Gas Phase Kinetics of 2, 2, 2-trifluoroethylbutyrate with Cl Atom: An Experimental and Theoretical Study.

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Table S-I: Optimized geometries in Cartesian Coordinates of reactants, transition states (TS) and products (P) at M06-2X/6-31+G(d,p) level of theory.

2,2,2-trifluoroethyl butyarte

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.696946	-0.790611	0.000072
2	1	0	4.654746	-1.434475	-0.884584
3	1	0	5.667123	-0.287356	0.000732
4	1	0	4.654203	-1.435622	0.883883
5	1	0	3.624114	0.875545	-0.874228
6	6	0	3.553941	0.220757	0.000374
7	1	0	3.623663	0.874525	0.875781
8	1	0	2.073104	-1.118832	0.874033
9	6	0	2.194125	-0.467361	-0.000352
10	1	0	2.073518	-1.117714	-0.875648
11	6	0	1.049931	0.511039	-0.000143
12	8	0	1.134491	1.713191	-0.000034
13	8	0	-0.146158	-0.127385	-0.000226
14	1	0	-1.294122	1.359096	-0.891783
15	6	0	-1.274946	0.726834	-0.000256
16	1	0	-1.293942	1.359421	0.891042
17	6	0	-2.492089	-0.168511	0.00006
18	9	0	-2.534804	-0.958123	-1.08091
19	9	0	-2.534652	-0.957523	1.081488
20	9	0	-3.60349	0.587432	-0.000097

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.999154	-0.306516	-0.672751
2	1	0	4.925712	0.247793	-1.611702
3	1	0	5.947199	-0.042826	-0.202334
4	1	0	5.030027	-1.371886	-0.914681
5	1	0	3.816867	1.078172	0.496931

6	6	0	3.82554	0.014453	0.247725
7	1	0	3.927029	-0.522045	1.194334
8	1	0	2.447084	-1.422448	-0.64374
9	6	0	2.496075	-0.356482	-0.396806
10	1	0	2.342419	0.174955	-1.342411
11	6	0	1.324539	-0.040512	0.479172
12	8	0	1.319089	0.464897	1.55491
13	8	0	0.140115	-0.424968	-0.145555
14	1	0	-1.339351	1.15418	0.162683
15	6	0	-1.016898	-0.124325	0.494242
16	1	0	-0.965637	-0.055563	1.580885
17	6	0	-2.162366	-0.939935	-0.050923
18	9	0	-2.258546	-0.840352	-1.372299
19	9	0	-2.005859	-2.235956	0.252584
20	9	0	-3.306117	-0.526798	0.494742
21	17	0	-1.556856	2.552241	-0.292589

TS2

Center Number	Atomic Number	Atomic Type	**Coordinates (Angstroms)**		
			X	Y	Z
1	6	0	4.407153	-0.334539	0.291362
2	1	0	4.441327	-0.28033	1.381457
3	1	0	5.312369	-0.836521	-0.051218
4	1	0	4.416501	0.684732	-0.101503
5	1	0	3.15992	-2.11839	0.199498
6	6	0	3.166791	-1.091255	-0.173636
7	1	0	3.157926	-1.170468	-1.269918
8	1	0	1.796586	0.866007	0.040959
9	6	0	1.888997	-0.416082	0.229007
10	1	0	1.885214	-0.432159	1.528017
11	6	0	0.622993	-1.154312	-0.048009
12	8	0	0.552739	-2.30434	-0.378831
13	8	0	-0.452536	-0.367448	0.144961
14	1	0	-1.883619	-1.734463	0.767312
15	6	0	-1.704391	-1.007097	-0.027128
16	1	0	-1.765342	-1.503164	-0.997197
17	6	0	-2.756159	0.074443	0.041825

18	9	0	-2.739627	0.718756	1.20885
19	9	0	-2.59991	0.980186	-0.927239
20	9	0	-3.966923	-0.47961	-0.106448
21	17	0	1.687255	2.382242	-0.181379

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.052751	-1.331416	-0.672755
2	1	0	3.959245	-0.946404	-1.690697
3	1	0	5.000296	-0.989865	-0.255638
4	1	0	4.087209	-2.42709	-0.731239
5	1	0	2.982315	0.500937	0.155062
6	6	0	2.895482	-0.903438	0.17664
7	1	0	2.986	-1.03549	1.254356
8	1	0	1.322289	-2.184586	-0.516339
9	6	0	1.514884	-1.111054	-0.372654
10	1	0	1.395487	-0.644518	-1.354052
11	6	0	0.447479	-0.591302	0.558919
12	8	0	0.583862	-0.376787	1.728671
13	8	0	-0.717876	-0.412414	-0.091341
14	1	0	-1.568578	1.086348	1.064039
15	6	0	-1.780768	0.076613	0.707566
16	1	0	-1.969654	-0.578447	1.559764
17	6	0	-3.005934	0.105482	-0.17442
18	9	0	-2.843601	0.897097	-1.235612
19	9	0	-3.325827	-1.112685	-0.620523
20	9	0	-4.046751	0.569863	0.52963
21	17	0	2.945868	1.93382	-0.116772

TS4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.817565	-0.972622	0.808044

2	1	0	-4.105523	0.371694	0.271603
3	1	0	-4.743805	-1.458549	0.513613
4	1	0	-3.745706	-0.718085	1.8637
5	1	0	-2.727321	-1.332407	-0.994869
6	6	0	-2.567048	-1.360532	0.08619
7	1	0	-2.336594	-2.409745	0.320527
8	1	0	-1.192761	-0.494635	1.538841
9	6	0	-1.374318	-0.488233	0.459585
10	1	0	-1.54383	0.557173	0.183493
11	6	0	-0.114354	-0.950776	-0.219555
12	8	0	-0.014283	-1.881165	-0.96839
13	8	0	0.936505	-0.175702	0.122726
14	1	0	2.131276	-0.458036	-1.553473
15	6	0	2.170377	-0.542436	-0.465837
16	1	0	2.452939	-1.560635	-0.192026
17	6	0	3.205865	0.417948	0.068173
18	9	0	2.938438	1.681171	-0.268355
19	9	0	3.300373	0.361284	1.398767
20	9	0	4.404738	0.102969	-0.441481
21	17	0	-4.25742	1.648779	-0.341534

TS5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.442347	-1.194724	-0.000368
2	1	0	3.58564	-1.762182	-0.917348
3	1	0	4.707113	-0.461212	0.000017
4	1	0	3.585403	-1.762681	0.916341
5	1	0	2.527103	0.531839	-0.877248
6	6	0	2.410313	-0.108631	-0.000209
7	1	0	2.526985	0.531455	0.877131
8	1	0	0.830712	-1.34392	0.874335
9	6	0	0.999482	-0.709124	-0.000443
10	1	0	0.83089	-1.343559	-0.875525
11	6	0	-0.059195	0.363154	-0.00038
12	8	0	0.127798	1.545451	-0.000621
13	8	0	-1.295596	-0.181291	-0.000043

14	1	0	-2.337164	1.381036	-0.890721
15	6	0	-2.361573	0.750572	-0.000035
16	1	0	-2.336961	1.38125	0.890494
17	6	0	-3.637802	-0.056138	0.000201
18	9	0	-3.735844	-0.837393	-1.077874
19	9	0	-3.735584	-0.837188	1.078447
20	9	0	-4.687546	0.776379	0.000219
21	17	0	5.887765	0.33811	0.000477

HCl

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	0	0	-1.209319
2	17	0	0	0	0.071136

P1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.677537	-0.794744	0.068245
2	1	0	4.709408	-1.31773	-0.892945
3	1	0	5.644348	-0.307732	0.215809
4	1	0	4.558163	-1.547015	0.854684
5	1	0	3.683393	0.980742	-0.675185
6	6	0	3.541527	0.224108	0.102834
7	1	0	3.540051	0.76073	1.057287
8	1	0	1.984885	-1.195776	0.679339
9	6	0	2.186862	-0.446301	-0.095837
10	1	0	2.14001	-0.984899	-1.051307
11	6	0	1.053434	0.533835	-0.090548
12	8	0	1.10339	1.725787	-0.009329
13	8	0	-0.163647	-0.133369	-0.205083
14	6	0	-1.276345	0.635797	-0.320041
15	1	0	-1.219767	1.637132	0.110495
16	6	0	-2.517077	-0.157488	0.010634
17	9	0	-2.577029	-1.296076	-0.679387

18	9	0	-2.547384	-0.466998	1.317974
19	9	0	-3.603816	0.570181	-0.264654

P2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.527265	0.714894	0.320511
2	1	0	-4.75492	1.158983	-0.65342
3	1	0	-5.424194	0.202905	0.675521
4	1	0	-4.299674	1.524772	1.019502
5	1	0	-3.605477	-1.087515	-0.461103
6	6	0	-3.357156	-0.25979	0.221444
7	1	0	-3.141033	-0.727697	1.18735
8	6	0	-2.106272	0.381927	-0.302227
9	1	0	-2.199794	1.04671	-1.164168
10	6	0	-0.870152	-0.451376	-0.30835
11	8	0	-0.774506	-1.5422	0.192505
12	8	0	0.138423	0.187444	-0.950077
13	1	0	1.878979	-0.259058	-1.903189
14	6	0	1.405333	-0.447216	-0.939104
15	1	0	1.310331	-1.517998	-0.74869
16	6	0	2.258206	0.173972	0.150428
17	9	0	2.476442	1.476247	-0.071843
18	9	0	1.683666	0.056551	1.351678
19	9	0	3.451923	-0.441412	0.192673

P3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.762737	-0.71963	-0.104763
2	1	0	4.598233	-1.670528	-0.620505
3	1	0	5.628165	-0.22551	-0.551094
4	1	0	5.009366	-0.946191	0.942643

5	6	0	3.544714	0.150734	-0.16573
6	1	0	3.657763	1.2004	0.110193
7	1	0	2.241137	-0.801778	1.246842
8	6	0	2.225115	-0.464338	0.197695
9	1	0	2.01098	-1.354541	-0.403618
10	6	0	1.08293	0.514917	0.063794
11	8	0	1.187291	1.713547	0.019891
12	8	0	-0.103471	-0.122888	0.022519
13	1	0	-1.226702	1.247862	-1.059941
14	6	0	-1.233455	0.72529	-0.099771
15	1	0	-1.269623	1.455033	0.712966
16	6	0	-2.451062	-0.167376	-0.022551
17	9	0	-2.469078	-1.079447	-1.001027
18	9	0	-2.516227	-0.820961	1.145261
19	9	0	-3.559778	0.581785	-0.136323

P4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.734002	-0.81107	-0.008271
2	1	0	-5.742802	-0.418984	0.105172
3	1	0	-4.646207	-1.681801	-0.658068
4	1	0	-3.701874	0.835092	0.890421
5	6	0	-3.596564	0.159688	0.034782
6	1	0	-3.650575	0.805626	-0.855726
7	1	0	-2.108829	-1.221274	-0.762865
8	6	0	-2.23452	-0.525658	0.075358
9	1	0	-2.1153	-1.120592	0.988551
10	6	0	-1.108945	0.472878	0.016468
11	8	0	-1.225475	1.67043	-0.057003
12	8	0	0.093873	-0.140694	0.050884
13	1	0	1.242982	1.395306	0.853666
14	6	0	1.21165	0.727837	-0.011469
15	1	0	1.19923	1.322778	-0.928398
16	6	0	2.440168	-0.15319	-0.00653
17	9	0	2.535592	-0.875125	1.116414
18	9	0	2.448941	-1.003829	-1.040751
19	9	0	3.538741	0.61485	-0.096312

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.717354	-0.809886	-0.000131
2	1	0	4.902241	-1.366918	-0.91812
3	1	0	4.903078	-1.365382	0.918618
4	1	0	3.683109	0.850279	-0.879657
5	6	0	3.611856	0.202611	-0.00049
6	1	0	3.683671	0.851554	0.877686
7	1	0	2.12301	-1.140876	0.877507
8	6	0	2.245366	-0.495268	0.000443
9	1	0	2.122398	-1.142129	-0.8756
10	6	0	1.112874	0.501057	0.000189
11	8	0	1.219241	1.700242	0.000092
12	8	0	-0.084217	-0.127018	0.000128
13	1	0	-1.227867	1.363508	-0.892117
14	6	0	-1.211543	0.732193	-0.000004
15	1	0	-1.228006	1.363596	0.892046
16	6	0	-2.429521	-0.163288	-0.000053
17	9	0	-2.470141	-0.952234	-1.081047
18	9	0	-2.470323	-0.952111	1.081021
19	9	0	-3.539551	0.592797	-0.000178

Table S-II: Vibrational frequencies of reactants (R), transition states (TSs), and products (P) at M06-2X/6-31+G(d,p) level of theory.

2,2,2-TFEB	TS1	TS2	TS3	TS4	TS5
21.6144	-1023.0477	-907.3829	-491.0936	-606.588	-672.7545
41.127	16.5275	21.8538	13.4121	23.8747	12.3048
50.5152	41.4101	32.8872	36.7224	33.5426	36.1272
80.3745	54.0532	44.9075	57.8678	46.9912	37.7648
93.8485	55.5237	55.2268	65.2139	57.7247	46.0669
177.0352	74.0256	65.0139	82.0511	81.382	59.1304
185.9047	81.236	86.8387	115.1858	99.0862	78.8635

249.3014	96.7503	128.0053	121.7403	135.0586	94.3263
249.4572	169.5142	148.3531	176.3808	178.7843	180.7945
312.2399	201.697	230.5585	182.1751	194.4186	188.6765
361.9196	252.9484	248.218	205.6815	251.2612	233.8767
362.874	253.7454	273.0343	253.1307	314.3402	309.4355
478.3891	303.6311	321.1126	314.5462	363.3316	343.6127
533.8392	313.862	367.5945	360.4152	367.0869	367.3451
574.7319	361.1787	394.0253	363.4821	400.4119	388.3532
580.9253	460.476	435.6768	476.3787	480.534	481.6315
642.924	496.8801	493.1118	536.8977	537.2347	536.4071
739.6285	541.7571	532.4129	567.3422	577.5341	576.5011
748.4497	567.0755	567.4035	585.0645	580.4912	581.5176
874.8446	578.496	635.6203	617.8845	641.8539	626.8179
883.5395	654.1825	681.2679	647.9407	645.2228	644.4491
923.2902	738.7247	715.3051	745.5353	735.8071	737.0161
981.5614	750.0624	734.8484	781.4965	749.4054	746.522
989.2755	864.7309	870.5093	849.5062	801.0592	783.1295
1071.9709	882.8379	873.3592	877.4295	857.7153	835.4879
1099.5468	889.1473	906.524	915.4015	876.0064	877.0348
1128.308	926.6957	922.4014	924.644	909.8273	883.168
1155.043	963.8247	975.7562	963.929	966.2199	984.53
1214.9764	983.8054	1018.6345	980.3371	984.2443	984.5731
1232.175	1071.7313	1053.234	995.5094	994.6665	1039.2986
1238.3335	1116.257	1088.2869	1097.4618	1100.6987	1078.9422
1251.1089	1126.9574	1097.6763	1129.9141	1103.5218	1118.2753
1318.4578	1141.2493	1169.9578	1149.6428	1141.2242	1118.9398
1323.0047	1154.2726	1180.2739	1191.595	1174.5491	1167.7583
1334.8886	1237.8756	1218.4108	1216.4248	1216.0498	1219.2964
1349.4505	1249.4563	1239.2068	1242.8565	1217.7568	1234.7341
1420.6208	1251.1953	1251.0509	1248.0191	1239.8943	1241.067
1430.3825	1266.9799	1272.0942	1264.8343	1246.1189	1251.6048
1464.6407	1320.759	1314.9097	1319.3735	1305.7626	1314.8501
1473.2978	1321.5456	1344.234	1338.8854	1322.7581	1318.7664
1498.0711	1329.4989	1363.0248	1352.7263	1337.4744	1338.56
1501.9985	1416.0087	1425.6896	1413.3271	1361.1284	1339.8672
1509.6741	1427.5083	1434.4781	1446.8751	1433.9938	1411.5674
1514.3723	1454.4461	1454.861	1447.6481	1463.7365	1461.8143
1873.2816	1458.9307	1462.6221	1475.6146	1466.1606	1472.026
3066.0297	1498.1717	1489.3069	1483.4563	1474.0095	1475.8091
3071.7724	1509.6402	1506.2438	1494.2614	1475.6344	1495.8198

3087.9497	1513.8154	1511.7949	1494.7737	1501.8461	1503.4058
3107.354	1916.3612	1857.5682	1878.4954	1868.9306	1878.715
3111.6766	3063.8876	3035.3209	3030.1179	3036.0738	3079.3524
3125.4315	3067.7633	3068.7529	3032.5016	3076.29	3092.4935
3145.0261	3087.0023	3114.7063	3115.1591	3107.0372	3120.0466
3153.8649	3107.1293	3134.1949	3119.7161	3117.4786	3120.9707
3171.9528	3126.6269	3147.9308	3123.7973	3126.6964	3131.5027
	3146.2893	3158.447	3163.7966	3136.3198	3144.7943
	3150.1453	3172.1942	3182.8557	3179.4222	3181.6392
	3196.2787	3203.3368	3187.8778	3238.8502	3232.5372

P1	P2	P3	P4	P5	HCl
34.25	29.8667	33.1953	17.8705	30.8250	3030.0679
46.9291	49.9102	48.6836	50.1973	10.6563	
71.7118	55.5069	70.5741	58.6637	51.4025	
77.6697	63.5368	79.6019	84.1304	58.728	
92.1073	113.034	85.5808	106.9755	81.1632	
156.0989	174.7671	150.7247	180.4499	107.5419	
186.8464	242.7314	174.5174	186.8354	179.1535	
249.951	257.7119	181.7005	220.7415	185.9051	
256.9694	282.9299	250.7936	251.9161	247.214	
312.5439	329.169	314.2614	315.4578	314.7749	
333.8694	383.3708	357.9694	367.1768	336.0986	
363.6725	393.5452	366.8879	368.1522	367.5061	
460.7738	499.9686	386.7553	477.0326	458.811	
478.7351	531.6494	479.6657	495.8292	491.4939	
568.3238	571.7858	537.4599	537.4718	537.6144	
585.0607	593.4272	572.4156	575.1777	576.9618	
591.4459	670.4787	579.4338	578.6067	577.8952	
652.184	688.567	645.0255	645.0842	645.2252	
741.3514	746.5989	740.0007	741.2182	741.8661	
751.6453	783.4187	874.7955	757.8985	748.5	
883.1153	867.9061	908.142	873.9649	876.3198	
893.8033	902.179	933.7803	905.7113	877.4261	
929.3431	955.398	984.7931	983.9248	985.2427	
968.772	1015.0164	991.3711	991.0782	986.4514	
1072.5823	1060.9759	994.748	1010.4162	1030.673	
1123.7066	1067.7561	1092.7897	1097.6685	1099.9936	
1124.5363	1119.8729	1135.1393	1113.3257	1115.7298	

1163.6078	1191.3607	1174.2172	1142.7555	1118.2911	
1178.974	1210.9226	1195.4959	1187.8127	1218.7636	
1234.5484	1238.0615	1217.8578	1218.3289	1222.3781	
1252.9065	1244.8898	1230.5722	1230.855	1237.0745	
1260.104	1274.3562	1238.2264	1238.1819	1242.2785	
1298.7055	1325.1336	1316.1254	1301.6134	1308.9968	
1327.32	1343.5878	1337.0411	1321.1532	1323.3075	
1339.4929	1358.0422	1345.2374	1337.2851	1336.6053	
1423.4178	1418.1929	1417.9511	1351.6201	1337.4815	
1433.3621	1447.6128	1448.0874	1429.4264	1406.3475	
1465.3472	1475.829	1452.8203	1464.067	1460.3117	
1497.6124	1484.2229	1477.5561	1475.585	1476.4949	
1502.5465	1494.8739	1487.7167	1478.9908	1481.1563	
1510.7609	1509.1273	1495.9487	1483.488	1501.0152	
1516.6614	1516.3174	1503.1991	1503.7087	1504.0287	
1894.9853	1781.13	1877.5495	1871.5744	1871.9791	
3062.9105	3037.5691	3001.2154	3013.5088	3075.5334	
3068.27	3069.771	3012.072	3074.6085	3084.1281	
3084.8277	3126.2852	3058.5812	3094.3305	3115.4915	
3108.4757	3128.7367	3068.1324	3119.101	3119.5925	
3125.3418	3150.0129	3118.5372	3120.4775	3135.4744	
3143.6672	3163.1119	3156.1672	3179.3294	3179.7782	
3155.291	3194.5038	3178.8171	3192.5158	3200.9846	
3283.5416	3237.9394	3257.6646	3299.2108	3309.6472	

Table S-III. Optimized geometries in Cartesian Coordinates of Haloalkoxy radical and its corresponding transition states (TS) and products (P) at M06-2X/6-31+G(d,p) level of theory

Haloalkoxy radical ($CH_3CH_2CH_2C(O)OCH(O^{\cdot})CF_3$)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.811405	-0.777686	0.186915
2	1	0	-4.76574	-1.188509	1.200779
3	1	0	-5.771662	-0.268072	0.07582
4	1	0	-4.795508	-1.618471	-0.514231

5	1	0	-3.691669	1.025799	0.617671
6	6	0	-3.649008	0.177341	-0.072692
7	1	0	-3.721133	0.600234	-1.079797
8	1	0	-2.212143	-1.369889	-0.611658
9	6	0	-2.303889	-0.523174	0.079582
10	1	0	-2.182691	-0.944516	1.085037
11	6	0	-1.137783	0.395646	-0.171012
12	8	0	-1.193587	1.563578	-0.462851
13	8	0	0.042205	-0.2564	-0.028023
14	6	0	1.192139	0.539012	-0.247398
15	1	0	1.212503	0.934995	-1.266101
16	6	0	2.386461	-0.363891	-0.041766
17	9	0	2.427822	-0.867344	1.198483
18	9	0	2.391419	-1.393091	-0.898571
19	9	0	3.515835	0.337677	-0.237257
20	8	0	1.258041	1.624042	0.681724

TSO_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.136623	-0.408066	-0.538443
2	1	0	-5.300065	-1.334438	0.004645
3	1	0	-6.02204	0.206373	-0.416694
4	1	0	-5.047006	-0.653382	-1.592777
5	1	0	-4.022162	0.585393	1.015464
6	6	0	-3.896118	0.3241	-0.029478
7	1	0	-3.772193	1.259267	-0.564931
8	1	0	-2.462491	-0.786585	-1.227817
9	6	0	-2.63363	-0.519025	-0.189007
10	1	0	-2.714084	-1.458556	0.351157
11	6	0	-1.395425	0.173811	0.308592
12	8	0	-1.322001	1.237605	0.810634
13	8	0	-0.297725	-0.599629	0.085953
14	6	0	0.914501	-0.237623	0.614525
15	1	0	1.114636	1.123929	0.241515

16	6	0	2.025487	-0.902779	-0.198199
17	9	0	1.953461	-2.211948	-0.077998
18	9	0	1.918097	-0.601478	-1.473851
19	9	0	3.19744	-0.507093	0.233305
20	8	0	1.067032	-0.145595	1.855901
21	8	0	1.286252	2.233845	-0.260119
22	8	0	2.43335	2.318793	-0.71132

TSα-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.921049	-0.697862	0.194017
2	1	0	-4.900251	-1.08767	1.216953
3	1	0	-5.858088	-0.15091	0.063852
4	1	0	-4.935493	-1.553905	-0.488449
5	1	0	-3.729375	1.066048	0.59458
6	6	0	-3.717483	0.201455	-0.076717
7	1	0	-3.764257	0.604582	-1.093379
8	1	0	-2.343287	-1.416389	-0.569824
9	6	0	-2.4043	-0.551453	0.10198
10	1	0	-2.30842	-0.955131	1.117366
11	6	0	-1.198623	0.311742	-0.158922
12	8	0	-1.202913	1.474231	-0.476644
13	8	0	-0.138008	-0.331602	-0.004959
14	6	0	1.336936	0.591794	-0.287885
15	1	0	0.029293	1.28942	-0.769756
16	6	0	2.490523	-0.35575	-0.052678
17	9	0	2.50144	-0.832885	1.198568
18	9	0	2.458343	-1.402984	-0.886739
19	9	0	3.649922	0.293205	-0.254054
20	8	0	1.441735	1.693419	0.617842

TSC-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.793767	-0.797615	0.125579
2	1	0	-4.748676	-1.28842	1.103258
3	1	0	-5.756705	-0.286188	0.052534
4	1	0	-4.770782	-1.579152	-0.640874
5	1	0	-3.686068	0.971704	0.703877
6	6	0	-3.636306	0.181804	-0.052353
7	1	0	-3.707949	0.683945	-1.022416
8	1	0	-2.188663	-1.308838	-0.70909
9	6	0	-2.287502	-0.521026	0.047706
10	1	0	-2.166792	-1.021209	1.016417
11	6	0	-1.126143	0.421601	-0.124143
12	8	0	-1.188026	1.608891	-0.321269
13	8	0	0.057273	-0.233111	-0.030008
14	6	0	1.177739	0.565821	-0.177386
15	1	0	1.211343	1.327343	-1.748204
16	6	0	2.376796	-0.343889	-0.040943
17	9	0	2.41746	-0.945263	1.15492
18	9	0	2.390425	-1.300763	-0.977745
19	9	0	3.502552	0.377551	-0.17547
20	8	0	1.225185	1.408833	0.671077

TSC-C

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.881592	-0.895455	0.270126
2	1	0	-4.995822	-0.723858	1.345488
3	1	0	-5.833875	-0.655218	-0.209037
4	1	0	-4.691214	-1.963318	0.121017
5	1	0	-3.964808	1.01661	-0.170752
6	6	0	-3.74944	-0.048289	-0.304748
7	1	0	-3.663343	-0.209321	-1.384203
8	1	0	-2.146435	-1.429966	0.225277

9	6	0	-2.415992	-0.374742	0.357225
10	1	0	-2.453559	-0.210101	1.441276
11	6	0	-1.281191	0.4511	-0.179234
12	8	0	-1.346052	1.294756	-1.03377
13	8	0	-0.104719	0.123518	0.438632
14	6	0	1.028284	0.873997	0.063042
15	1	0	0.875257	1.339235	-0.930713
16	6	0	2.60909	-0.468975	-0.09149
17	9	0	2.871998	-1.044636	1.083389
18	9	0	2.31737	-1.428283	-0.975328
19	9	0	3.706346	0.16537	-0.506822
20	8	0	1.320448	1.878985	0.902759

TSC-O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.185912	-0.608113	0.231208
2	1	0	-5.07978	-1.460137	0.910686
3	1	0	-6.056407	-0.031198	0.553017
4	1	0	-5.395975	-1.002606	-0.76832
5	1	0	-3.742846	0.661749	1.229142
6	6	0	-3.926531	0.254379	0.229813
7	1	0	-4.055755	1.116327	-0.432694
8	1	0	-2.83524	-0.947657	-1.227506
9	6	0	-2.705484	-0.540795	-0.216963
10	1	0	-2.5293	-1.407147	0.43271
11	6	0	-1.44546	0.277688	-0.21868
12	8	0	-1.338823	1.43557	0.088126
13	8	0	-0.376874	-0.472575	-0.629027
14	6	0	1.715707	0.596602	-0.607505
15	1	0	2.081455	0.757414	-1.64084
16	6	0	2.692844	-0.3595	0.100352
17	9	0	2.33015	-0.572142	1.366876
18	9	0	2.728594	-1.536804	-0.531487
19	9	0	3.921867	0.158497	0.093445
20	8	0	1.705368	1.805219	-0.024731

Table S-IV. Vibartional frequencies of haloalkoxy radical and its corresponding transition states (TS) and products (P) at M06-2X/6-31+G(d,p) level of theory.

Haloalkoxy radical	TSO_2(O_2 reaction)	TSα-H(α-ester rearrangement)	TSC-H(C-H bond scission)	TSC-C(C-C bond scission)	TSC-O(C-O bond scission)
18.5393	-1650.4571	-1112.7272	-937.069	-396.4396	-619.672
41.5901	38.2772	20.7603	40.5862	27.7032	9.9269
45.2432	49.9292	52.7916	54.768	31.3889	46.9648
59.3451	58.2641	54.8997	59.1931	46.8729	74.8893
101.1867	64.4424	89.987	82.2553	89.4941	86.1607
125.4384	83.5724	115.0419	105.0721	97.2895	123.0334
207.7081	85.2335	152.8152	116.3515	121.7052	140.6273
216.7969	107.2025	229.3744	200.0841	160.9319	226.3937
238.2458	148.4664	233.2812	227.6972	169.6498	236.8708
265.3325	177.6199	242.6909	243.9531	217.4856	259.8013
313.8954	188.6048	278.6203	269.186	238.4369	268.5103
361.9539	231.1978	333.5439	306.8721	282.9282	316.9185
378.5433	252.8401	371.4256	357.5409	331.0406	385.6545
458.0442	266.1534	395.4089	396.2933	343.3863	455.8624
522.2721	290.7933	487.2695	451.87	421.7206	472.2494
566.3948	312.0292	526.9014	512.3303	522.5951	540.7816
591.9899	361.4459	566.5749	533.7716	532.4252	598.3065
636.4753	392.2149	587.3264	558.1827	570.934	638.9305
676.0513	467.8322	643.9718	572.4913	573.9256	659.8946
749.0568	529.0225	712.7075	605.4114	659.5804	709.5806
750.2569	541.5033	747.8844	663.898	747.0736	781.6635
875.3307	569.6354	756.551	734.5658	749.0369	818.1915
883.6244	598.3839	779.4441	756.9687	883.3508	914.6749
926.7041	664.0129	890.5829	775.0375	916.9907	970.1838
976.8628	723.6214	924.088	872.3836	949.6297	977.0741
1058.6831	752.7541	932.2746	889.6501	987.2676	1048.966
1072.4166	762.1926	1015.4317	933.3308	1043.2378	1095.128
1119.5211	878.819	1073.4611	944.7376	1073.2616	1124.104
1128.2172	886.7567	1135.2998	1070.9311	1101.5114	1222.963
1149.4181	931.9994	1138.8818	1117.1465	1126.8277	1241.596
1182.7423	977.2545	1186.5814	1125.593	1148.6203	1274.246
1194.37	1044.4649	1255.9316	1133.1151	1183.5171	1321.688
1251.4759	1072.5151	1264.1543	1160.1663	1251.6283	1375.853

1270.9642	1105.2885	1269.1901	1253.1024	1321.2452	1422.077
1306.7324	1128.2325	1290.1607	1257.5106	1326.4218	1426.865
1314.5739	1142.8514	1323.5473	1305.2651	1332.3375	1448.531
1323.8895	1184.9639	1330.4882	1325.7555	1353.2505	1486.707
1339.9285	1251.1957	1394.3653	1330.2909	1361.1343	1535.517
1351.1124	1267.2906	1428.9958	1371.7072	1422.142	1568.071
1422.6948	1289.1078	1458.1144	1420.8919	1431.4089	1576.683
1431.8102	1324.1536	1496.4447	1431.2554	1460.5368	1605.992
1463.9374	1328.66	1502.8863	1463.8973	1498.8024	1635.105
1499.8153	1338.0582	1508.8425	1502.6281	1508.0866	1644.435
1507.568	1364.6823	1517.1205	1508.2963	1514.4548	1652.179
1515.1886	1420.0374	1600.1836	1517.2575	1659.8531	1667.986
1883.577	1430.5693	1678.0957	1794.8501	1890.422	1761.661
2999.7527	1462.0833	1792.8961	1926.1378	3061.217	3195.695
3060.9876	1501.1979	3063.8	3062.9143	3068.2774	3215.029
3070.9895	1509.9474	3070.5689	3068.9879	3086.1278	3226.217
3086.7333	1517.4543	3088.1167	3087.4039	3104.7556	3239.123
3107.971	1617.1851	3120.7596	3109.456	3105.412	3247.756
3124.5961	1694.9093	3134.0996	3126.2644	3124.0572	3264.688
3143.5832	1888.8555	3148.901	3145.3299	3143.6021	3275.489
3151.1666	3062.8913	3154.7679	3151.7899	3147.1805	3392.194
	3068.9852				
	3088.4202				
	3106.6376				
	3125.783				
	3144.9791				
	3151.968				

Table S-V: Summary of average values of the rate coefficients of different bath gases and various fluence its corresponding rate coefficients relative to ethane as a reference compound at 298 K.

	Buffer gas	($k_{2,2,2\text{-TFEB}}/k_{ethane}$)	$k\times10^{11}$
	N_2	1.11± 0.63	6.60 ± 3.74
Ethane	N_2-O_2	1.00 ± 0.05	6.01 ± 0.31
	Laser fluence		
	50 mJ pulse^{-1}	0.99 ± 0.04	5.87 ± 0.24
	75 mJ pulse^{-1}	1.15 ± 0.02	6.82 ± 0.13
	100 mJ pulse^{-1}	1.18 ± 0.06	6.94 ± 0.36

33: Complete Reference

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