8\text{-}O3\text{-}Si6\text{-}O2}$	$\varphi_{O3\text{-}Si6\text{-}O2\text{-}Si7}$	relative E
1 (4)[b]	-81.2	45.3	45.3	-81.2	81.2	0.00
2 (6)	-62.3	62.3	44.7	-79.0	62.2	0.05
3 (2)	62.3	-62.3	79.0	-44.7	-62.3	0.19
4 (2)	53.8	-53.8	-54.0	53.9	54.0	0.98

[a]: the number of enantiomeric isomers is indicated in parenthesis
[b]: conformer used in this study

Table S5: Torsion angle φ (°) and relative conformational energy (kcal mol^{-1}) for D_5 conformers within 1.2 kcal mol^{-1} of the global minima with the MMFF method.

conformer #[a]	$\varphi_{Si1\text{-}O2\text{-}Si4\text{-}O6}$	$\varphi_{O2\text{-}Si4\text{-}O6\text{-}Si8}$	$\varphi_{Si4\text{-}O6\text{-}Si8\text{-}O10}$	$\varphi_{O6\text{-}Si8\text{-}O10\text{-}Si9}$	$\varphi_{Si8\text{-}O10\text{-}Si9\text{-}O7}$	$\varphi_{O10\text{-}Si9\text{-}O7\text{-}Si5}$	$\varphi_{Si9\text{-}O7\text{-}Si5\text{-}O3}$	relative E
1 (20)[b]	50.5	-171.8	160.7	-43.3	87.3	-53.3	-36.6	0.00
2 (16)	-123.8	80.8	-53.9	-67.9	134.3	-1.3	-69.7	0.38
3 (4)	77.1	77.0	-93.5	-56.3	129.2	-46.4	-46.5	0.48
4 (13)	-95.7	154.4	-102.9	54.0	-56.9	-69.4	151.3	0.60
5 (8)	166.7	-64.0	47.7	63.2	-131.1	131.1	-63.2	0.75
6 (5)	-137.5	84.9	-88.7	50.6	28.7	-155.2	96.9	0.83
7 (13)	176.6	45.6	-41.4	103.5	-153.8	41.5	53.8	1.06
8 (3)	48.1	-104.4	131.4	41.4	-97.0	62.0	-69.9	1.19

[a]: the number of enantiomeric isomers is indicated in parenthesis
[b]: conformer used in this study

Table S6: Cartesian coordinates for TS species at H16 on D_3 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	-1.82097	0.557924	-0.0861
O	0.798329	0.949328	-0.4318
Si	-0.63702	1.725884	-0.10472
Si	1.254305	-0.62872	-0.20525
Si	-1.73241	-1.08465	0.155702
O	-0.11375	-1.47217	0.216374
C	-2.51299	-1.52551	1.785473
H	-3.57374	-1.25736	1.795748
H	-2.42827	-2.59875	1.981196
H	-2.01845	-0.99095	2.602374
C	-2.53208	-1.94943	-1.28563
H	-2.48139	-3.0362	-1.16918
H	-3.58429	-1.66226	-1.37479
H	-2.02753	-1.68238	-2.21935
C	2.470474	-0.72105	1.209917
H	2.223596	-0.09191	2.068493
H	2.692864	-1.74116	1.532564
C	1.995018	-1.30673	-1.76527
H	2.898462	-0.74799	-2.02728
H	2.268896	-2.35868	-1.64053
H	1.285328	-1.23187	-2.5947
C	-0.99328	2.950763	-1.45374
H	-1.94564	3.459169	-1.27643
H	-0.20432	3.706843	-1.50812
H	-1.04999	2.44599	-2.42239
C	-0.5308	2.504469	1.586132
H	0.281096	3.236453	1.634435
H	-1.46564	3.008599	1.849173
H	-0.33923	1.735443	2.34261
O	4.761719	0.014071	0.330132
H	3.459134	-0.29085	0.740939
H	5.240005	-0.18562	1.154731

Table S7: Cartesian coordinates for TS species at H18 on D_3 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	-1.46474	0.770924	-0.22648
O	1.211516	0.735779	-0.18836
Si	-0.12387	1.745147	-0.17132
Si	1.351683	-0.89301	-0.53101
Si	-1.60902	-0.86948	0.033093
O	-0.16936	-1.54159	-0.47735
C	-1.82918	-1.19838	1.850622
H	-2.71679	-0.68774	2.237142
H	-1.94048	-2.27021	2.042857
H	-0.9533	-0.84454	2.406974
C	-2.98957	-1.52712	-1.01989
H	-3.07566	-2.61258	-0.91246
H	-3.94429	-1.07788	-0.73029
H	-2.80948	-1.29969	-2.07432
C	2.384283	-1.62764	0.835189
H	2.228144	-2.69487	1.010589
H	3.451477	-1.39653	0.796793
C	2.074065	-1.13116	-2.22744
H	3.065071	-0.67367	-2.29949
H	2.166995	-2.19508	-2.46458
H	1.427462	-0.67062	-2.98096
C	-0.09996	2.838651	-1.67544
H	-0.98851	3.476391	-1.70533
H	0.78526	3.481546	-1.6796
H	-0.08697	2.232598	-2.58653
C	-0.098	2.701476	1.427283
H	0.848758	3.235672	1.558539
H	-0.9059	3.439612	1.444918
H	-0.24269	2.031035	2.281632
O	1.518376	-0.10149	2.649112
H	1.62886	0.622374	2.001801
H	1.982649	-1.09712	1.824144

Table S8: Cartesian coordinates for TS species at H11 on D_4 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	0.605318	1.632767	0.753122
O	-1.93055	0.796432	0.41123
O	-1.06397	-1.55876	-0.56831
O	1.481121	-0.72336	-0.24234
Si	1.948169	0.747154	0.385071
Si	-2.41161	-0.66187	-0.20917
Si	-0.86408	2.018662	0.087115
Si	0.394046	-1.93087	0.1145
C	2.954228	1.520976	-0.97911
H	3.639914	2.317636	-0.68071
H	2.388401	1.808727	-1.86858
C	2.939199	0.507029	1.936683
H	3.807085	-0.12892	1.736126
H	3.29796	1.467519	2.318718
H	2.334502	0.03844	2.718794
C	0.203337	-2.05425	1.968769
H	-0.50931	-2.84128	2.236353
H	1.159133	-2.2874	2.448895
H	-0.16488	-1.10814	2.383674
C	1.030442	-3.48294	-0.68328
H	2.011254	-3.75894	-0.28377
H	0.345273	-4.3194	-0.5176
H	1.128384	-3.33803	-1.76373
C	-3.41954	-1.51232	1.105588
H	-4.35547	-0.97438	1.284815
H	-3.66529	-2.53762	0.812807
H	-2.86722	-1.54583	2.049861
C	-3.34753	-0.41693	-1.80025
H	-3.74088	-1.36982	-2.16755
H	-4.18853	0.269283	-1.66127
H	-2.69094	-0.00619	-2.57333
C	-1.4761	3.558824	0.923259
H	-1.58017	3.384574	1.998213
H	-0.77579	4.3867	0.778766
H	-2.45214	3.859093	0.531015
C	-0.66802	2.192326	-1.76382
H	-1.62787	2.413868	-2.2416
H	0.02657	3.001236	-2.01272
H	-0.27963	1.263783	-2.19985
O	4.108131	-0.62669	-1.61573
H	3.267262	-1.08569	-1.41896
H	3.664483	0.628268	-1.34437

Table S9: Cartesian coordinates for TS species at H23 on D_4 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	2.246171	-0.04504	0.509298
O	0.189624	1.685924	0.593954
O	-1.7587	0.15367	-0.46404
O	0.309561	-1.58257	-0.54667
Si	1.884845	-1.57078	-0.02579
Si	-1.37556	1.686358	0.065994
Si	1.756023	1.480075	0.091372
Si	-1.23885	-1.3641	-0.01859
C	2.946367	-2.00263	-1.49323
H	4.009017	-1.93189	-1.24215
H	2.741532	-3.02171	-1.83543
H	2.744807	-1.32163	-2.3258
C	2.120926	-2.7391	1.405118
H	1.792636	-3.75183	1.151415
H	3.178032	-2.78462	1.685386
H	1.559002	-2.40058	2.280564
C	-1.32459	-1.52883	1.836173
H	-2.35086	-1.36509	2.18131
H	-1.01047	-2.52559	2.161719
H	-0.67501	-0.79048	2.321023
C	-2.3785	-2.53636	-0.90283
H	-2.43381	-3.54912	-0.49676
H	-2.25381	-2.56019	-1.98776
C	-2.46018	2.120442	1.515225
H	-2.28013	3.148582	1.843945
H	-3.51994	2.024233	1.258454
H	-2.25408	1.455656	2.359666
C	-1.6061	2.837865	-1.37972
H	-2.66489	2.902945	-1.65048
H	-1.25611	3.847455	-1.14274
H	-1.0595	2.477806	-2.25621
C	2.827137	2.690915	1.004469
H	2.721726	2.544998	2.083488
H	3.880808	2.553998	0.744208
H	2.544956	3.721671	0.770071
C	1.827607	1.668292	-1.76738
H	1.514693	2.671228	-2.07547
H	2.843142	1.501289	-2.14077
H	1.164628	0.941424	-2.25219
O	-4.44466	-1.16691	-0.46602
H	-3.89034	-0.37598	-0.61669
H	-3.46853	-2.07841	-0.71979

Table S10: Cartesian coordinates for TS species at H24 on D_4 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	-1.0589	1.636871	-0.61048
O	1.612614	1.291212	-0.4767
O	1.07297	-1.32811	-0.82414
O	-1.36238	-0.90028	0.271722
Si	-2.15618	0.440415	-0.3266
Si	2.238557	-0.23302	-0.36703
Si	0.351789	2.228972	0.033339
Si	-0.28226	-2.05805	-0.24577
C	-3.34328	0.963886	1.010068
H	-3.87308	1.878339	0.727088
H	-4.08574	0.184583	1.207013
H	-2.80653	1.164017	1.943976
C	-2.98243	0.027911	-1.94305
H	-3.61676	-0.85942	-1.85445
H	-3.60474	0.862326	-2.28056
H	-2.23078	-0.1583	-2.71648
C	-1.02512	-3.07768	-1.61374
H	-0.35978	-3.90509	-1.87814
H	-1.98965	-3.49656	-1.31131
H	-1.17764	-2.47066	-2.51092
C	0.108367	-3.05432	1.28622
H	-0.62035	-3.83332	1.524387
H	1.123486	-3.45602	1.338046
C	3.639348	-0.36679	-1.58031
H	4.429628	0.351206	-1.34212
H	4.072275	-1.37142	-1.56928
H	3.283875	-0.15823	-2.59344
C	2.748203	-0.58112	1.393481
H	3.237669	-1.5579	1.472003
H	3.454894	0.177189	1.746069
H	1.885375	-0.58135	2.069797
C	0.604301	3.942874	-0.63759
H	0.650078	3.917233	-1.73012
H	-0.21809	4.602546	-0.34553
H	1.539486	4.372921	-0.26726
C	0.250762	2.172666	1.897495
H	1.178223	2.542998	2.346549
H	-0.57335	2.792094	2.266928
H	0.100736	1.148663	2.260069
O	-0.37894	-1.24957	2.984576
H	0.035889	-2.28812	2.198491
H	-1.04576	-0.91971	2.348525

Table S11: Cartesian coordinates for TS species at H40 on D_4 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
O	0.730996	-1.46867	0.760682
O	1.009684	1.224042	0.77569
O	-1.52403	1.715131	0.01011
O	-1.41395	-0.85781	-0.74795
Si	-0.30793	-2.04002	-0.40111
Si	0.060468	2.137057	-0.23544
Si	1.715937	-0.2079	1.153972
Si	-2.32845	0.269446	0.057074
C	0.627624	-2.42929	-1.96043
H	1.322122	-3.25985	-1.79496
H	-0.0602	-2.71481	-2.76238
H	1.212928	-1.56694	-2.29803
C	-1.16319	-3.52496	0.329787
H	-1.92304	-3.91711	-0.35296
H	-0.4433	-4.32319	0.535213
H	-1.65104	-3.2618	1.273509
C	-2.53409	-0.25097	1.838882
H	-3.03255	0.535258	2.414064
H	-3.13022	-1.16532	1.924009
H	-1.55547	-0.43618	2.295877
C	-3.94541	0.467058	-0.83887
H	-4.5191	-0.4645	-0.82897
H	-4.55252	1.251138	-0.37652
H	-3.76448	0.746193	-1.88112
C	0.257582	3.918016	0.257813
H	1.292871	4.247052	0.127584
H	-0.38567	4.560111	-0.35122
H	-0.01776	4.056418	1.307309
C	0.527368	1.799595	-2.00522
H	-0.07849	2.412105	-2.68121
H	1.584215	2.007366	-2.19625
H	0.345987	0.748029	-2.25327
C	2.029716	-0.26221	2.986805
H	1.081592	-0.19111	3.528933
H	2.518059	-1.19767	3.274559
H	2.663981	0.572414	3.298899
C	3.31336	-0.36981	0.185786
H	4.063423	0.384564	0.438068
H	3.753911	-1.36947	0.233333
O	3.145051	-0.03317	-2.33324
H	4.028404	-0.42026	-2.46829
H	3.026225	-0.17335	-0.93873

Table S12: Cartesian coordinates for TS species at H17 on D_5 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
Si	-2.3172	-1.13149	-0.1486
O	-1.04159	-2.11906	0.193057
O	-1.92656	0.441873	0.209096
Si	0.568868	-2.35729	-0.09088
Si	-1.12036	1.345242	1.353178
O	1.315391	-0.89942	0.116194
O	0.144853	2.099622	0.61618
Si	2.749226	-0.06391	0.148321
Si	1.010389	2.186518	-0.79555
O	2.455891	1.398902	-0.56175
C	0.82844	-2.94174	-1.84365
H	0.595293	-2.14544	-2.55869
H	0.19084	-3.80156	-2.07153
H	1.86994	-3.24015	-2.00467
C	-2.72654	-1.12442	-1.97023
H	-1.87136	-1.09756	-2.65004
H	-3.44831	-1.87945	-2.29242
C	-2.30682	2.646616	1.95862
H	-2.65257	3.269273	1.127035
H	-1.82962	3.302775	2.69273
H	-3.18377	2.188368	2.42689
C	0.084164	1.334685	-2.17437
H	0.636344	1.414517	-3.11648
H	-0.0152	0.273206	-1.92444
H	-0.92055	1.74179	-2.32672
C	4.025387	-0.98078	-0.85415
H	4.224144	-1.97233	-0.43241
H	4.970911	-0.43098	-0.88348
H	3.676647	-1.10693	-1.88423
C	1.200532	-3.56783	1.175147
H	2.277393	-3.72921	1.055627
H	0.700546	-4.53671	1.084507
H	1.022337	-3.18686	2.185849
C	-3.76274	-1.66726	0.888582
H	-3.52805	-1.58182	1.954275
H	-4.02958	-2.7081	0.683053
H	-4.63359	-1.0392	0.67568
C	-0.51282	0.238199	2.724192
H	0.187983	-0.50133	2.326744
H	-1.34633	-0.29163	3.198152
H	-0.00125	0.820014	3.497709
C	1.389215	3.971422	-1.14729
H	2.019762	4.064847	-2.03657
H	1.919427	4.422423	-0.30362
H	0.469604	4.539252	-1.31778
C	3.243953	0.177626	1.926543
H	3.313025	-0.78192	2.450142
H	2.494461	0.792868	2.434715
H	4.210648	0.683689	2.007035
O	-3.71175	1.200841	-1.98439
H	-3.17582	1.388218	-1.18757
H	-3.28283	-0.07815	-2.14756

Table S13: Cartesian coordinates for TS species at H30 on D_5 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
Si	-2.87942	0.35762	0.422012
O	-2.10344	1.713038	-0.13156
O	-1.85292	-0.93507	0.300009
Si	-0.57613	2.32499	0.021748
Si	-1.12352	-1.90992	-0.82532
O	0.442167	1.383187	-0.89566
O	0.453666	-2.10523	-0.36033
Si	1.987071	0.816267	-0.73911
Si	1.482058	-1.71386	0.875235
O	2.067436	-0.17545	0.598425
C	-0.03263	2.249576	1.809981
H	0.080846	1.211571	2.141757
H	-0.76236	2.744298	2.459434
H	0.934203	2.743333	1.954975
C	-3.29224	0.550619	2.228577
H	-3.85579	-0.31491	2.590703
H	-3.89332	1.448519	2.401933
H	-2.37964	0.63128	2.827848
C	-1.96229	-3.57222	-0.78466
H	-1.91285	-3.99931	0.221854
H	-1.48694	-4.27349	-1.47707
H	-3.01756	-3.48133	-1.0627
C	0.585043	-1.71996	2.506835
H	1.196014	-1.2695	3.295139
H	-0.35146	-1.16014	2.420285
H	0.336509	-2.74258	2.809214
C	3.187484	2.194945	-0.36502
H	3.540906	2.763394	-1.22909
H	2.902875	2.86829	0.447732
C	-0.57662	4.053655	-0.66167
H	0.429984	4.483373	-0.62894
H	-1.24507	4.703818	-0.08945
H	-0.91216	4.049371	-1.70288
C	-4.38618	0.105336	-0.64291
H	-4.11122	0.083772	-1.70205
H	-5.09922	0.923522	-0.50265
H	-4.89246	-0.83326	-0.39663
C	-1.16338	-1.12611	-2.51354
H	-0.74558	-0.11515	-2.47028
H	-2.18705	-1.06608	-2.89779
H	-0.57482	-1.71603	-3.22403
C	2.923563	-2.88933	0.816327
H	3.648305	-2.66919	1.606933
H	3.437639	-2.80921	-0.14709
H	2.591198	-3.92438	0.939657
C	2.45427	-0.11394	-2.27742
H	2.288136	0.494527	-3.17148
H	1.862002	-1.02974	-2.36592
H	3.513824	-0.38774	-2.23689
O	4.92355	0.649532	0.602966
H	4.18025	0.134166	0.975024
H	4.158155	1.622074	0.038706

Table S14: Cartesian coordinates for TS species at H33 on D_5 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
Si	-1.2285	-1.45772	1.213216
O	-2.27149	-0.53083	0.298126
O	0.071767	-1.88289	0.298774
Si	-2.18597	1.053843	-0.20405
Si	0.9229	-1.8506	-1.11815
O	-0.5981	1.415853	-0.44067
O	2.185212	-0.79008	-0.92823
Si	0.788783	2.241827	-0.07534
Si	2.826675	0.021686	0.367737
O	1.782586	1.244201	0.793933
C	-2.93262	2.164594	1.090829
H	-2.40212	2.073122	2.044015
H	-3.98061	1.894128	1.255504
H	-2.89635	3.214249	0.781753
C	-0.6339	-0.46603	2.676765
H	-0.03058	-1.08515	3.348787
H	-1.4795	-0.07552	3.252546
H	-0.00655	0.371163	2.347662
C	1.619329	-3.55498	-1.39606
H	2.209584	-3.86468	-0.52761
H	2.270822	-3.57273	-2.27488
H	0.82217	-4.28979	-1.54426
C	3.009106	-1.10466	1.839481
H	3.308167	-0.53867	2.727111
H	2.058192	-1.60224	2.051345
H	3.7654	-1.87369	1.652582
C	0.378209	3.699631	1.009645
H	-0.34398	4.366586	0.528271
H	1.278687	4.278189	1.237336
H	-0.04834	3.360016	1.959271
C	-3.13661	1.116072	-1.80327
H	-3.58295	2.081486	-2.0544
H	-2.6247	0.688275	-2.66824
C	-2.16115	-2.99339	1.696136
H	-2.50037	-3.53192	0.805622
H	-3.03958	-2.74607	2.300008
H	-1.52594	-3.66855	2.277242
C	-0.14485	-1.25056	-2.52089
H	-0.33447	-0.18004	-2.39871
H	-1.10623	-1.77475	-2.54257
H	0.351994	-1.40345	-3.4841
C	4.445166	0.753376	-0.19268
H	4.875699	1.396619	0.580699
H	4.302238	1.35188	-1.09775
H	5.167179	-0.03596	-0.42335
C	1.591664	2.698643	-1.69305
H	0.921495	3.311074	-2.30397
H	1.830494	1.790459	-2.25812
H	2.51843	3.259758	-1.5366
O	-4.85451	-0.59179	-1.10782
H	-4.16852	-1.00446	-0.5454
H	-4.07391	0.392349	-1.61197

Table S15: Cartesian coordinates for TS species at H45 on D_5 molecule

atom	X-Coord.	Y-Coord.	Z-Coord.
Si	-2.82588	-0.69317	0.414617
O	-2.51082	0.805264	-0.22334
O	-1.48941	-1.65183	0.258456
Si	-1.41444	2.027502	-0.08427
Si	-0.34483	-2.05118	-0.87214
O	0.093364	1.340958	-0.13624
O	1.143778	-1.69552	-0.25208
Si	1.699813	1.694016	-0.33431
Si	1.961763	-0.98484	0.986301
O	2.531561	0.497482	0.463105
C	-1.61907	2.895301	1.554938
H	-1.41834	2.20837	2.384046
H	-2.63576	3.282071	1.674964
H	-0.92347	3.736828	1.64072
C	-3.20113	-0.54856	2.234436
H	-3.51792	-1.51462	2.639893
H	-4.0004	0.177116	2.414595
H	-2.315	-0.2293	2.792198
C	-0.42938	-3.88891	-1.15842
H	-0.29489	-4.42891	-0.21627
H	0.35121	-4.21465	-1.85248
H	-1.40042	-4.17352	-1.57644
C	0.842919	-0.72534	2.453303
H	1.398571	-0.33534	3.311576
H	0.071916	0.001146	2.176012
H	0.344389	-1.65384	2.746759
C	2.097352	3.333087	0.457549
H	1.552282	4.150713	-0.02703
H	3.166591	3.554242	0.383745
H	1.828174	3.320397	1.518587
C	-1.62653	3.17411	-1.53668
H	-0.89027	3.985205	-1.51073
H	-2.62368	3.624625	-1.53987
H	-1.50104	2.627085	-2.4766
C	-4.24107	-1.40661	-0.56272
H	-3.9949	-1.43056	-1.6292
H	-5.14555	-0.80252	-0.44268
H	-4.4653	-2.42802	-0.24059
C	-0.61353	-1.08347	-2.44461
H	-0.53819	-0.01005	-2.24868
H	-1.60275	-1.28686	-2.86891
H	0.136471	-1.35244	-3.19574
C	3.488476	-1.98927	1.338167
H	3.998483	-1.74422	2.272658
H	3.366503	-3.0699	1.234303
C	2.128024	1.632581	-2.1443
H	1.515526	2.335597	-2.71909
H	1.951517	0.624748	-2.53374
H	3.180137	1.882028	-2.3155
O	4.947437	-0.95189	-0.43603
H	4.386731	-0.15456	-0.35981
H	4.265661	-1.68673	0.479408

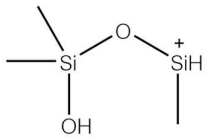
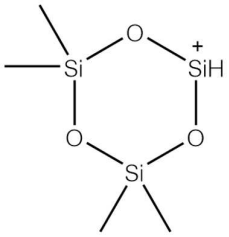
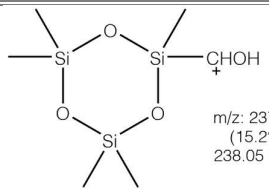
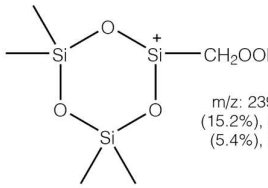
Table S16: Imaginary frequencies (cm^{-1}) for the reactions between different cyclic methylsiloxanes and •OH at the M06–2X/6–311++G** // M06–2X/6–31+G** level of theory at 298 K in gas phase.

cyclosiloxanes	H atom number/position	imaginary frequencies
D_3	H16/axial pointing outward	–776.4 *i*
	H18/ axial pointing inward	–1115.2 *i*
D_4	H11/axial pointing outward	–1180.0 *i*
	H40/axial pointing inward	–752.2 *i*
	H23/equatorial side ways	–1172.9 *i*
	H24/equatorial up or down	–1143.4 *i*
D_5	H17/axial pointing outward	–1199.7 *i*
	H30/axial pointing inward	–1180.1 *i*
	H33/equatorial side ways	–1198.8 *i*
	H45/equatorial up or down	–1169.8 *i*

Table S17: The temperature-dependent free energy barriers (kcal mol^{-1}) for the D chemicals.

chemical	H atom number/position	temperature-dependent free energy barriers							
		238.15 K	258.15 K	278.15 K	298.15 K	318.15 K	338.15 K	353.15 K	358.15 K
D_3	H16/axial pointing outward	8.90	9.48	10.06	10.63	11.21	11.79	12.23	12.37
	H18/ axial pointing inward	7.81	8.56	9.32	10.07	10.83	11.59	12.16	12.35
D_4	H11/axial pointing outward	8.36	9.12	9.88	10.64	11.41	12.18	12.75	12.95
	H40/axial pointing inward	8.40	9.07	9.74	10.42	11.09	11.76	12.27	12.44
	H23/equatorial side ways	8.54	9.26	9.99	10.72	11.45	12.18	12.73	12.92
	H24/equatorial up or down	8.03	8.82	9.61	10.40	11.20	11.99	12.59	12.79
D_5	H17/axial pointing outward	8.35	9.12	9.88	10.66	11.43	12.20	12.79	12.98
	H30/axial pointing inward	8.67	9.42	10.17	10.92	11.67	12.42	12.99	13.17
	H33/equatorial side ways	8.34	9.15	9.97	10.78	11.60	12.42	13.04	13.25
	H45/equatorial up or down	8.25	8.95	9.65	10.36	11.07	11.77	12.31	12.48

Table S18: Identification of D_3 product fragments

m/z	Rel. Int.*	ratio†	comments and possible structure	
135	2.4%	1.000	Advanced degradation product (n^{th} step product) or lower fragment of any of the expected products. Si–H and O–H bonds are formed via intramoleclar H shifts after EI. Si–O bonds are probably broken during EI.	 m/z: 135.03 (100.0%), 136.03 (10.2%), 137.03 (3.3%), 137.03 (3.3%), 136.03 (3.2%)
136	0.4%	0.165		
137	0.3%	0.122		
193	17.0%	1.000	Removal of methyl via EI and a hydrogen shift. Such as would be possible of the alcohol or even the silanol. EI would induce a hydride shift and loss of CH_2O or H_2O	 m/z: 193.02 (100.0%), 194.02 (10.2%), 195.01 (6.7%), 194.02 (5.1%), 194.02 (4.3%), 195.01 (3.3%)
194	3.5%	0.205		
195	2.5%	0.144		
227	0.7%	1.000	The ratio for m/z 227 to 229 is not concordant with expectations. On further examination a different species over laps in the m/z 229 to 231 region. This results in a higher intensity for 229 since 2 different species are overlapping. Both Fragments could not be assigned to a structure.	
228	0.2%	0.235		
229	0.3%	0.477		
230	<0.2%	0.124		
231	<0.1%	0.090		
237	10.6%	1.000	Likewise m/z 239 seems to be an overlap of 2 species, produced from fragmentation of the alcohol and the peroxide.	 m/z: 237.04 (100.0%), 238.04 (15.2%), 239.04 (10.0%), 238.05 (6.5%), 240.04 (1.0%)
238	2.4%	0.226		
239	1.8%	0.165		
240	0.3%	0.030		
241	0.2%	0.016		 m/z: 239.02 (100.0%), 240.02 (15.2%), 241.02 (10.0%), 240.03 (5.4%), 241.03 (1.0%), 242.02 (1.0%)

* Rel. Int.: The maximum intensity of the fragment relative to maximum for m/z 207 which is $[D_3 – CH_3]^+$. This serves as an indication of the prominence of the fragment relative to the initial concentration of D_3

† ratio: The ratio of intensities showing the Si isotope ratios.

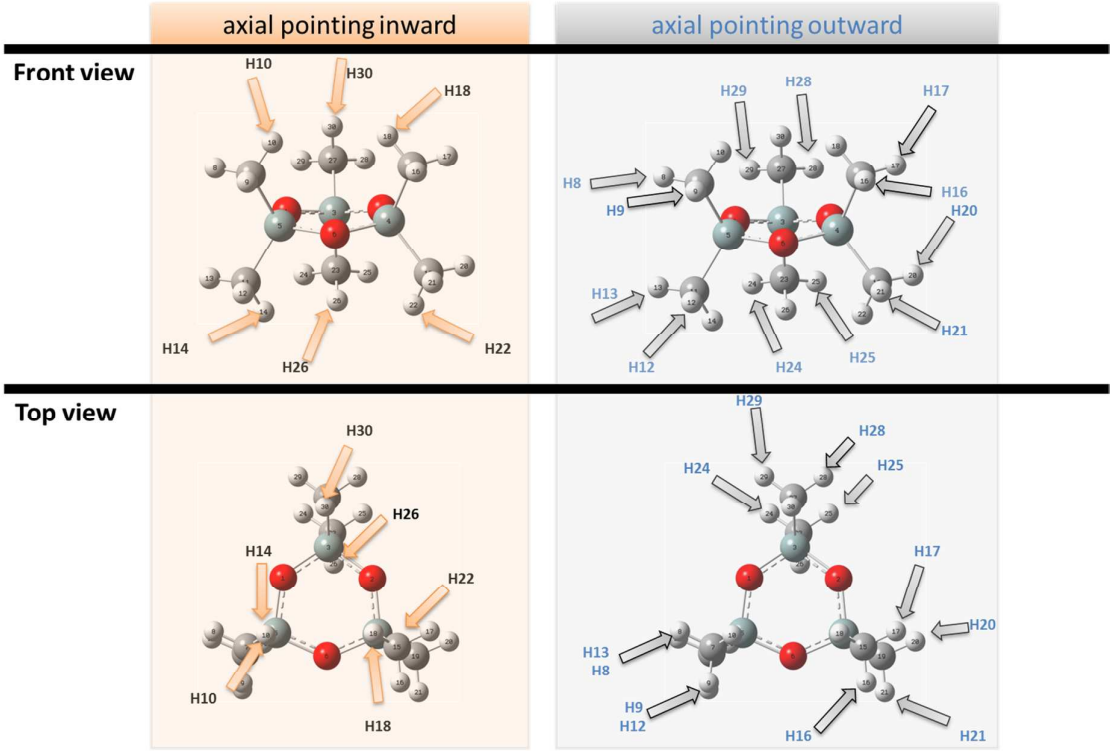


Figure S1: Geometry of D_3 was optimized at M06-2X/6-31+G** level of theory and the single-point energy for the optimized geometry was calculated at M06-2X/6-311++G** level of theory; all the eighteen hydrogen atoms on the optimized D_3 were grouped into two categories, axial pointing inward (H10, H14, H18, H22, H26, and H30) and axial pointing outward (H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, and H29)

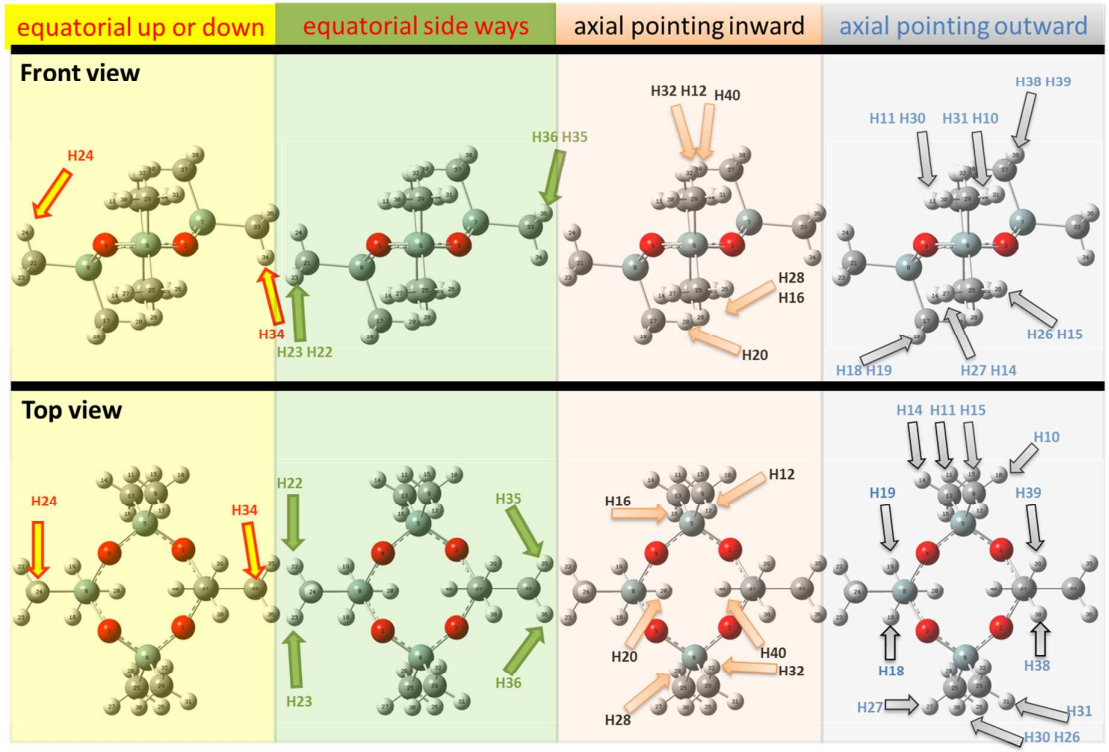


Figure S2: Geometry of D_4 was optimized at M06-2X/6-31+G** level of theory and the single-point energy for the optimized geometry was calculated at M06-2X/6-311++G** level of theory; all the twenty-four hydrogen atoms on the optimized molecule were grouped into four categories, equatorial up or down (H24 and H34), equatorial sideway (H22, H23, H35, and H36), axial pointing inward ones (H12, H16, H20, H28, H32, H40) and axial pointing outward (H10, H11, H14, H15, H18, H19, H26, H27, H30, H31, H38, and H39).

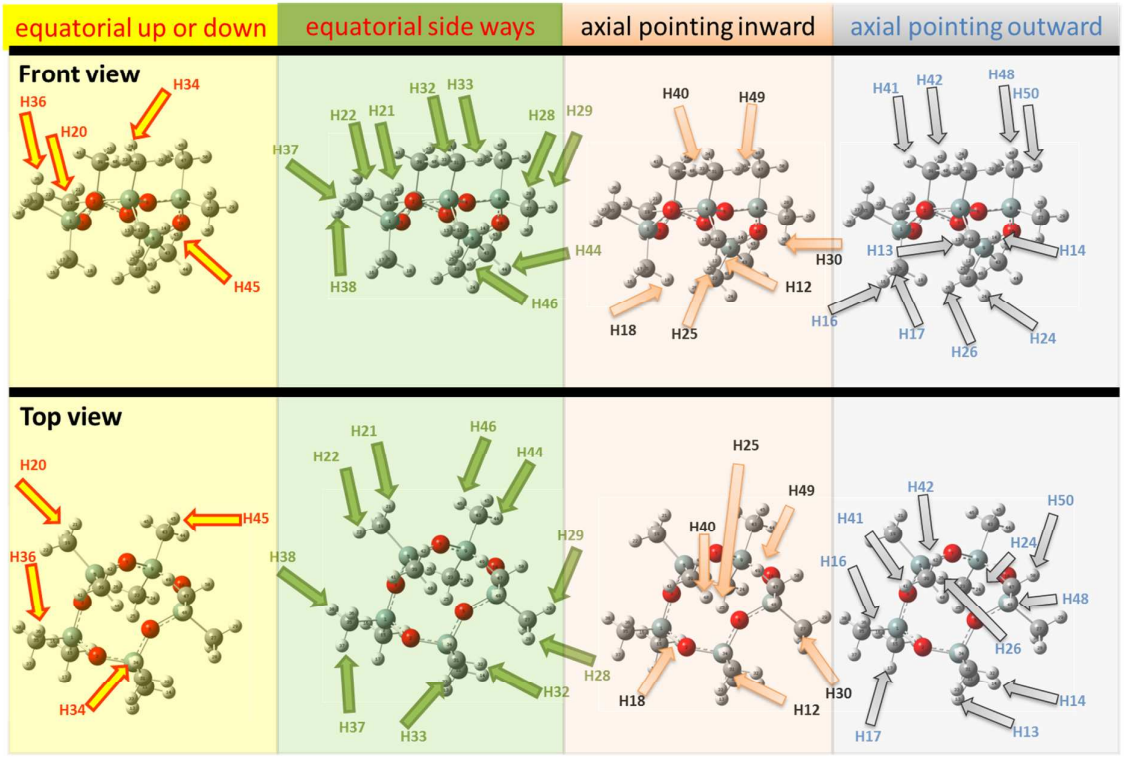


Figure S3: Geometry of D_5 was optimized at M06-2X/6-31+G** level of theory and the single-point energy for the optimized geometry was calculated at M06-2X/6-311++G** level of theory; all the thirty-six hydrogen atoms on the optimized molecule were also grouped into four categories, equatorial up or down (H20, H34, H36, and H45), equatorial sideway (H21, H22, H28, H29, H32, H33, H37, H38, H44, and H46), axial pointing inward (H12, H18, H25, H30, H40, and H49) and axial pointing outward (H13, H14, H16, H17, H24, H26, H41, H42, H48, H50).

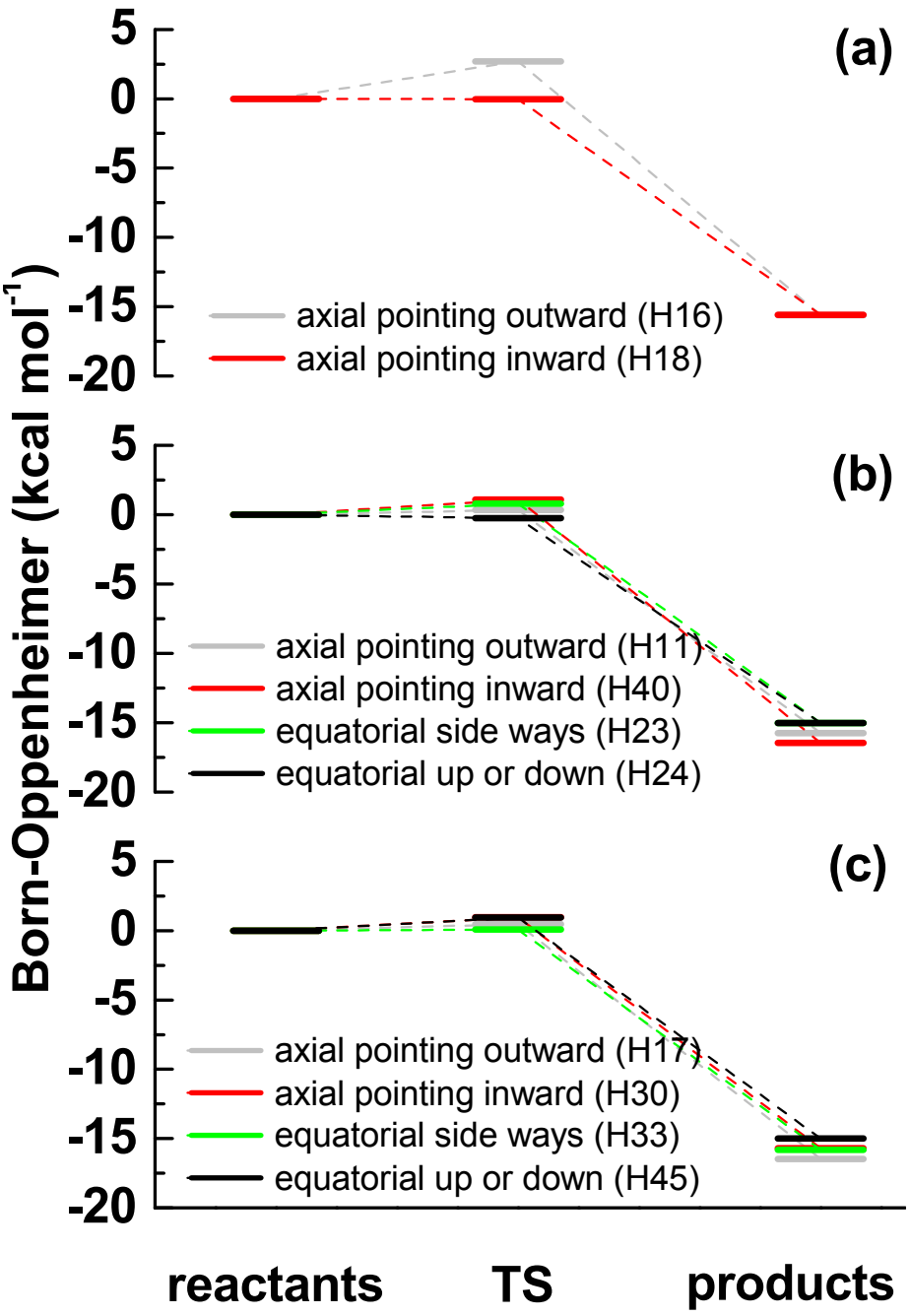


Figure S4: Calculated zero-point corrected Born-Oppenheimer energies of reaction and barrier heights (kcal mol^{-1}) of the first step of reactions between different cyclosiloxanes (a: D_3; b: D_4, and c: D_5) and •OH at the M06-2X/6-311++G** // M06-2X/6-31+G** level of theory.

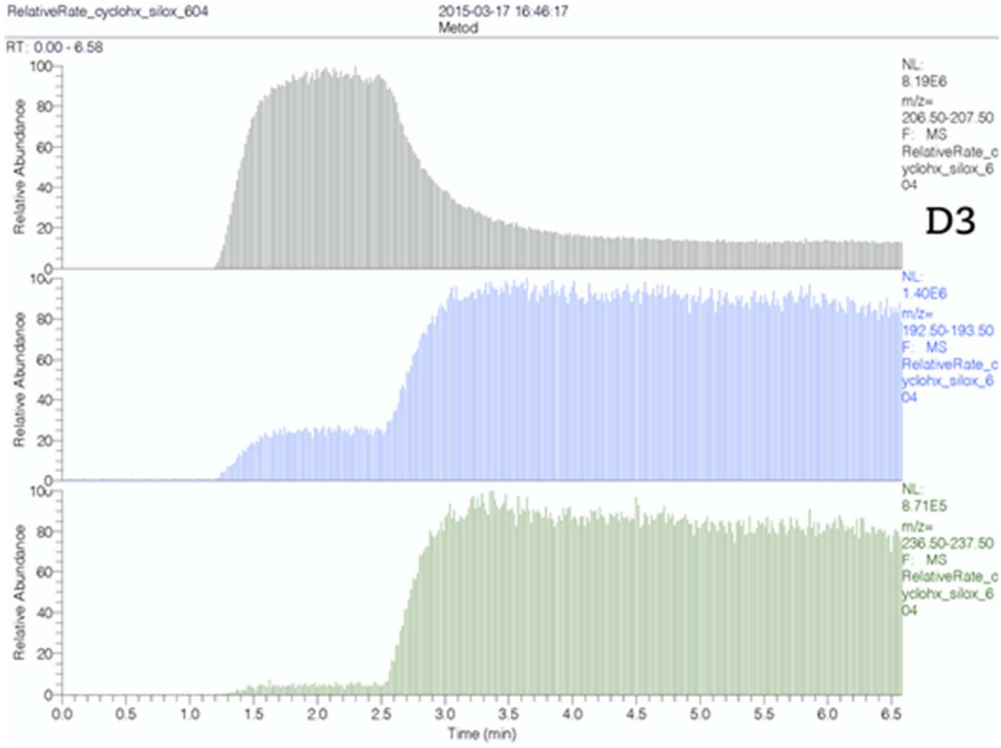


Figure S5: Example of PID run show increase in m/z 193 and m/z 237.