

Supplementary material for:

Relative rate and product studies of the reactions of atomic chlorine with tetrafluoroethylene, 1,2-dichloro-1,2-difluoroethylene, 1,1-dichloro-2,2-difluoroethylene and hexafluoro-1,3-butadiene in the presence of oxygen

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**Table 1S. Geometries computed with B3LYP/6-311G(2d,d,p) theory.
Atomic numbers and cartesian coordinates in 10^{-10} m.**

C2F4

6	0.000000000	0.000000000	0.660977000
6	0.000000000	0.000000000	-0.660977000
9	0.000000000	1.103884000	1.386891000
9	0.000000000	-1.103884000	1.386891000
9	0.000000000	1.103884000	-1.386891000
9	0.000000000	-1.103884000	-1.386891000

CF2ClCF2

6	0.803229000	0.843694000	0.000000000
6	0.193692000	-0.535589000	0.000000000
9	0.596951000	1.549554000	1.096618000
9	0.596951000	1.549554000	-1.096618000
9	0.596951000	-1.200111000	1.092095000
9	0.596951000	-1.200111000	-1.092095000
17	-1.615985000	-0.478742000	0.000000000

CF2ClCF2OO

6	-0.600135000	-0.560285000	-0.045678000
6	0.558719000	0.475569000	-0.131977000
9	-0.375407000	-1.568173000	-0.884818000
9	-0.740618000	-1.009664000	1.195822000
9	0.628282000	0.928540000	-1.391452000

9	0.297968000	1.505602000	0.680159000
8	-1.836434000	0.012171000	-0.509198000
8	-2.403354000	0.785000000	0.405047000
17	2.110281000	-0.269165000	0.323632000

CF2ClCF2O

6	-0.715416000	0.767415000	0.000000000
6	0.052678000	-0.662695000	0.000000000
9	-0.299372000	1.459940000	1.089871000
9	-0.299372000	1.459940000	-1.089871000
9	-0.299372000	-1.347894000	1.087016000
9	-0.299372000	-1.347894000	-1.087016000
8	-1.983325000	0.469860000	0.000000000
17	1.801202000	-0.376709000	0.000000000

ClO

17	0.000000000	0.000000000	0.515230000
8	0.000000000	0.000000000	-1.094864000

CF2Cl

6	-0.515074000	-0.179779000	0.000000000
9	-0.515074000	-0.933471000	1.088073000
9	-0.515074000	-0.933471000	-1.088073000
17	0.727163000	1.051832000	0.000000000

COF2

6	0.000000000	0.000000000	0.145768000
8	0.000000000	0.000000000	1.316401000
9	0.000000000	1.066187000	-0.633657000
9	0.000000000	-1.066187000	-0.633657000

TS for $\text{CF}_2\text{ClCF}_2\text{O} \rightarrow \text{CF}_2\text{Cl} + \text{CF}_2\text{O}$

6	-0.816409000	0.891242000	0.000000000
6	0.087211000	-0.745306000	0.000000000
9	-0.291587000	1.501707000	1.086354000
9	-0.291587000	1.501707000	-1.086354000
9	-0.291587000	-1.389682000	1.084483000
9	-0.291587000	-1.389682000	-1.084483000
8	-1.977024000	0.491340000	0.000000000
17	1.805206000	-0.401340000	0.000000000

CF₂ClOO

6	-0.036989000	-0.200817000	0.000000000
8	-0.773090000	1.029903000	0.000000000
9	-0.343936000	-0.909342000	-1.079768000
9	-0.343936000	-0.909342000	1.079768000
17	1.665354000	0.258702000	0.000000000
8	-2.077361000	0.783596000	0.000000000

CF₂ClO

6	0.374324000	0.058766000	0.000000000
8	0.840622000	1.324207000	0.000000000
9	0.840622000	-0.554696000	1.098431000
9	0.840622000	-0.554696000	-1.098431000
17	-1.417772000	-0.056572000	0.000000000

CCl₂FCFCIO

6	0.584091000	0.120889000	0.316528000
6	-0.699029000	-0.569151000	-0.264879000
9	0.451775000	0.218219000	1.648014000
9	-0.627960000	-0.556503000	-1.615873000
17	1.976194000	-0.945573000	-0.042569000
17	0.834855000	1.741599000	-0.367111000
17	-2.217021000	0.352244000	0.246298000
8	-0.977897000	-1.723306000	0.272292000

CFCI₂

6	-0.159699000	0.442599000	0.000000000
9	0.709772000	1.445801000	0.000000000
17	-0.159699000	-0.460818000	1.481369000
17	-0.159699000	-0.460818000	-1.481369000

COFCI

8	-0.804840000	1.367819000	0.000000000
6	0.000000000	0.516592000	0.000000000
9	1.314412000	0.718003000	0.000000000
17	-0.317117000	-1.206125000	0.000000000

CCI2FCFO

6	-0.222931000	0.332529000	0.000000000
6	-0.476095000	-1.186113000	0.000000000
9	-1.404940000	0.962068000	0.000000000
9	0.677190000	-1.863299000	0.000000000
17	0.677190000	0.788556000	1.476100000
17	0.677190000	0.788556000	-1.476100000
8	-1.535071000	-1.697292000	0.000000000

TS for CCI2FCFCIO $\rightarrow$ CFCI2 + COFCI

6	-0.670256000	-0.163998000	0.337867000
6	0.838617000	0.734864000	-0.210501000
9	-0.557874000	-0.263935000	1.653052000
9	0.737580000	0.689693000	-1.565802000
17	-2.070521000	0.790617000	-0.113322000
17	-0.659477000	-1.742514000	-0.422506000

17	2.233501000	-0.329959000	0.269091000
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8	0.726617000	1.816815000	0.373133000
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TS for CCl₂FCFCIO → CCl₂FCFO + Cl

6	-0.603150000	-0.123089000	0.313901000
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6	0.587511000	0.689009000	-0.288149000
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9	-0.430242000	-0.220718000	1.637917000
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9	0.555445000	0.646504000	-1.624547000
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17	-2.081285000	0.844241000	-0.000518000
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17	-0.755463000	-1.745633000	-0.388506000
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17	2.311459000	-0.333157000	0.237650000
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8	0.987113000	1.719965000	0.287315000
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F₂C(O)CFCICFO

6	1.030749000	-0.715206000	-0.215725000
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6	-0.149483000	0.247770000	0.393000000
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6	-1.495807000	-0.125641000	-0.256482000
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8	0.607927000	-1.922856000	0.042696000
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8	-1.928404000	0.289107000	-1.277873000
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17	0.284602000	1.925222000	0.039613000
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9	2.190764000	-0.370317000	0.386627000
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9	1.155700000	-0.423895000	-1.532977000
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9	-0.188389000	0.047136000	1.723321000
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9	-2.112205000	-1.041847000	0.498943000
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TS F2C(O)CFClCFO → OCF2CFC(F)O + Cl

6	1.281453000	-0.511784000	-0.074253000
6	-0.144791000	-0.180348000	0.452213000
6	-1.415522000	-0.551489000	-0.297101000
8	0.774026000	-1.648971000	0.318803000
8	-1.477133000	-0.965972000	-1.394148000
17	-0.149553000	2.000704000	-0.322526000
9	2.268424000	0.020480000	0.646059000
9	1.551278000	-0.352818000	-1.362896000
9	-0.255880000	0.048338000	1.733344000
9	-2.470441000	-0.341634000	0.494665000

OCF2CFC(F)O

6	-1.155088000	-0.194648000	-0.052914000
6	0.121567000	0.503014000	0.118872000
6	1.488716000	-0.107723000	-0.086853000
8	-0.668748000	0.002743000	1.211481000
8	2.436199000	0.453374000	-0.503416000
9	1.483403000	-1.405790000	0.248548000
9	0.150771000	1.835043000	0.000432000
9	-1.261670000	-1.452624000	-0.471968000
9	-2.247034000	0.484172000	-0.392472000

CF2CFH

6	0.000000000	0.431789000	0.000000000
6	-0.700690000	-0.690042000	0.000000000
9	1.316307000	0.507667000	0.000000000
9	-0.565016000	1.629166000	0.000000000
9	-0.086452000	-1.885953000	0.000000000
1	-1.779411000	-0.708411000	0.000000000

TS CF2CFH + HO2 → CF2CFH(OOH)

6	0.271372000	-0.504974000	0.115879000
6	1.088201000	0.433466000	0.680282000
9	0.616730000	-1.170766000	-0.963146000
9	-0.572097000	-1.182154000	0.888746000
9	2.073419000	0.962222000	-0.044735000
1	0.862397000	0.917463000	1.617777000
8	-1.077315000	0.614524000	-0.775446000
8	-2.114235000	0.885722000	0.084543000
1	-2.549898000	0.025902000	0.204697000

CF2CFH(OOH)

6	-0.054638000	-0.454572000	0.023582000
6	1.041568000	0.283341000	0.706173000
9	0.418840000	-1.417935000	-0.795134000
9	-0.820329000	-1.045162000	0.988247000

9	1.918647000	0.879637000	-0.099527000
1	0.929838000	0.710745000	1.692132000
8	-0.871485000	0.295658000	-0.829550000
8	-1.405958000	1.394126000	-0.054314000
1	-2.286299000	1.049498000	0.157970000

CF2(O)CFH

6	-0.503138000	0.015259000	-0.012829000
6	0.817433000	-0.526173000	-0.266382000
9	-0.712863000	1.325189000	0.128255000
9	-1.624566000	-0.567532000	-0.454504000
9	1.878861000	0.300185000	-0.296661000
1	1.007101000	-1.464854000	-0.775823000
8	0.154280000	-0.623779000	1.007160000

Table 2S. Enthalpies at 298 K computed via the CBS-QB3 method.

CCl ₂ FCFCIO	-1729.906376
CFCI ₂	-1057.222993
COFCI	-672.695608
CCl ₂ FCFO	-1270.234151
TS for CCl ₂ FCFCIO → CFCI ₂ + COFCI	-1729.897915
TS for CCl ₂ FCFCIO → CCl ₂ FCFO + Cl	-1729.904253
F ₂ C(O)CFCICFO	-1123.116457
TS F ₂ C(O)CFCICFO → OCF ₂ CFC(F)O + Cl	-1123.074067
OCF ₂ CFC(F)O + Cl	-1123.091521
CF ₂ CFH + HO ₂	-526.64167
TS CF ₂ CFH + HO ₂ → CF ₂ CFH(OOH)	-526.62157
CF ₂ CFH(OOH)	-526.663811
CF ₂ (O)CFH + OH	-526.704881