Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Oxidation Pathways and Kinetics of 1,1,2,3-Tetrafluoropropene (CF_2=CF-CH_2F) Reaction with Cl-atoms and Subsequent Aerial Degradation of its Product Radicals in Presence of NO

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Table S1: T1 diagnostic values of all the species involved in the CF_2=CF-CH_2F + Cl reaction at CCSD(T) level of theory.

Species	T1 diagnostic value	
	CCSD(T)/6-31+G(d,p)	CCSD(T)/6-311++G(d,p)
CF_2=CF-CH_2F	0.01473491	0.01345089
Cl	0.00527446	0.00570653
RC	0.01565944	0.0146616
TS1	0.02116631	0.02042312
TS2	0.02108053	0.0204491
TS3	0.02086858	0.02013525
TS4	0.02141117	0.0207179
P1	0.01550945	0.0144888
P2	0.01552919	0.01448403
P3	0.02297249	0.02213417
HCl	0.0052296	0.00563986
O_2	0.01537337	0.01508543
CF_2(Cl)CF($OO^{\bullet}$)CH_2F	0.02046753	0.01922937

NO	0.02456795	0.02667502
$CF_2(Cl)CF(O^{\bullet})CH_2F$	0.01683104	0.01574364
NO_2	0.02721841	0.02722437
TS5	0.02171073	0.02088449
TS6	0.02370382	0.0228951
$CF_2ClC(O)F$	0.0159805	0.0150309
$^{\bullet}CH_2F$	0.0161872	0.01528372
$^{\bullet}CF_2Cl$	0.01675709	0.01571724
$FCOCH_2F$	0.01665727	0.01583061
$CF_2(^{\bullet}OO)CF(Cl)CH_2F$	0.02013456	0.01888494
$CF_2(^{\bullet}O)CF(Cl)CH_2F$	0.01608492	0.0149374
TS7	0.02348482	0.02254609
FCFO	0.01687326	0.0158009
$^{\bullet}CF(Cl)CH_2F$	0.01576691	0.01506226
$(^{\bullet}OO)CF(Cl)CH_2F$	0.02262843	0.02155744
$(^{\bullet}O)CF(Cl)CH_2F$	0.01772215	0.01677315
TS8	0.01855898	0.01764473
FCOCl	0.01642332	0.01585598

Table S2: Coordinate of all the optimized species obtained at the MP2/6-31+G(d,p) level of theory.

SPECIES	**Coordinate**			
	Atom	**X-Axis**	**Y-Axis**	**Z-Axis**
CF_2=CF-CH_2F	C	1.008104000	-0.185921000	0.005271000
	C	-0.195832000	0.358692000	0.205844000
	C	-1.437275000	-0.380277000	0.514929000
	H	-1.996153000	0.133310000	1.295509000

	H	-1.214051000	-1.402461000	0.811952000
	F	-2.267244000	-0.431557000	-0.623901000
	F	-0.307902000	1.710925000	0.097502000
	F	1.238041000	-1.497708000	0.075826000
	F	2.110463000	0.497695000	-0.267618000
RC	C	0.415979000	0.921293000	-0.094284000
	C	-0.485522000	0.011535000	0.381856000
	C	-1.493391000	-0.703387000	-0.438651000
	H	-1.636376000	-1.708770000	-0.049536000
	H	-1.191834000	-0.732541000	-1.482271000
	F	-2.719687000	-0.018679000	-0.345688000
	F	-0.556610000	-0.133681000	1.714825000
	F	0.483899000	1.251251000	-1.365478000
	F	1.209138000	1.626418000	0.671667000
	Cl	1.556185000	-1.380183000	-0.214097000
Cl	Cl	0.000000000	0.000000000	0.000000000
TS1	C	0.510017000	0.772469000	-0.130172000
	C	-0.548344000	0.079111000	0.368567000
	C	-1.549364000	-0.657268000	-0.443116000
	H	-1.696477000	-1.650354000	-0.023979000
	H	-1.235618000	-0.717957000	-1.481210000
	F	-2.768901000	0.036162000	-0.374452000
	F	-0.665998000	0.009140000	1.693135000
	F	0.603831000	1.068086000	-1.404051000
	F	1.304270000	1.481914000	0.623185000
	Cl	1.541143000	-1.303251000	-0.123932000
TS2	C	-0.419229000	-0.983254000	-0.076874000
	C	0.359027000	0.027757000	0.362346000
	C	1.443401000	0.659500000	-0.440690000
	H	1.610497000	1.671909000	-0.084412000
	H	1.197511000	0.654452000	-1.498174000
	F	2.621279000	-0.083007000	-0.246094000
	F	0.410603000	0.211372000	1.689445000
	F	-0.463450000	-1.350098000	-1.328367000
	F	-1.230548000	-1.654522000	0.685113000
	Cl	-1.361656000	1.490348000	-0.275705000
TS3	C	1.680287000	-0.283217000	-0.123953000
	C	0.586882000	0.336262000	0.245663000
	C	-0.514649000	0.665589000	-0.658138000
	H	-1.531965000	-0.106805000	-0.276639000
	H	-0.380025000	0.401383000	-1.703343000
	F	-0.971003000	1.942208000	-0.506728000
	F	0.414591000	0.672453000	1.544782000
	F	1.930544000	-0.642850000	-1.374603000
	F	2.660192000	-0.622492000	0.685445000

	Cl	-2.641885000	-0.985309000	0.121088000
TS4	C	1.498363000	-0.148239000	0.327592000
	C	0.636837000	0.436468000	-0.471909000
	C	-0.577470000	-0.145795000	-1.050932000
	H	-0.906165000	0.338080000	-1.969032000
	H	-1.546171000	0.101339000	-0.231815000
	F	-0.550385000	-1.504103000	-1.169197000
	F	0.820952000	1.745831000	-0.790554000
	F	1.400865000	-1.396049000	0.737349000
	F	2.572790000	0.446508000	0.805247000
	Cl	-2.652473000	0.298606000	0.772162000
P1	C	-0.715546000	-0.143909000	0.403699000
	C	0.692519000	0.298781000	0.188143000
	C	1.690374000	-0.521426000	-0.543312000
	H	1.746966000	-0.220552000	-1.591526000
	H	1.448372000	-1.578282000	-0.461771000
	F	2.960439000	-0.311557000	0.016083000
	F	0.796385000	1.630907000	0.011657000
	F	-0.716292000	-1.445586000	0.809948000
	F	-1.305072000	0.597093000	1.374731000
	Cl	-1.695209000	-0.014091000	-1.067627000
P2	C	0.464375000	1.070295000	0.123031000
	C	-0.174626000	-0.291344000	0.214785000
	C	-1.514821000	-0.363803000	-0.489816000
	H	-1.966318000	-1.333314000	-0.289271000
	H	-1.396374000	-0.198364000	-1.558226000
	F	-2.343115000	0.633009000	0.028003000
	F	-0.343839000	-0.568843000	1.555325000
	F	0.576877000	1.522805000	-1.135587000
	F	1.615902000	1.194219000	0.785321000
	Cl	0.891806000	-1.528818000	-0.490475000
P3	C	1.070892000	-0.128241000	-0.018708000
	C	-0.253787000	0.198444000	0.001550000
	C	-1.289705000	-0.709686000	0.014970000
	H	-1.179226000	-1.779220000	0.023350000
	F	-2.557690000	-0.249857000	-0.003673000
	F	-0.545031000	1.520625000	-0.004623000
	F	1.485796000	-1.396021000	-0.004961000
	F	2.063017000	0.749266000	0.012121000
HCl	H	0.000000000	0.000000000	-1.206906000
	Cl	0.000000000	0.000000000	0.070994000
O_2	O	0.000000000	0.000000000	0.637176000
	O	0.000000000	0.000000000	-0.637176000
$CF_2(Cl)CF(OO^{\bullet})CH_2F$	C	0.997029000	-0.367594000	0.210796000
	C	-0.459401000	0.007899000	-0.133787000

	C	-0.919126000	1.307838000	0.506835000
	H	-0.374499000	2.144499000	0.074764000
	H	-0.771252000	1.257041000	1.584125000
	F	-2.273238000	1.481822000	0.248020000
	F	-0.573871000	0.070748000	-1.490040000
	F	1.101068000	-0.501440000	1.562122000
	F	1.296056000	-1.558782000	-0.350927000
	Cl	2.134105000	0.842105000	-0.348163000
	O	-2.383350000	-1.240149000	-0.245852000
	O	-1.216048000	-1.114517000	0.375134000
$NO^{\bullet}$	O	0.000000000	0.000000000	0.533411000
	N	0.000000000	0.000000000	-0.609613000
$CF_2(Cl)CF(O^{\bullet})CH_2F$	C	-0.858342000	0.325899000	0.170802000
	C	0.639147000	0.278423000	-0.232752000
	C	1.448297000	-0.696539000	0.633220000
	H	1.098780000	-1.708370000	0.441590000
	H	1.358122000	-0.429302000	1.682932000
	F	2.784624000	-0.606830000	0.258089000
	F	0.683938000	-0.152298000	-1.556199000
	F	-0.940492000	0.653180000	1.489069000
	F	-1.468075000	1.307962000	-0.536512000
	Cl	-1.681737000	-1.192336000	-0.102519000
	O	1.152259000	1.517820000	-0.087418000
NO_2	N	0.000000000	0.333213000	0.000000000
	O	1.118269000	-0.145791000	0.000000000
	O	-1.118269000	-0.145770000	0.000000000
TS5	C	-0.907915000	0.299600000	0.177569000
	C	0.532050000	0.595162000	-0.346169000
	C	1.581216000	-0.620814000	0.766643000
	H	1.006411000	-1.531826000	0.646385000
	H	1.599664000	-0.101005000	1.713939000
	F	2.775170000	-0.684096000	0.169515000
	F	0.712603000	-0.053436000	-1.555841000
	F	-0.908417000	0.490572000	1.524451000
	F	-1.721279000	1.232440000	-0.373458000
	Cl	-1.536415000	-1.294593000	-0.178920000
	O	1.069772000	1.640988000	-0.098618000
TS6	C	-1.008837000	0.291393000	0.204349000
	C	0.862614000	0.444804000	-0.264877000
	C	1.500026000	-0.609394000	0.645359000
	H	1.086725000	-1.597455000	0.468645000
	H	1.394995000	-0.294310000	1.680024000
	F	2.855716000	-0.640153000	0.319956000
	F	0.795252000	-0.045313000	-1.564553000
	F	-1.064852000	0.552573000	1.513561000
	F	-1.635109000	1.235851000	-0.482398000

	Cl	-1.582192000	-1.289029000	-0.183241000
	O	0.966708000	1.639727000	-0.077706000
$CF_2ClC(O)F$	C	-0.292432000	-0.350734000	0.202112000
	C	1.139997000	0.067107000	-0.154466000
	F	1.427022000	1.241117000	0.456585000
	F	-0.490095000	-1.623691000	-0.199353000
	F	-0.445172000	-0.306350000	1.550754000
	Cl	-1.453598000	0.708941000	-0.567270000
	O	1.899997000	-0.518740000	-0.864270000
$^{\bullet}CH_2F$	C	-0.032709000	-0.669335000	0.000000000
	H	0.245315000	-1.098798000	0.948208000
	H	0.245315000	-1.098798000	-0.948208000
	F	-0.032709000	0.690401000	0.000000000
$^{\bullet}CF_2Cl$	C	0.504949000	-0.164759000	0.000000000
	F	0.504949000	-0.933795000	1.096118000
	F	0.504949000	-0.933795000	-1.096118000
	Cl	-0.712870000	1.046874000	0.000000000
$FCOCH_2F$	C	-0.622074000	0.078546000	0.000358000
	C	0.734812000	0.745413000	0.049830000
	H	0.819849000	1.278293000	0.996489000
	H	0.800169000	1.451662000	-0.776043000
	F	1.776698000	-0.165700000	-0.048633000
	F	-0.548768000	-1.276962000	0.022164000
	O	-1.668477000	0.663783000	-0.035419000
$CF_2(^{\bullet}OO)CF(Cl)CH_2F$	C	0.656304000	-0.461603000	-0.111695000
	C	-0.713183000	0.158639000	0.224571000
	C	-1.037735000	1.444914000	-0.518187000
	H	-2.016627000	1.786346000	-0.186237000
	H	-1.028255000	1.272442000	-1.592549000
	F	-0.097229000	2.422154000	-0.208013000
	F	-0.719710000	0.395066000	1.581297000
	F	0.773039000	-0.617377000	-1.451569000
	F	0.802921000	-1.667965000	0.467030000
	Cl	-1.965794000	-1.017813000	-0.175509000
	O	1.660617000	0.420116000	0.363940000
	O	2.864367000	-0.094437000	0.098010000
$CF_2(^{\bullet}O)CF(Cl)CH_2F$	C	0.085930000	1.048566000	-0.047464000
	C	0.003510000	-0.479677000	0.216515000
	C	-1.103115000	-1.178029000	-0.551121000
	H	-1.115702000	-2.227062000	-0.261674000
	H	-0.954800000	-1.065276000	-1.622691000
	F	-2.324511000	-0.603384000	-0.200326000
	F	-0.202452000	-0.644641000	1.567543000
	F	0.282011000	1.242007000	-1.391770000
	F	1.163528000	1.588439000	0.583314000
	Cl	1.542875000	-1.206153000	-0.233591000

	O	-1.042938000	1.651248000	0.389872000
TS7	C	0.760550000	1.015862000	-0.027123000
	C	-0.341104000	-0.452369000	0.212648000
	C	-1.568376000	-0.327728000	-0.666048000
	H	-2.095534000	-1.282902000	-0.635331000
	H	-1.272727000	-0.084075000	-1.684649000
	F	-2.412089000	0.649693000	-0.174294000
	F	-0.635833000	-0.466493000	1.521881000
	F	1.144752000	0.855191000	-1.331844000
	F	1.841867000	0.684393000	0.727027000
	Cl	0.646763000	-1.802643000	-0.230450000
	O	-0.022675000	1.886533000	0.304480000
FCFO	C	0.000000000	0.000000000	0.147899000
	F	0.000000000	1.073742000	-0.642604000
	F	0.000000000	-1.073742000	-0.642604000
	O	0.000000000	0.000000000	1.334936000
$^{\bullet}CF(Cl)CH_2F$	C	0.070080000	0.204173000	-0.226681000
	C	-1.016605000	-0.681719000	0.289804000
	H	-1.081158000	-0.627064000	1.379639000
	H	-0.845955000	-1.706827000	-0.030665000
	F	-2.241061000	-0.247690000	-0.226962000
	F	-0.081974000	1.504506000	0.112250000
	Cl	1.677269000	-0.359540000	-0.040901000
$(^{\bullet}OO)CF(Cl)CH_2F$	C	0.090592000	-0.207712000	0.218976000
	C	-0.912869000	-0.575726000	-0.853349000
	H	-0.739919000	-1.606833000	-1.155134000
	H	-0.823750000	0.105876000	-1.694784000
	F	-2.191361000	-0.470827000	-0.314833000
	F	-0.043150000	-1.008636000	1.306577000
	Cl	1.725050000	-0.321810000	-0.412114000
	O	-0.150956000	1.106927000	0.773767000
	O	-0.188785000	2.016515000	-0.181718000
$(^{\bullet}O)CF(Cl)CH_2F$	C	-0.051233000	0.239238000	0.065424000
	C	0.980204000	-0.861058000	-0.150315000
	H	0.880731000	-1.244214000	-1.163512000
	H	0.842374000	-1.643137000	0.591956000
	F	2.251320000	-0.312989000	0.003939000
	F	0.091613000	1.189157000	-0.926215000
	Cl	-1.688747000	-0.443208000	-0.058930000
	O	0.040671000	0.783412000	1.297900000
TS8	C	-0.071556000	0.303501000	0.071177000
	C	1.124052000	-0.252926000	-0.739481000
	H	1.455753000	0.519589000	-1.428445000
	H	0.833761000	-1.157806000	-1.265700000
	F	2.176832000	-0.563911000	0.115813000

	F	-0.374704000	1.559119000	-0.447242000
	Cl	-1.552727000	-0.674071000	-0.083094000
	O	0.196590000	0.354638000	1.387428000
FCOCl	C	0.000000000	0.496115000	0.000000000
	O	0.794121000	1.384551000	0.000000000
	F	-1.337301000	0.689249000	0.000000000
	Cl	0.334279000	-1.191549000	0.000000000

Table S3: Harmonic vibrational frequency of species involved in the reaction channel (R1- R3) at MP2/6-31+G(d,p) level of theory.

Species	**Vibrational frequencies (cm^{-1})**
CF_2=CF-CH_2F	75.1697, 135.6016, 215.8526, 255.0294, 349.3843, 461.7407, 506.5227, 554.0713, 633.7794, 786.6422, 984.3992, 1028.4969, 1165.3581, 1288.2105, 1314.9158, 1343.1116, 1442.7695, 1537.2192, 1846.9506, 3166.8966, 3244.5919
RC	78.3611, 103.8177, 139.2484, 181.813, 186.0103, 219.9076, 273.0452, 349.9061, 495.469, 504.0486, 615.4647, 779.0304, 989.5642, 1032.2245, 1172.4908, 1278.1514, 1325.9051, 1391.2112, 1418.9993, 1527.9215, 1639.3389, 2718.4721, 3185.5719, 3264.3142
Cl	–
TS1	*i*614.4424, 72.5099, 105.6282, 167.6199, 212.5088, 235.2054, 286.66, 345.475, 368.747, 512.9643, 518.3038, 649.1065, 813.7326, 1003.459, 1044.7774, 1178.6773, 1278.3091, 1351.7722, 1398.3042, 1436.1233, 1534.2239, 1669.6654, 3183.2464, 3268.0071
TS2	*i*356.282, 94.6373, 130.7203, 146.8836, 179.2838, 229.7914, 262.2506, 358.5682, 446.4289, 525.791, 576.5656, 638.6786, 808.0975, 998.4165, 1042.5583, 1190.9519, 1281.6893, 1341.7974, 1411.0852, 1437.9144, 1533.6223, 1787.6379, 3196.3567, 3279.9762
TS3	*i*1509.0558, 37.4048, 60.7878, 128.4556, 164.7592, 203.6216, 258.8368, 368.157, 453.4038, 491.9666, 535.2107, 639.7992, 756.5671, 844.9412, 958.1072, 1061.5662, 1113.2245, 1156.659, 1237.1609, 1317.0194, 1362.863, 1430.4614, 2057.965, 3242.1032
TS4	*i*1546.71, 24.4978, 62.1609, 132.8056, 166.7284, 201.2549, 280.7678, 391.7192, 432.3258, 476.9976, 524.6367, 637.6736, 750.8609, 815.1756, 993.291, 1087.2845, 1152.2988,1197.6323, 1244.3253, 1291.0156, 1362.3977, 1445.1586, 1970.3307, 3214.7049

P1	49.8695, 57.698, 144.6631, 208.2467, 283.145, 324.3178, 351.5235, 421.3285, 483.5289, 513.331, 633.8362, 724.8693, 915.6917, 1001.9105, 1044.6041,1116.8945, 1170.6538, 1270.835, 1322.025,1408.6832, 1452.1252, 1533.7995, 3140.847, 3238.4322
P2	77.3871, 120.0027, 177.8838, 182.7194, 235.6698, 337.5332, 343.2226, 409.0848, 498.2582, 558.6477, 652.7549, 732.4454, 950.5425, 963.9627, 1085.9151, 1154.2404, 1222.8986, 1262.1327, 1294.2579, 1399.4908, 1441.785, 1536.5513, 3175.1351, 3257.6729
P3	71.5696, 153.5063, 167.7183, 197.751, 270.6499, 395.7958, 508.9041, 520.0483, 562.2384, 612.2458, 862.7223, 1034.0463, 1199.3926, 1315.7993, 1365.6252, 1468.0907, 1647.6259, 3369.0214
HCl	3043.888
O_2	1200.675
$CF_2(Cl)CF(OO^{\bullet})CH_2F$	63.6367, 78.914, 99.8718, 160.451,183.4455, 259.3659,270.1261, 326.3919, 336.0852, 360.6589, 398.3334, 448.2432,491.9044, 594.264, 639.0406, 801.1265, 897.9242, 985.6529, 1076.6617,1120.3358,1147.043,1180.4563, 1199.2292,1255.4674, 1300.0423, 1340.3444, 1456.7504, 1537.9446, 3170.5349, 3251.7331
NO	3853.923
$CF_2(Cl)CF(O^{\bullet})CH_2F$	65.9177, 85.3712, 155.3069, 206.9609, 271.3926, 300.2328, 329.1097, 340.0051, 413.035, 448.9925, 482.3773, 562.0881, 631.6296, 758.6606, 919.4314, 985.2797, 1072.3864, 1113.2055, 1152.3273, 1177.28, 1210.2734, 1237.187, 1316.8649, 1432.0237, 1539.3249, 3178.5916, 3265.43
NO_2	752.2909, 1369.6107, 2305.834
TS5	*i*702.2466, 60.1895, 73.3698, 148.3302, 206.7799, 228.8738, 269.8783, 295.6447, 351.2001, 380.0237, 436.146, 463.7038, 605.5799, 620.7434, 714.2663, 764.0747, 980.116, 1085.085, 1124.573, 1156.124, 1207.3913, 1230.8399, 1236.6955,1528.1091, 1707.2344, 3206.8337, 3369.5976
TS6	*i*1044.1524, 39.561, 75.0454, 145.631, 171.8733, 229.9016, 277.9961, 297.0052, 311.2559, 400.3895, 417.5611, 457.3534, 588.9535, 645.6086, 806.9784, 808.1659, 1021.1495,1087.4127, 1157.3436, 1170.4946, 1248.4382, 1299.8298, 1431.4896, 1531.6297, 1567.0562, 3186.9388, 3277.4758
$CF_2ClC(O)F$	55.125, 187.564, 239.7131, 346.4294, 370.5409, 439.3061, 524.2209, 612.335, 691.3085, 766.8546, 996.1453, 1105.0794,

	1194.4307, 1296.0445, 1901.6509
$^{\bullet}CH_2F$	763.1004, 1163.1481, 1201.4039,1515.6961,3249.8412, 3415.4991
$^{\bullet}CF_2Cl$	370.9895, 428.9747, 595.0564, 814.85, 1167.1308, 1210.871
$FCOCH_2F$	13.7825, 257.3625, 490.0537, 544.1875, 622.5675, 833.0273, 1053.0083, 1107.3782, 1254.0161, 1285.3992, 1426.9849, 1525.6363, 1884.9501, 3162.6847, 3235.0205
$CF_2(^{\bullet}OO)CF(Cl)CH_2F$	54.6633, 106.5314, 137.0115, 167.3084, 189.1717, 247.5331, 261.3699, 331.8705, 334.3791, 367.2638, 410.466, 457.0067, 527.7265, 577.0054, 651.0813, 816.6742, 917.1443, 980.196, 1070.888, 1108.734, 1131.9521,1197.9832,1205.9619,1232.1536, 1292.9815,1381.8102,1444.2968,1533.4187,3169.9239, 3251.7154
$CF_2(^{\bullet}O)CF(Cl)CH_2F$	64.0942, 120.2767, 178.8704, 205.5281, 241.2375, 306.2795, 333.1666, 336.0657, 376.3323, 451.3549, 528.0356, 559.2601, 620.3286, 745.1353, 937.2389, 979.6653, 1080.3311, 1113.562, 1158.3712, 1205.8253, 1224.3837, 1260.8052, 1325.346, 1439.428, 1533.5596, 3174.0116, 3257.5868
TS7	*i*1115.5765, 57.2098, 126.7125, 172.9014, 199.9336, 221.9173, 268.298, 301.3751, 326.0264, 370.882, 463.7217, 550.8235, 579.6551, 601.995, 824.5502, 878.1039,1008.8295, 1074.7966, 1127.7829, 1139.3623, 1266.0657,1295.4792, 1434.1291, 1522.7542, 1537.1155, 3148.4455,3237.3712
FCFO	565.3045, 601.4673, 758.575, 949.5368, 1226.7184, 1958.4574
$^{\bullet}CF(Cl)CH_2F$	102.9613, 220.7331, 344.5497, 419.7061, 454.26, 816.2831, 987.8065, 1070.1755, 1139.3631, 1262.8293, 1299.3294, 1441.0818, 1534.6674, 3130.08, 3231.9184
$(^{\bullet}OO)CF(Cl)CH_2F$	93.317, 149.1522, 192.4778, 300.4056, 338.4066, 347.4281, 433.5334, 496.4806, 564.9893, 781.456, 938.4908, 1002.9406, 1095.0924, 1148.2296, 1218.218, 1273.7998, 1317.1442, 1445.0846, 1531.7535, 3180.4356, 3265.8481
$(^{\bullet}O)CF(Cl)CH_2F$	122.2661, 193.365, 221.7514, 330.1817, 420.4984, 432.2618, 540.7982, 796.0593, 916.1634, 975.7616, 1090.8558, 1179.2978, 1215.9165, 1315.9543, 1430.3151, 1537.3822, 3177.5603, 3264.376
TS8	*i*130.1437, 226.7789, 264.2377, 296.4212, 409.5777, 449.9181, 550.959, 737.5062, 878.3042, 1045.7988, 1100.6669, 1130.532, 1210.8938, 1292.951, 1433.308, 1539.175, 3181.6163,3266.9587
FCOCl	416.6972, 507.647, 662.5333, 764.8904, 1087.261, 1885.2167

Table S4: The zero point corrected total energy (E_0) [in hartree] and relative energy (RE) [kcal mol^{-1}] of CF_2=CF−CH_2F + Cl-atom reaction at MP2/6-31+G(d,p) level of theory.

Species	**MP2/6-31 + G(d,p)**	
	E_0	**RE**
R(CF_2=CF−CH_2F) + Cl	-973.0807813	0
RC	-973.0830539	-1.42
TS1	-973.0801622	0.38
TS2	-973.0818103	-0.64
TS3	-973.0617143	11.96
TS4	-973.0598015	13.16
P1	-973.1217419	-25.70
P2	-973.1208363	-25.13
P3+HCl	-973.0799146	0.54

Table S5: The zero point corrected total energy (E_0) [in hartree] and relative energy (RE) [kcal mol^{-1}] of CF_2=CF−CH_2F + Cl-atom reaction at CCSD(T)//MP2/6-31+G(d,p), and CCSD(T)/6-311++G(d,p)//MP2/6-31+G(d,p) level of theories.

Species	**Methods**			
	CCSD(T)//MP2/ 6-31+G(d,p)		**CCSD(T)/ 6-311++G(d,p)//MP2/6-31+G(d,p)**	
	E_0	**RE**	**E_0**	**RE**
R(CF_2=CF−CH_2F) + Cl	-973.1546509	0	-973.457234	0
RC	-973.1556221	-0.61	-973.461719	-2.81
TS1	-973.1584769	-2.41	-973.465335	-5.08

TS2	-973.160115	-3.43	-973.466984	-6.12
TS3	-973.1413239	8.36	-973.449992	4.54
TS4	-973.140521	8.87	-973.448746	5.33
P1	-973.1938774	-24.61	-973.497455	-25.24
P2	-973.1921358	-23.52	-973.496282	-24.50
P3+HCl	-973.1633966	-5.48	-973.470998	-8.64

Table S6: Rate coefficients (in $cm^3molecule^{-1}s^{-1}$) of each reaction pathway (R1, R2, R3a and R3b) of CF_2=CF−CH_2F + Cl reaction over the temperature range 200-1000 K at MP2/6-31+G (d,p).

Temperature (in K)	**Rate coefficients (in $cm^3molecule^{-1}s^{-1}$)**				
	k_1 (R1)	**k_2 (R2)**	**k_3 (R3a)**	**k_4 (R3b)**	**k_{total}**
200	1.61×10^{-13}	1.30×10^{-12}	5.89×10^{-25}	3.88×10^{-26}	1.46×10^{-12}
250	1.93×10^{-13}	9.90×10^{-13}	2.19×10^{-22}	2.63×10^{-23}	1.18×10^{-12}
298.15	2.28×10^{-13}	8.70×10^{-13}	1.04×10^{-20}	1.83×10^{-21}	1.10×10^{-12}
300	2.29×10^{-13}	8.68×10^{-13}	1.17×10^{-20}	2.10×10^{-21}	1.10×10^{-12}
350	2.69×10^{-13}	8.17×10^{-13}	2.09×10^{-19}	4.96×10^{-20}	1.09×10^{-12}
400	3.14×10^{-13}	8.02×10^{-13}	1.88×10^{-18}	5.50×10^{-19}	1.12×10^{-12}
450	3.61×10^{-13}	8.06×10^{-13}	1.07×10^{-17}	3.68×10^{-18}	1.17×10^{-12}
500	4.12×10^{-13}	8.22×10^{-13}	4.39×10^{-17}	1.73×10^{-17}	1.23×10^{-12}
550	4.66×10^{-13}	8.47×10^{-13}	1.43×10^{-16}	6.26×10^{-17}	1.31×10^{-12}
600	5.22×10^{-13}	8.78×10^{-13}	3.91×10^{-16}	1.87×10^{-16}	1.40×10^{-12}
650	5.81×10^{-13}	9.13×10^{-13}	9.29×10^{-16}	4.78×10^{-16}	1.50×10^{-12}
700	6.43×10^{-13}	9.52×10^{-13}	1.98×10^{-15}	1.09×10^{-15}	1.60×10^{-12}
750	7.06×10^{-13}	9.94×10^{-13}	3.86×10^{-15}	2.24×10^{-15}	1.71×10^{-12}
800	7.73×10^{-13}	1.04×10^{-12}	7.01×10^{-15}	4.26×10^{-15}	1.82×10^{-12}
850	8.41×10^{-13}	1.09×10^{-12}	1.20×10^{-14}	7.59×10^{-15}	1.95×10^{-12}
900	9.12×10^{-13}	1.13×10^{-12}	1.94×10^{-14}	1.28×10^{-14}	2.08×10^{-12}

950	9.84×10^{-13}	1.18×10^{-12}	3.01×10^{-14}	2.05×10^{-14}	2.22×10^{-12}
1000	1.06×10^{-12}	1.24×10^{-12}	4.51×10^{-14}	3.17×10^{-14}	2.37×10^{-12}

Table S7: The Branching ratios in terms of % contribution for all the involved reaction pathways (R1-R3a,b) of CF_2=CF−CH_2F + Cl reaction between the 200-1000 K at MP2/6-31+G(d,p).

%Branching Ratio	**k_1 (R1)**	**k_2 (R2)**	**k_3 (R3a)**	**k_4 (R3b)**
200	11	89	0	0
250	16.3	83.7	0	0
298.15	20.7	79.3	0	0
300	20.9	79.1	0	0
350	24.8	75.2	0	0
400	28.1	71.9	0	0
450	31	69	0	0
500	33.4	66.6	0	0
550	35.5	64.5	0	0
600	37.3	62.7	0	0
650	38.8	61.1	0	0
700	40.2	59.6	0.1	0
750	41.4	58.2	0.2	0.1
800	42.4	57	0.3	0.2
850	43.2	55.8	0.6	0.3
900	43.9	54.6	0.9	0.6
950	44.3	53.4	1.36	0.9
1000	44.6	52.1	1.9	1.34

Table S8: Rate coefficients (in $cm^3molecule^{-1}s^{-1}$) of each reaction pathway (R1, R2, R3a and R3b) of CF_2=CF−CH_2F + Cl reaction over the temperature range 200-1000 K at CCSD(T)//MP2/6-31+G(d,p).

Temperature (in K)	**Rate coefficients (in $cm^3molecule^{-1}s^{-1}$)**				
	k_1 (R1)	**k_2 (R2)**	**k_3 (R3a)**	**k_4 (R3b)**	**k_{total}**
200	1.80×10^{-10}	1.43×10^{-09}	5.08×10^{-21}	1.93×10^{-21}	1.61×10^{-09}
250	5.29×10^{-11}	2.68×10^{-10}	3.08×10^{-19}	1.50×10^{-19}	3.21×10^{-10}
298.15	2.52×10^{-11}	9.54×10^{-11}	4.52×10^{-18}	2.59×10^{-18}	1.21×10^{-10}
300	2.46×10^{-11}	9.24×10^{-11}	4.93×10^{-18}	2.84×10^{-18}	1.17×10^{-10}
350	1.49×10^{-11}	4.47×10^{-11}	3.71×10^{-17}	2.40×10^{-17}	5.95×10^{-11}
400	1.05×10^{-11}	2.66×10^{-11}	1.74×10^{-16}	1.23×10^{-16}	3.71×10^{-11}

450	8.18×10^{-12}	1.81×10^{-11}	5.99×10^{-16}	4.50×10^{-16}	2.63×10^{-11}
500	6.83×10^{-12}	1.35×10^{-11}	1.65×10^{-15}	1.31×10^{-15}	2.04×10^{-11}
550	5.98×10^{-12}	1.08×10^{-11}	3.87×10^{-15}	3.20×10^{-15}	1.68×10^{-11}
600	5.42×10^{-12}	9.06×10^{-12}	8.01×10^{-15}	6.86×10^{-15}	1.45×10^{-11}
650	5.04×10^{-12}	7.88×10^{-12}	1.51×10^{-14}	1.33×10^{-14}	1.29×10^{-11}
700	4.77×10^{-12}	7.04×10^{-12}	2.64×10^{-14}	2.39×10^{-14}	1.19×10^{-11}
750	4.59×10^{-12}	6.43×10^{-12}	4.33×10^{-14}	4.00×10^{-14}	1.11×10^{-11}
800	4.47×10^{-12}	5.98×10^{-12}	6.75×10^{-14}	6.36×10^{-14}	1.06×10^{-11}
850	4.39×10^{-12}	5.64×10^{-12}	1.01×10^{-13}	9.67×10^{-14}	1.02×10^{-11}
900	4.34×10^{-12}	5.38×10^{-12}	1.45×10^{-13}	1.41×10^{-13}	1.00×10^{-11}
950	4.31×10^{-12}	5.17×10^{-12}	2.03×10^{-13}	2.00×10^{-13}	9.89×10^{-12}
1000	4.31×10^{-12}	5.02×10^{-12}	2.76×10^{-13}	2.76×10^{-13}	9.88×10^{-12}

Table S9: The Branching ratios in terms of % contribution for all the involved reaction pathways (R1-R3a,b) of CF_2=CF−CH_2F + Cl reaction between the 200-1000 K at CCSD(T)//MP2/6-31+G(d,p).

%Branching Ratio	**k_1 (R1)**	**k_2 (R2)**	**k_3 (R3a)**	**k_4 (R3b)**
200	11.2	88.8	0	0
250	16.5	83.5	0	0
298.15	20.9	79.1	0	0
300	21.1	78.9	0	0
350	25	75	0	0
400	28.3	71.7	0	0
450	31.1	68.9	0	0
500	33.5	66.5	0	0
550	35.6	64.4	0	0
600	37.4	62.5	0	0
650	38.9	60.9	0.1	0.1
700	40.2	59.3	0.2	0.2
750	41.3	57.9	0.3	0.3
800	42.2	56.5	0.6	0.6
850	42.9	55.2	0.9	0.9
900	43.4	53.8	1.45	1.41
950	43.6	52.3	2.05	2.02
1000	43.6	50.8	2.8	2.79

Table S10: Rate coefficients (in $cm^3molecule^{-1}s^{-1}$) of each reaction pathway (R1, R2, R3a and R3b) of CF_2=CF−CH_2F + Cl reaction over the temperature range 200-1000 K at CCSD(T)/6-311++G(d,p)//MP2/6-31+G(d,p).

Temperature (in K)	Rate coefficients (in $cm^3molecule^{-1}s^{-1}$)				
	k_1 (R1)	k_2 (R2)	k_3 (R3a)	k_4 (R3b)	k_{total}
200	1.54×10^{-07}	1.24×10^{-06}	7.55×10^{-17}	1.43×10^{-17}	1.39×10^{-06}
250	1.17×10^{-08}	6.24×10^{-08}	6.71×10^{-16}	1.87×10^{-16}	7.19×10^{-08}
298.15	2.33×10^{-09}	8.94×10^{-09}	2.85×10^{-15}	1.02×10^{-15}	1.13×10^{-08}
300	2.22×10^{-09}	8.42×10^{-09}	2.98×10^{-15}	1.08×10^{-15}	1.06×10^{-08}
350	7.04×10^{-10}	2.14×10^{-09}	8.99×10^{-15}	3.90×10^{-15}	2.84×10^{-09}
400	3.06×10^{-10}	7.84×10^{-10}	2.13×10^{-14}	1.06×10^{-14}	1.09×10^{-09}
450	1.64×10^{-10}	3.67×10^{-10}	4.28×10^{-14}	2.36×10^{-14}	5.31×10^{-10}
500	1.02×10^{-10}	2.03×10^{-10}	7.69×10^{-14}	4.61×10^{-14}	3.05×10^{-10}
550	6.96×10^{-11}	1.27×10^{-10}	1.27×10^{-13}	8.16×10^{-14}	1.96×10^{-10}
600	5.14×10^{-11}	8.65×10^{-11}	1.97×10^{-13}	1.34×10^{-13}	1.38×10^{-10}
650	4.02×10^{-11}	6.32×10^{-11}	2.90×10^{-13}	2.06×10^{-13}	1.04×10^{-10}
700	3.28×10^{-11}	4.87×10^{-11}	4.10×10^{-13}	3.04×10^{-13}	8.22×10^{-11}
750	2.78×10^{-11}	3.91×10^{-11}	5.61×10^{-13}	4.30×10^{-13}	6.79×10^{-11}
800	2.41×10^{-11}	3.25×10^{-11}	7.46×10^{-13}	5.90×10^{-13}	5.80×10^{-11}
850	2.15×10^{-11}	2.77×10^{-11}	9.68×10^{-13}	7.86×10^{-13}	5.09×10^{-11}
900	1.94×10^{-11}	2.42×10^{-11}	1.23×10^{-12}	1.02×10^{-12}	4.59×10^{-11}
950	1.79×10^{-11}	2.15×10^{-11}	1.54×10^{-12}	1.31×10^{-12}	4.22×10^{-11}
1000	1.66×10^{-11}	1.94×10^{-11}	1.89×10^{-12}	1.64×10^{-12}	3.96×10^{-11}

Table S11: The Branching ratios in terms of % contribution for all the involved reaction pathways (R1-R3a,b) of CF_2=CF−CH_2F + Cl reaction between the 200-1000 K at CCSD(T)/6-311++G(d,p)//MP2/6-31+G(d,p).

%Branching Ratio	TS1	TS2	TS3	TS4
200	11	89	0	0
250	16.3	83.7	0	0
298.15	20.7	79.3	0	0
300	20.9	79.1	0	0

350	24.8	75.2	0	0
400	28.1	71.9	0	0
450	30.9	69.1	0	0
500	33.4	66.6	0	0
550	35.4	64.5	0	0
600	37.2	62.6	0.1	0
650	38.7	60.8	0.2	0.1
700	39.9	59.2	0.5	0.3
750	40.9	57.6	0.8	0.6
800	41.7	56	1.29	1.02
850	42.1	54.4	1.9	1.54
900	42.4	52..7	2.68	2.23
950	42.3	50.9	3.64	3.09
1000	42	49.1	4.77	4.14

Table S12: The zero point corrected total energy (E_0) [in hartree] and relative energy (RE) [kcal mol^{-1}] of degradation of two product radicals (P1 and P2) with atmospheric O_2 in the presence of NO radicals at MP2/6-31 + G(d,p) level of theory.

Species	**MP2/6-31 + G(d,p)**	
P1 degradation	**E_0**	**RE**
P1+O_2+NO	-1252.586635	0
$CF_2(Cl)CF(OO^{\bullet})CH_2F$ +NO	-1252.665731	-49.63
$CF_2(Cl)CF(O^{\bullet})CH_2F$+$NO_2$	-1252.712608	-79.05
TS5+ NO_2	-1252.689394	-64.48
TS6+NO_2	-1252.687439	-63.25
$CF_2ClC(O)F$+$^{\bullet}CH_2F$+NO_2	-1252.71888	-82.98
$^{\bullet}CF_2Cl$+$FCOCH_2F$+NO_2	-1252.724566	-86.55
P2 degradation	**E_0**	**RE**
P2+O_2+NO+O_2+NO	-1532.050622	0
$CF_2(^{\bullet}OO)CF(Cl)CH_2F$+NO+ O_2+NO	-1532.137927	-54.78
$CF_2(^{\bullet}O)CF(Cl)CH_2F$+$NO_2$+$O_2$+NO	-1532.178484	-80.23
TS7+NO_2+O_2+NO	-1532.160789	-69.13

FCFO+•CF(Cl)CH_2F+NO_2+O_2 +NO	-1532.1956	-90.97
(•OO)CF(Cl)CH_2F+FCFO+ NO_2+NO	-1532.281674	-144.98
(•O)CF(Cl)CH_2F+FCFO+NO_2+NO_2	-1532.323139	-171.01
TS8+FCFO+NO_2+NO_2	-1532.31557	-166.26
FC(O)Cl+•CH_2F+NO_2+NO_2 +FCFO	-1532.335555	-178.79

Table S13: The zero point corrected total energy (E_0) [in hartree] and relative energy (RE) [kcal mol^{-1}] of degradation of two product radicals (P1 and P2) with atmospheric O_2 in the presence of NO radicals at CCSD(T)//MP2/6-31+G(d,p), and CCSD(T)/6-311++G(d,p)//MP2/6-31+G(d,p) level of theories.

Species	**Methods**			
	CCSD(T)//MP2/ 6-31+G(d,p)		**CCSD(T)/ 6-311++G(d,p)//MP2/6-31+G(d,p)**	
P1 degradation	**E_0**	**RE**	**E_0**	**RE**
P1+O_2+NO	-1252.687605	0	-1253.127441	0
CF_2(Cl)CF(OO•)CH_2F +NO	-1252.781858	-59.14	-1253.216728	-56.03
CF_2(Cl)CF(O•)CH_2F+NO_2	-1252.813311	-78.88	-1253.246769	-74.88
TS5+ NO_2	-1252.792021	-65.52	-1253.229473	-64.03
TS6+NO_2	-1252.794145	-66.85	-1253.230981	-64.97
CF_2ClC(O)F+•CH_2F+NO_2	-1252.808592	-75.92	-1253.244703	-73.58
•CF_2Cl+$FCOCH_2F$+NO_2	-1252.814869	-79.86	-1253.250013	-76.91
P2 degradation	**E_0**	**RE**	**E_0**	**RE**
P2+O_2+NO+O_2+NO	-1532.179592	0	-1532.756254	0
CF_2(•OO)CF(Cl)CH_2F+NO+ O_2+NO	-1532.282631	-64.66	-1532.853807	-61.21

$CF_2(^{\bullet}O)CF(Cl)CH_2F+NO_2+O_2+NO$	-1532.307263	-80.11	-1532.877384	-76.01
$TS7+NO_2+O_2+NO$	-1532.294464	-72.08	-1532.868138	-70.21
$FCFO+^{\bullet}CF(Cl)CH_2F+NO_2+O_2+NO$	-1532.314478	-84.64	-1532.88828	-82.85
$(^{\bullet}OO)CF(Cl)CH_2F+FCFO+NO_2+NO$	-1532.414985	-147.71	-1532.983681	-142.71
$(^{\bullet}O)CF(Cl)CH_2F+FCFO+NO_2+NO_2$	-1532.441722	-164.49	-1533.00907	-158.64
$TS8+FCFO+NO_2+NO_2$	-1532.43449	-159.95	-1533.001258	-153.74
$FC(O)Cl+^{\bullet}CH_2F+NO_2+NO_2+FCFO$	-1532.442869	-165.21	-1533.012945	-161.07

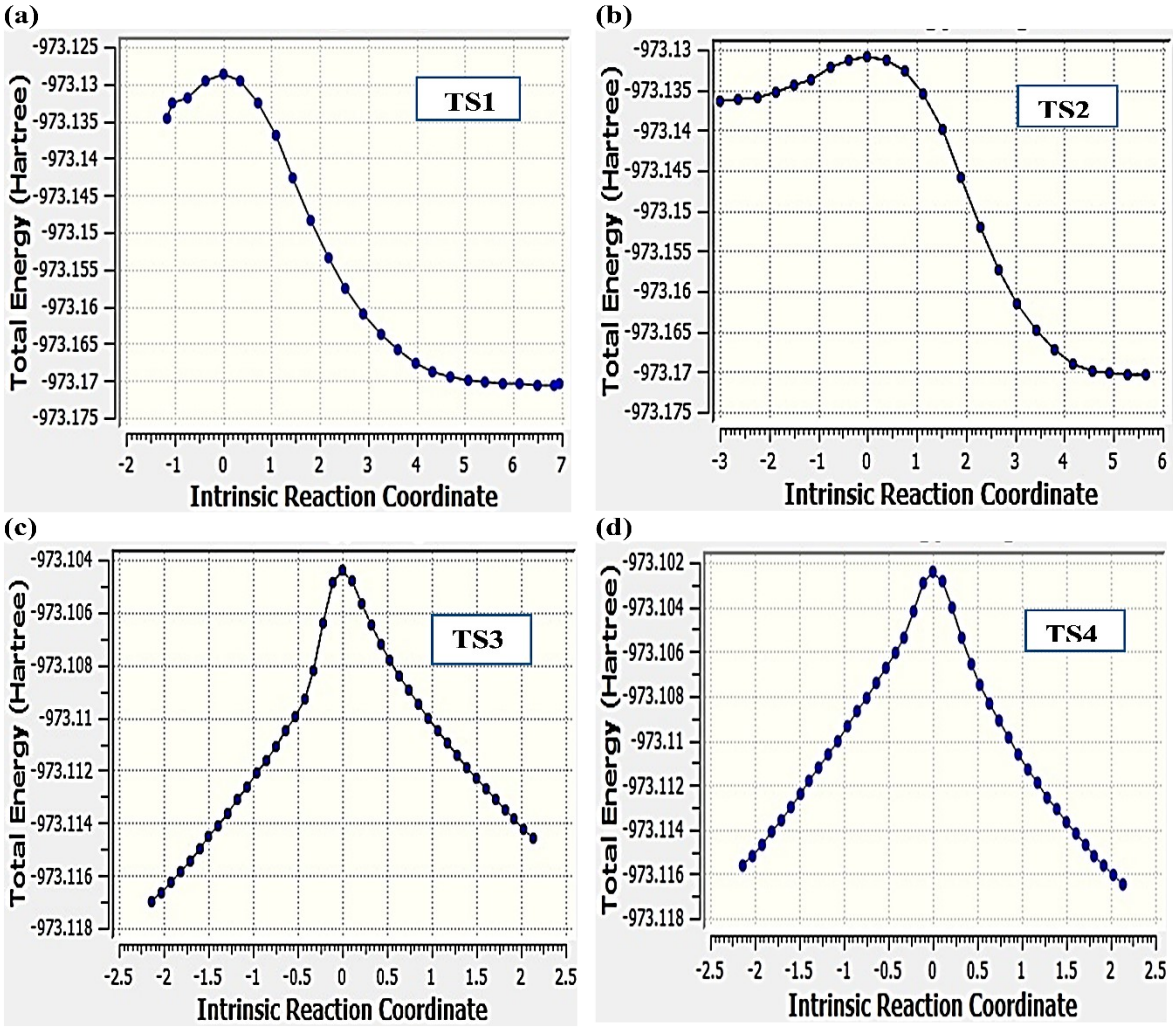

Figure S1: IRC plot for all the TSs at the MP2/6-31+G(d,p) level of theory