A Computational Study on the Atmospheric Oxidation of CF₃OCHFCF₃ (HFE-227)

Initiated by ˙OH radical: Mechanism, Kinetics, Degradation of Product Radicals and

Ecotoxicity

Geetaraj Dutta[a], Udeshna Priya Kakati[a], Nand Kishor Gour[b] and Subrata Paul[a*]

[a]Department of Chemistry, Assam University, Silchar-788011, Assam, India

[b]Department of Chemical Sciences, Tezpur University, Tezpur-784028, Assam, India

Email: subrata.paul@aus.ac.in

Table S1: Cartesian coordinate of all species calculated at M06-2X/6-311+G(d,p).

Species		X-axis	Y-axis	Z-axis
CF₃OCFHCF₃ (R)	O	-0.546625000	-0.118087000	0.524518000
	C	0.416870000	0.481236000	-0.279521000
	H	0.173668000	0.408575000	-1.342682000
	F	0.559969000	1.782687000	0.058580000
	C	-1.812189000	-0.131658000	0.028152000
	F	-1.887171000	-0.868918000	-1.082722000
	F	-2.232796000	1.092115000	-0.283479000
	F	-2.601682000	-0.648444000	0.941911000
	C	1.736332000	-0.239613000	0.001621000
	F	2.051485000	-0.190204000	1.287587000
	F	2.711386000	0.332975000	-0.701242000
	F	1.638059000	-1.513951000	-0.371188000
˙OH	O	0.000000000	0.000000000	0.108003000
	H	0.000000000	0.000000000	-0.864026000
TS1	C	1.923887000	-0.044519000	0.119331000
	F	2.541868000	-1.073195000	0.605705000
	F	1.896363000	0.937378000	1.046634000
	F	2.628338000	0.556157000	-0.846933000
	O	1.037310000	-0.968263000	-1.149262000
	H	0.575590000	-0.319143000	-1.710151000
	O	0.255124000	-0.480912000	0.590927000
	C	-0.678235000	0.508975000	0.450287000
	F	-0.336348000	1.367839000	-0.571212000
	C	-2.032632000	-0.099197000	0.071572000
	F	-1.961295000	-0.710132000	-1.109445000
	F	-2.956045000	0.859593000	-0.007704000
	F	-2.415945000	-0.978817000	0.989183000
	H	-0.765623000	1.091579000	1.373649000
TS1a	O	-1.528233000	1.178454000	-0.120252000
	C	-1.233441000	0.150031000	0.427162000
	H	-1.032131000	0.029976000	1.501352000
	F	-1.590480000	-1.048748000	-0.100787000
	C	0.753652000	-0.001770000	-0.005968000
	F	1.335759000	1.054273000	0.499345000

	F	0.866968000	-0.051826000	-1.302469000
	F	1.180723000	-1.103386000	0.563188000
TS2	C	-0.914485000	0.975032000	-0.217312000
	F	-0.924400000	1.514025000	0.970004000
	C	-1.613001000	-0.398912000	-0.105342000
	F	-1.077753000	-1.205951000	0.788189000
	F	-1.689263000	-0.998786000	-1.282181000
	F	-2.865154000	-0.110450000	0.285102000
	H	-1.389362000	1.550520000	-1.005474000
	O	0.655997000	1.945753000	-0.628448000
	H	0.863299000	1.915631000	-1.576771000
	O	0.640676000	-0.079882000	-0.809952000
	C	1.651451000	-0.346502000	0.036522000
	F	1.823486000	-1.670098000	0.085205000
	F	1.419192000	0.082760000	1.279644000
	F	2.803770000	0.191741000	-0.369715000
RC	O	-0.292097000	-0.788083000	0.326621000
	C	0.490809000	0.352966000	0.141082000
	H	0.126746000	0.977182000	-0.677422000
	F	0.514753000	1.081392000	1.279522000
	C	-1.606198000	-0.673493000	0.023968000
	F	-1.794018000	-0.386508000	-1.266936000
	F	-2.200697000	0.295524000	0.727897000
	F	-2.190331000	-1.819608000	0.296674000
	C	1.907988000	-0.141167000	-0.148364000
	F	2.361831000	-0.920399000	0.824038000
	F	2.723955000	0.902831000	-0.274550000
	F	1.919965000	-0.827551000	-1.290139000
	O	-1.512233000	2.583826000	-0.504435000
	H	-2.466799000	2.495897000	-0.668741000
TS3	O	-0.550612000	-0.774280000	-0.050245000
	C	0.425762000	0.042732000	0.479035000
	H	0.208767000	1.230544000	0.299451000
	F	0.551312000	-0.143009000	1.798373000
	C	-1.822101000	-0.281539000	-0.109301000
	F	-1.927354000	0.638551000	-1.073839000
	F	-2.186615000	0.286786000	1.030370000
	F	-2.626850000	-1.280135000	-0.389060000
	C	1.744414000	-0.270962000	-0.228587000
	F	2.054112000	-1.557885000	-0.116414000
	F	2.721221000	0.451897000	0.300671000
	F	1.630415000	0.030995000	-1.520022000
	O	0.065315000	2.472135000	-0.016023000
	H	-0.361012000	2.400437000	-0.886895000
CFHO˙CF$_3$(P1)	O	-1.435451000	-1.209737000	0.074742000
	C	-0.904526000	-0.092811000	-0.390654000
	H	-0.962754000	-0.123116000	-1.493665000
	F	-1.515910000	1.044739000	0.052926000
	C	0.592139000	0.005654000	-0.004100000

	F	0.742108000	-0.028316000	1.313634000
	F	1.105925000	1.141013000	-0.463222000
	F	1.259065000	-1.010330000	-0.540643000
CF$_3$OH(P1)	C	-0.002790000	0.024129000	0.000000000
	F	-1.121055000	0.725688000	0.000000000
	F	-0.002790000	-0.778075000	1.073472000
	F	-0.002790000	-0.778075000	-1.073472000
	O	1.037185000	0.870367000	0.000000000
	H	1.858971000	0.366453000	0.000000000
COFH (P1a)	O	1.120162000	-0.246996000	-0.000001000
	C	0.127393000	0.377310000	0.000002000
	H	0.017903000	1.465961000	0.000008000
	F	-1.082618000	-0.194873000	-0.000001000
CF$_3$O$^\cdot$ (P2)	C	-0.006812000	0.000234000	0.034295000
	F	0.772096000	1.070873000	-0.035093000
	F	-0.848916000	-0.006313000	-0.990368000
	F	0.772087000	-1.071250000	-0.022208000
	O	-0.777066000	0.007350000	1.152906000
CHFOHCF$_3$(P2)	C	-0.852258000	0.017663000	-0.426262000
	H	-0.909377000	0.068567000	-1.518103000
	F	-1.389759000	1.178797000	0.066220000
	C	0.616834000	-0.021241000	-0.005552000
	F	0.749666000	-0.069713000	1.313129000
	F	1.244737000	1.067112000	-0.454686000
	F	1.213074000	-1.090818000	-0.535013000
	O	-1.463047000	-1.077524000	0.110412000
	H	-2.333160000	-1.195302000	-0.281156000
CF$_3$OC$^\cdot$FCF$_3$(P3)	O	-0.582053000	-0.011331000	0.631742000
	C	0.417835000	0.521646000	-0.108584000
	F	0.550625000	1.827551000	0.017069000
	C	-1.803251000	-0.128586000	0.010882000
	F	-1.731745000	-0.957432000	-1.021625000
	F	-2.231238000	1.045791000	-0.432541000
	F	-2.648402000	-0.601397000	0.897355000
	C	1.719051000	-0.236350000	-0.012638000
	F	2.214439000	-0.200140000	1.228317000
	F	2.617583000	0.298438000	-0.831694000
	F	1.523695000	-1.507211000	-0.344871000
H$_2$O	O	0.000000000	0.000000000	0.116566000
	H	0.000000000	0.761418000	-0.466263000
	H	0.000000000	-0.761418000	-0.466263000
O$_2$	O	0.000000000	0.000000000	0.593573000
	O	0.000000000	0.000000000	-0.593573000
NO	O	0.000000000	0.000000000	0.531240000
	N	0.000000000	0.000000000	-0.607132000
CF$_3$OCF(OO·)CF$_3$	O	-0.668094000	-0.493178000	-0.455675000
	C	0.364394000	0.222274000	0.085024000
	F	0.185035000	0.515934000	1.370934000
	C	-1.960976000	-0.190332000	-0.081869000
	F	-2.162805000	1.117106000	-0.019049000

	F	-2.241993000	-0.715379000	1.099609000
	F	-2.752307000	-0.717828000	-0.988574000
	C	1.639435000	-0.640558000	-0.070284000
	F	1.491419000	-1.765523000	0.615370000
	F	2.691175000	0.014759000	0.394690000
	F	1.834368000	-0.928007000	-1.348220000
	O	0.473522000	1.428288000	-0.672238000
	O	1.236929000	2.310158000	-0.087095000
CF$_3$OCF(O$^\bullet$)CF$_3$	O	-0.548575000	-0.563800000	-0.160375000
	C	0.403632000	0.445941000	-0.069760000
	F	0.238091000	1.128126000	1.086554000
	C	-1.863391000	-0.202378000	-0.021880000
	F	-2.101056000	0.976513000	-0.595368000
	F	-2.212729000	-0.119569000	1.251683000
	F	-2.592132000	-1.128868000	-0.606160000
	C	1.790202000	-0.281305000	-0.001215000
	F	1.825105000	-1.030625000	1.086014000
	F	2.756617000	0.622482000	0.058246000
	F	1.963077000	-1.041745000	-1.067718000
	O	0.439149000	1.260004000	-1.134892000
NO$_2$	N	0.000000000	0.315490000	0.000000000
	O	1.090756000	-0.138027000	0.000000000
	O	-1.090756000	-0.138027000	0.000000000
TS3a	O	-0.433795000	0.471432000	1.036223000
	C	0.591674000	0.718855000	0.426326000
	F	0.838542000	1.921010000	-0.075110000
	C	-1.904384000	-0.111287000	-0.020732000
	F	-1.365530000	-0.343881000	-1.194614000
	F	-2.806333000	0.828462000	-0.076706000
	F	-2.359290000	-1.197246000	0.534146000
	C	1.634132000	-0.300480000	0.003515000
	F	2.816672000	-0.022348000	0.553255000
	F	1.790872000	-0.297724000	-1.320847000
	F	1.256382000	-1.512051000	0.386048000
$\cdot$CF$_3$	C	-0.275567000	0.176010000	0.000000000
	F	-0.275567000	-0.566221000	1.083542000
	F	-0.275567000	-0.566221000	-1.083542000
	F	0.734845000	1.015102000	0.000000000
COFCF$_3$	O	1.551286000	1.157909000	-0.000054000
	C	0.946125000	0.156367000	-0.000013000
	F	1.497373000	-1.049972000	0.000024000
	C	-0.588234000	0.017567000	0.000005000
	F	-0.980554000	-0.652499000	-1.080070000
	F	-1.153799000	1.209715000	-0.000016000
	F	-0.980535000	-0.652452000	1.080116000
TS3b	O	0.641103000	-0.547150000	-0.265436000
	C	-0.644133000	0.642776000	0.213930000
	F	-0.581454000	1.549172000	-0.745520000
	C	1.950886000	-0.182060000	-0.050383000
	F	2.342533000	-0.435000000	1.183830000

	F	2.163643000	1.097573000	-0.311115000
	F	2.652183000	-0.924999000	-0.894580000
	C	-1.848020000	-0.300802000	-0.024709000
	F	-1.854239000	-0.763586000	-1.263443000
	F	-2.958112000	0.407968000	0.174738000
	F	-1.817855000	-1.306810000	0.826855000
	O	-0.175188000	0.849857000	1.319196000
TS4	O	-0.885743000	0.583008000	0.508399000
	C	0.087950000	0.838421000	-0.396288000
	H	-0.101453000	0.450966000	-1.394674000
	F	0.403832000	2.121426000	-0.431410000
	C	-1.926411000	-0.191149000	0.071000000
	F	-1.498875000	-1.345180000	-0.431159000
	F	-2.614873000	0.430365000	-0.885902000
	F	-2.712638000	-0.418069000	1.095099000
	C	1.681887000	-0.365822000	-0.049188000
	F	3.008499000	-0.280929000	0.099399000
	F	1.616430000	-0.655668000	-1.402612000
	F	1.180511000	-1.420589000	0.551639000
	O	1.450175000	0.732851000	1.376637000
	H	2.079465000	1.451272000	1.205772000
TS4a	O	-0.660375000	-0.716885000	0.639540000
	C	-1.662836000	-0.578104000	-0.056233000
	H	-1.997960000	-1.232006000	-0.855388000
	F	-2.373272000	0.548184000	0.023208000
	C	0.902806000	0.038841000	-0.001716000
	F	1.836266000	-0.873871000	0.070010000
	F	1.200255000	1.086108000	0.721465000
	F	0.652434000	0.373208000	-1.249487000
CF$_3$OC·FH	O	0.364316000	0.085475000	-0.804163000
	C	1.491104000	0.580455000	-0.213807000
	H	1.371350000	1.327116000	0.564294000
	F	2.374612000	-0.369050000	0.062919000
	C	-0.739581000	-0.034983000	-0.017650000
	F	-1.132963000	1.151129000	0.454059000
	F	-0.510307000	-0.820292000	1.033016000
	F	-1.708566000	-0.548870000	-0.743577000
TS5	O	-0.848097000	0.538776000	0.585747000
	C	0.212835000	0.773611000	-0.262991000
	H	0.058782000	0.188183000	-1.183659000
	F	0.241813000	2.037797000	-0.761682000
	C	-1.865331000	-0.207300000	0.073856000
	F	-1.444726000	-1.426623000	-0.274947000
	F	-2.396309000	0.352805000	-1.012500000
	F	-2.789098000	-0.318125000	1.000536000
	C	1.668907000	-0.516942000	-0.068618000
	F	2.877515000	-0.020413000	-0.220982000
	F	1.422155000	-1.321870000	-1.096881000
	F	1.535882000	-1.192708000	1.036884000
	O	1.219704000	1.286719000	1.156350000

	H	1.844796000	1.913863000	0.759552000
CF₃OC(OH)FH	O	-0.154216000	-0.361365000	-0.569954000
	C	-1.269754000	-0.061646000	0.209986000
	H	-1.021013000	-0.051845000	1.275235000
	F	-1.701028000	1.194621000	-0.107470000
	C	1.046507000	-0.048737000	-0.035232000
	F	1.294585000	-0.760142000	1.071734000
	F	1.128952000	1.238166000	0.306690000
	F	1.976363000	-0.317875000	-0.927709000
	O	-2.205683000	-0.982521000	-0.137668000
	H	-3.050145000	-0.727704000	0.248001000

Table S2: Frequency analysis of all species calculated at M06-2X/6-311+G(d,p) level of theory.

Species	M06-2X/6-311+G(d,p) level of theory Frequencies (cm^{-1})
CF₃OCFHCF₃	34.1769, 54.0259, 73.8924, 161.3739, 200.3201, 248.9358, 325.3116, 345.2134, 428.1915, 459.5323, 526.6559, 549.3247, 585.231, 637.423, 660.7839, 691.3451, 749.5468, 907.0962, 944.5034, 1158.6475, 1176.3462, 1230.9057, 1243.8721, 1274.9536, 1280.0086, 1346.7222, 1352.7257, 1409.0932, 1482.1743, 3128.8349
˙OH	3790.097
TS1	633.1286i, 41.2909, 60.7679, 86.0545, 112.8464, 179.5781, 198.3505, 246.2085, 304.4665, 362.8518, 415.4062, 416.8037, 484.4391, 524.8386, 567.8097, 591.7517, 597.4657, 615.9049, 625.5674, 691.6148, 726.0056, 740.2399, 882.7118, 920.3269, 934.1955, 1021.9032, 1096.295, 1174.3031, 1222.9537, 1269.346
TS1a	388.5735i, 45.0317, 141.0044, 168.5538, 254.8413, 340.1729, 532.1641, 537.7653, 653.6487, 666.9557, 946.5521, 1043.41, 1102.3735, 1321.6606, 1337.7175, 1354.5807, 1684.5353, 3050.6466
TS2	666.2466i, 34.9714, 70.4403, 76.0014, 118.4119, 163.5177, 214.4448, 248.1613, 278.3485, 344.8162, 394.6923, 420.6392, 463.481, 487.2808, 512.887, 556.0644, 566.5452, 634.2052, 639.7032, 657.1406, 671.7359, 690.5599, 845.6425, 884.4599, 932.1022, 1184.575, 1199.6123, 1219.1071, 1229.9718, 1246.6544, 1255.751, 1291.4068, 1370.6713, 1431.4262, 3201.3271, 3802.5512
RC	19.9551, 52.5979, 57.0228, 69.5427, 91.6254, 126.2981,133.6564, 162.281, 199.3469, 247.6455, 253.451, 325.0349, 345.3856, 427.9476, 459.9196, 528.5291, 549.3961, 585.2691, 636.4499, 660.9542, 692.5195, 748.6723, 907.7292, 940.3582, 1160.8554, 1166.9816, 1227.5406, 1241.7204, 1272.5975, 1283.8393, 1343.1933, 1352.6015, 1413.528, 1486.4189, 3149.108, 3787.1109
TS3	1652.3402i, 34.5263, 49.2835, 64.2071, 76.9503, 127.0628, 148.7185, 161.0917, 199.4927, 248.9766, 324.2902, 346.405,

	406.5342, 439.4876, 476.7832, 547.298, 554.2656, 589.5643, 631.8213, 668.6792, 706.2005, 761.371, 805.6325, 908.8863, 943.2878, 1175.446, 1189.4784, 1214.2702, 1237.0284, 1281.4446, 1289.6393, 1304.0837, 1348.9132, 1403.0399, 1429.7609, 3792.7186
CFHO˙CF$_3$	75.5076, 222.9803, 241.4399, 369.9202, 409.6732, 529.1513, 579.3196, 606.7538, 703.7371, 848.3697, 1072.6628, 1133.6454, 1171.6023, 1238.1336, 1287.7665, 1312.817, 1336.6142, 2981.9342
CF$_3$OH	201.6106, 446.4758, 454.532, 607.1671, 629.6752, 642.1447, 929.2255, 1131.4153, 1220.7266, 1333.2191, 1429.2364, 3881.3593
COFH	682.4861, 1056.8665, 1113.9115, 1385.1925, 1950.4329, 3137.4962
CF$_3$O˙	278.3, 420.7744, 589.0803, 605.5419, 628.8799, 924.7608, 1251.6273, 1271.3196, 1313.2978
CHFOHCF$_3$	78.5961, 222.3481, 250.8782, 286.5738, 375.4334, 424.8371, 532.4549, 587.0073, 597.0796, 726.8894, 867.0796, 1112.5926, 1179.2927, 1219.9382, 1254.4412, 1279.7273, 1346.6104, 1390.176, 1517.7397, 3097.5887, 3900.5713
CF$_3$OC˙FCF$_3$	28.3595, 41.1709, 59.9133, 143.8076, 194.0692, 231.4903, 323.9394, 351.3952, 432.7428, 461.6375, 517.2296, 554.1837, 593.1132, 632.5148, 646.3014, 685.7915, 747.9243, 881.8051, 931.0843, 1155.3468, 1220.3332, 1231.6851, 1266.4546, 1291.4539, 1338.44, 1348.0636, 1448.6366
H$_2$O	1597.8993, 3895.0952, 4000.8932
O$_2$	1762.8482
NO	2086.4877
CF$_3$OCF(OO˙)CF$_3$	46.1102, 50.4713, 78.7181, 106.1047, 146.6784, 216.5844, 222.5036, 275.2692, 307.4583, 354.8636, 367.1294, 375.4494, 432.8162, 507.6774, 551.967, 562.6684, 600.5141, 637.9711, 659.9439, 727.6461, 777.5933, 842.8284, 931.6075, 1073.2909, 1176.7454, 1212.6501, 1248.2643, 1280.4359, 1294.7229, 1298.6571, 1317.0337, 1350.4236, 1418.6657
CF$_3$OCF(O˙)CF$_3$	44.757, 53.9619, 89.8291, 121.8528, 209.3299, 234.9626, 307.0725, 319.3839, 350.6361, 375.1869, 422.0962, 513.7631, 531.1481, 560.6179, 590.8103, 635.5826, 660.0782, 678.0321, 765.2157, 864.7866, 915.9817, 1059.0298, 1162.8399, 1172.44, 1264.5746, 1272.5525, 1293.2246, 1301.9607, 1321.0477, 1345.5488
NO$_2$	783.541, 1475.6982, 1797.0777
TS3a	544.4383i, 20.6527, 24.1859, 47.7979, 96.3922, 167.1406, 207.8467, 237.9445, 282.4046, 400.7315, 441.3079, 505.7156, 529.1698, 541.8584, 598.2825, 639.9052, 684.0497, 711.4086, 824.8519, 1028.0491, 1150.5805, 1223.5041, 1281.6819, 1339.8589, 1364.0625, 1384.166, 1585.3864
·CF$_3$	518.7006, 518.9451, 708.1057, 1115.497, 1305.4375, 1305.7606
COFCF$_3$	46.7558, 229.4933, 241.7337, 389.3416, 432.6283, 523.7173, 601.6546, 705.9957, 783.0062, 832.9641, 1139.2637, 1248.5205,

	1303.8376, 1380.7965, 2014.3465
TS3b	647.1995i, 43.5621, 50.6714, 82.8385, 105.8096, 162.3061, 231.7447, 253.9328, 293.2952, 359.5187, 385.0402, 429.4407, 454.7603, 516.2948, 571.7958, 602.6372, 618.2081, 652.2026, 672.921, 709.6438, 831.9469, 925.7958, 1142.9003, 1199.6713, 1262.2399, 1281.8336, 1292.6045, 1313.4996, 1369.9782, 1607.8881
TS4	604.2236i, 31.2362, 39.943, 53.0495, 87.5614, 190.8019, 213.2806, 239.3019, 310.14, 345.5054, 384.972, 399.8665, 452.3971, 472.0501, 480.4313, 538.5964, 563.2445, 590.9651, 626.3462, 655.3104, 715.9463, 724.7953, 846.1876, 934.0491, 951.7157, 1053.05, 1152.0285, 1228.3403, 1234.4575, 1250.7649, 1275.4023, 1310.0166, 1360.0084, 1455.775, 3171.2127, 3808.2494
TS4a	598.7678i, 30.3566, 83.779, 176.3715, 216.1052, 373.6766, 528.5074, 541.2353, 628.2779, 666.0384, 767.8091, 1026.9823, 1129.0865, 1327.0231, 1342.2218, 1345.1018, 1501.1357, 3204.8321
CF$_3$OC·FH	56.5966, 79.4133, 263.817, 377.6385, 442.2661, 529.0524, 613.0931, 664.6606, 671.2931, 865.1673, 942.8977, 1188.0527, 1207.0245, 1238.6327, 1265.0664, 1338.6196, 1389.4911, 3198.15
TS5	752.8676i, 36.3469, 48.783, 58.8364, 91.3063, 178.917, 225.126, 272.1654, 278.1146, 324.7991, 349.5445, 391.0726, 452.1913, 463.1578, 505.6038, 536.81, 553.9232, 557.9043, 627.5371, 669.2885, 699.8011, 741.1284, 911.194, 959.376, 1023.4842, 1058.2825, 1192.4297, 1225.1875, 1239.0938, 1286.0953, 1333.7792, 1347.5229, 1468.5158, 1491.6408, 2970.8068, 3802.6161
CF$_3$OC(OH)FH	45.5974, 78.9174, 188.9171, 226.9861, 360.5077, 389.0365, 466.4187, 527.0629, 598.0881, 630.7885, 673.3853, 733.8657, 927.4805, 1080.0378, 1119.588, 1226.1602, 1236.97, 1272.9504, 1317.1588, 1355.4885, 1398.646, 1494.9158, 3111.1573, 3892.5505

Table S3: T1 diagnostic value of all the species at CCSD(T)//M06-2x/6-311+G(d,p) level of theory.

Species	T1 diagnostic value
$CF_3OCFHCF_3$ (R)	0.012906
$\cdot OH$	0.010184
TS1	0.02455
TS1a	0.02321747
TS2	0.025911
RC	0.014857
TS3	0.017038
$CFHO\cdot CF_3$ (P1)	0.017063
CF_3OH (P1)	0.012289
COFH (P1a)	0.0168613
$CF_3O\cdot$ (P2)	0.014453
$CHFOHCF_3$(P2)	0.012913
$CF_3OC\cdot FCF_3$(P3)	0.014189
H_2O	0.010478
O_2	0.01306012
NO	0.02114424
$CF_3OCF(OO\cdot)CF_3$	0.01762259
$CF_3OCF(O\cdot)CF_3$	0.01985792
NO_2	0.02479014
TS3a	0.02118661
$\cdot CF_3$	0.015318
$COFCF_3$	0.01469563

TS3b	0.01985792
TS4	0.023266
TS4a	0.02353597
$CF_3OC^.FH$	0.014263
TS5	0.021706
$CF_3OC(OH)FH$	0.012825

Table S4: The zero point corrected total energy (E_0) [in hartree] and relative energy (ΔE) [kcal mol^{-1}] of $CF_3OCFHCF_3$+ $^.OH$ reaction calculated at M06-2x/6-311+G(d,p) and CCSD(T)// M06-2x/6-311+G(d,p) level of theory.

Species	M06-2x /6-311+G(d,p)		CCSD(T)// M06-2x /6-311+G(d,p)	
	E_0	ΔE	E_0	ΔE
R ($CF_3OCFHCF_3$)+ $^.OH$	-964.7133487	0	-963.0397577	0
TS1	-964.5968688	73.09	-962.9196767	75.35
TS2	-964.607475	66.44	-962.9259291	71.43
RC	-964.7193407	-3.76	-963.0407644	-0.63
TS3	-964.7075766	3.62	-963.0324027	4.62
TS4	-964.6088325	65.58	-962.9319217	67.67
TS5	-964.6130159	62.96	-962.9344321	66.09
$CFHO^.CF_3$(P1) + CF_3OH(P1)	-964.7372514	-14.99	-963.0616605	-13.74
$CF_3O^.$ (P2) + $CHFOHCF_3$(P2)	-964.7166544	-2.07	-963.0417114	-1.23
$CF_3OC^.FCF_3$(P3) + H_2O	-964.7361258	-14.29	-963.0607166	-13.15
$CF_3OC^.FH$ + CF_3OH (P4)	-964.7377158	-15.29	-963.0628656	-14.50

CF$_3$OC(OH)FH + ·CF$_3$ (P5)	-964.729246	-9.98	-963.0494215	-6.06

Table S5: The zero point corrected total energy (E$_0$) [in hartree] and relative energy (ΔE) [kcal mol^{-1}] of aerial degradation of product radicals CFHO˙CF$_3$ (P1), CF$_3$OC˙FCF$_3$ (P3) in the presence of NO radical and CF$_3$OC˙FH (P4) M06-2x/6-311+G(d,p) and CCSD(T)// M06-2x/6-311+G(d,p) level of theory.

Species	M06-2x/6-311+G(d,p)		CCSD(T)//M06-2x/6-311+G(d,p)	
P1 degradation	E$_0$	ΔE	E$_0$	ΔE
CFHO˙CF$_3$ (P1)	-551.28997	0	-550.331519	0
TS1a	-551.27069	12.10	-550.307344	15.17
˙CF$_3$ + HFCO	-551.282784	4.51	-550.324906	4.15
P3 degradation	E$_0$	ΔE	E$_0$	ΔE
CF$_3$OC˙FCF$_3$ + O$_2$ + NO	-1168.45621	0	-1166.50126	0
CF$_3$OCF(OO˙)CF$_3$+ NO	-1168.51344	-35.91	-1166.54660	-28.45
CF$_3$OCF(O˙)CF$_3$+ NO$_2$	-1168.59316	-85.94	-1166.61198	-69.48
TS3a + O$_2$ + NO	-1168.41347	26.82	-1166.46128	25.09
˙CF$_3$+ COFCF$_3$ + O$_2$+ NO	-1168.43388	14.01	-1166.48778	8.46
TS3b + NO$_2$	-1168.50315	-29.46	-1166.53422	-20.68
CF$_3$O˙ + COFCF$_3$ + NO$_2$	-1168.56918	-70.89	-1166.60317	-63.95
P4 degradation	E$_0$	ΔE	E$_0$	ΔE
CF$_3$OC˙FH (P4)	-551.292435	0	-550.332725	0
TS4a	-551.257481	21.93	-550.291615	25.32
˙CF$_3$ + HFCO	-551.282784	6.06	-550.324907	4.91

Table S6: The excitation energy (T$_V$) (in eV), oscillator strength (f) (in atomic units) and wavelength (λ) (in nm) of the first five excited states of title compound and intermediates and products

Species	Parameters	Excited states				
		1	2	3	4	5
$CF_3OCHFCF_3$	T_v	12.3185	12.9365	13.2696	13.4557	13.5932
	λ	100.65	95.84	93.44	92.14	91.21
	f	0.0338	0.0492	0.0030	0.0164	0.0638
$CFHO^{\cdot}CF_3$(P1)	T_v	0.6366	4.7331	9.1122	10.8470	11.2058
	λ	1947.49	261.95	136.06	114.30	110.64
	f	0.0001	0.0020	0.0432	0.0187	0.0111
CF_3OH(P1)	T_v	10.6861	12.5630	13.4907	13.9950	14.1129
	λ	116.02	98.69	91.90	88.59	87.85
	f	0.0192	0.0537	0.0261	0.0046	0.0000
$CF_3O^{\cdot}$ (P2)	T_v	0.1932	4.4640	11.5795	11.8526	12.0154
	λ	6417.80	277.74	107.07	104.60	103.19
	f	0.0000	0.0016	0.0010	0.0101	0.0161
$CHFOHCF_3$(P2)	T_v	9.8276	11.0272	11.9173	12.1256	12.6094
	λ	126.16	112.44	104.04	102.25	98.33
	f	0.0085	0.0276	0.1135	0.0251	0.0024
$CF_3OC^{\cdot}FCF_3$(P3)	T_v	8.5439	9.2593	9.9301	10.1563	10.5634
	λ	145.11	133.90	124.86	122.08	117.37
	f	0.0083	0.0165	0.0013	0.0187	0.0468
$CF_3OCF(OO\cdot)CF_3$	T_v	0.8107	7.1684	7.8481	8.2526	8.8812
	λ	1529.28	172.96	157.98	150.24	139.60
	f	0.0000	0.0079	0.0009	0.0373	0.0002

CF$_3$OCF(O$^{\cdot}$)CF$_3$	T$_v$	0.3162	4.4214	9.6310	10.1231	11.1591
	λ	3920.68	280.42	128.73	122.48	111.11
	f	0.0000	0.0008	0.0339	0.0048	0.0116
$^{\cdot}$CF$_3$	T$_v$	9.6824	10.4623	10.4631	11.0673	11.1828
	λ	128.05	118.51	118.50	112.03	110.87
	f	0.0254	0.0545	0.0545	0.0521	0.0000
COFCF$_3$	T$_v$	6.3465	10.0566	10.3216	11.4376	12.5370
	λ	195.36	123.29	120.12	108.40	98.89
	f	0.0015	0.2175	0.0000	0.0651	0.0328
CF$_3$OC$^{\cdot}$FH (P4)	T$_v$	8.2595	8.7340	9.1157	9.2163	9.7168
	λ	150.11	141.96	136.01	134.53	127.60
	f	0.0257	0.0088	0.0043	0.0125	0.0335
CF$_3$OC(OH)FH(P5)	T$_v$	9.8743	11.6378	11.9508	12.3824	13.0057
	λ	125.56	106.54	103.75	100.13	95.33
	f	0.0085	0.0235	0.0941	0.0271	0.0470
HFCO	T$_v$	6.4586	10.0198	10.6133	10.7595	11.5058
	λ	191.97	123.74	116.82	115.23	107.76
	f	0.0025	0.1612	0.0002	0.0244	0.1479

Table S7. Classification of acute and chronic toxicity. The concentrations are expressed in milligrams per liter (mg/L).

Classification	Acute toxicity[1]	Chronic toxicity[2]
Not harmful	$LC_{50}/EC_{50} > 100$	$ChV > 10$
Harmful	$10 < LC_{50}/EC_{50} < 100$	$1 < ChV < 10$
Toxic	$1 < LC_{50}/EC_{50} < 10$	$0.1 < ChV < 1$
Very Toxic	$LC_{50}/EC_{50} < 1$	$ChV < 0.1$

[1]Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC);

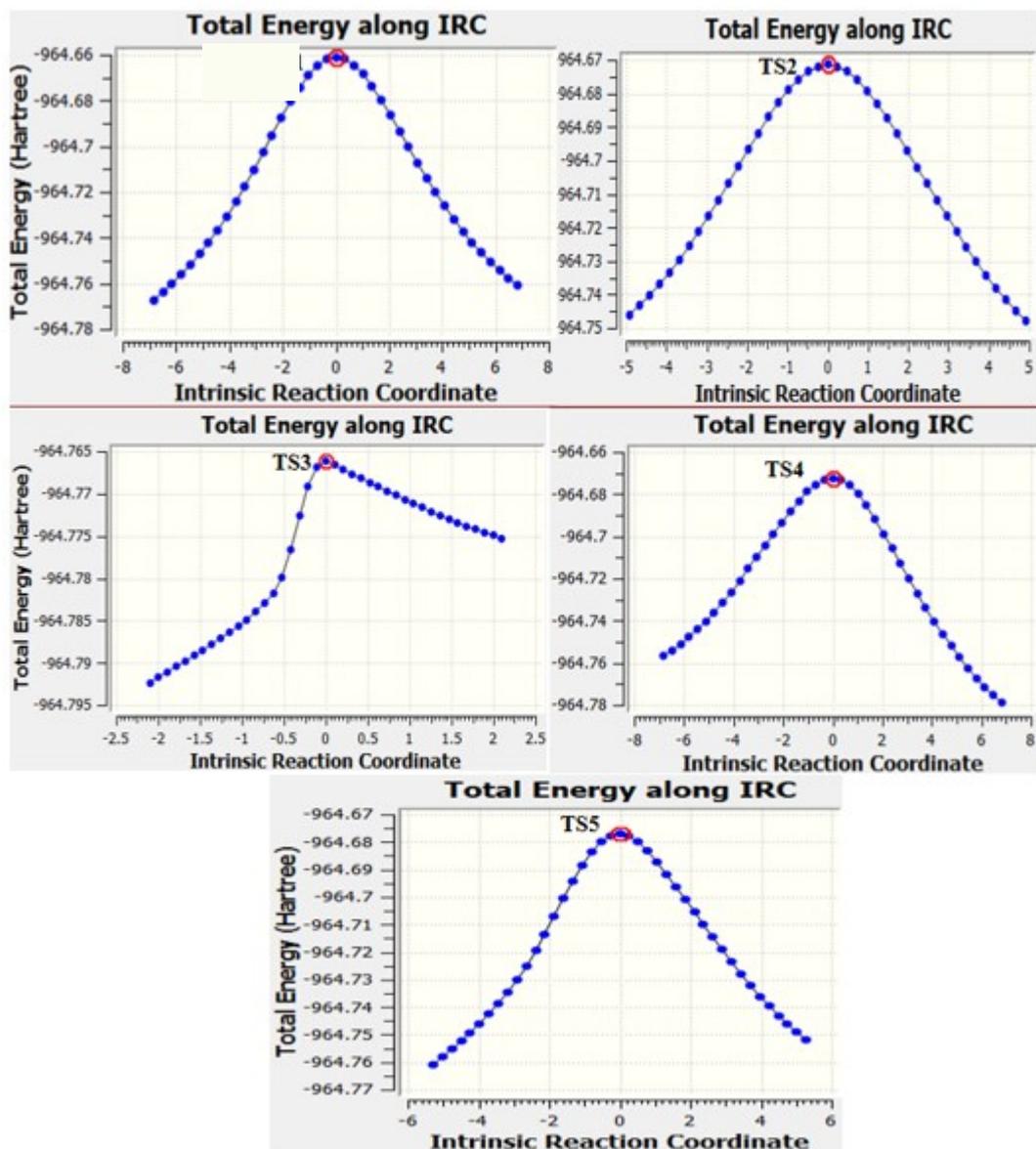[2]Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004).

Figure S1: IRC plots for R1-R5 reaction pathways.