Supporting Information

Unraveling the Mechanism and Structure-Activity Relationship of Swarts Reaction

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S1. Cartesian coordinates and single point energies

CCl_4

E = -1879.083110538000 Hartree

C	0.00000000	0.00000000	0.00000000
Cl	0.00000000	1.45282200	1.02732800
Cl	-1.45282200	0.00000000	-1.02732800
Cl	1.45282200	0.00000000	-1.02732800
Cl	0.00000000	-1.45282200	1.02732800

$CFCl_3$

E = -1518.736177693373 Hartree

C	0.10112200	0.22802000	0.00000000
Cl	-1.66682200	0.39982000	0.00000000
Cl	0.64486600	-0.62511900	1.46001000
Cl	0.64486600	-0.62511900	-1.46001000
F	0.64486600	1.45433100	0.00000000

CF_2Cl_2

E = -1158.392576657332 Hartree

C	0.00000000	0.00000000	0.33860400
Cl	0.00000000	1.46813000	-0.65537500
Cl	0.00000000	-1.46813000	-0.65537500
F	-1.07915400	0.00000000	1.12506200
F	1.07915400	0.00000000	1.12506200

CF_3Cl

E = -798.051645063101 Hartree

C	0.35166600	-0.00014800	0.00000000
Cl	-1.41645700	0.00030100	0.00000000
F	0.81369500	-0.62400000	1.08062400
F	0.81369500	-0.62400000	-1.08062400
F	0.81369500	1.24753000	0.00000000

CF_4

E = -437.712827622297 Hartree

C	0.00000000	0.00000000	0.00000000
F	0.00000000	1.08259400	0.76570700
F	-1.08259400	0.00000000	-0.76570700
F	0.00000000	-1.08259400	0.76570700
F	1.08259400	0.00000000	-0.76570700

SbF_5

E = -739.908609715463 Hartree

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Sb	0.00010100	0.00026500	0.00000000
F	1.61222200	0.93464800	0.00000000
F	0.00216500	0.00249400	1.87499700
F	-1.61928800	0.92263000	0.00000000
F	0.00216500	-1.86376900	0.00000000
F	0.00216500	0.00249400	-1.87499700

SbF_4Cl

E = -1100.269232076595 Hartree

Sb	0.00006500	0.19059200	0.00000000
F	0.00040200	0.26621500	1.88765900
F	1.59079700	1.16970500	0.00000000
F	-1.59272800	1.16628800	0.00000000
F	0.00040200	0.26621500	-1.88765900
Cl	0.00040200	-2.09035100	0.00000000

SbF_3Cl_2

E = -1460.628871923994 Hartree

Sb	-0.00101500	0.17587300	0.00000000
Cl	-1.98802300	-0.95597500	0.00000000
Cl	1.99976300	-0.93008000	0.00000000
F	-0.00547500	0.25836600	1.90058600
F	-0.00547500	2.04920400	0.00000000
F	-0.00547500	0.25836600	-1.90058600

SbF_2Cl_3

E = -1820.988468001699 Hartree

Sb	0.00162000	-0.00076300	0.00000000
Cl	1.97740500	1.16615200	0.00000000
Cl	-1.99230100	1.13314600	0.00000000
Cl	0.00487500	-2.29527700	0.00000000
F	0.00487500	-0.00163400	1.91531900
F	0.00487500	-0.00163400	-1.91531900

$SbFCl_4$

E = -2181.344962814291 Hartree

Sb	-0.00100800	0.00030700	-0.14563000
Cl	0.01569200	-0.01940300	2.22039600
Cl	-1.84722400	-1.38699500	-0.23008700
Cl	2.12736300	-0.89516600	-0.25076700
Cl	-0.28669400	2.29286700	-0.21124700
F	-0.01154800	0.01468700	-2.06154100

$SbCl_5$

E = -2541.699427003219 Hartree

Sb	-0.00004100	0.00421800	0.00000000
Cl	-0.00124600	0.01745300	2.37308400
Cl	-0.00124600	2.33434700	0.00000000
Cl	-0.00124600	0.01745300	-2.37308400
Cl	-1.99407600	-1.19578500	0.00000000
Cl	1.99793800	-1.18612500	0.00000000

ts1-a

E = -4060.410525565118 Hartree

Sb	-0.02331400	-0.15975300	0.94352100
F	-0.19539900	0.90340200	2.55563500
Cl	-0.29834300	2.01197000	-0.25931300
C	0.09567900	3.98683100	1.64826000
Cl	1.52817800	3.40603400	2.23175700
Cl	0.11519400	5.17490300	0.46965100
Cl	-1.31401100	3.70119300	2.47649800
Cl	2.32405400	0.32952400	1.02725100
Cl	0.26145000	-2.12623100	2.21579600
Cl	-2.38865800	-0.36906000	0.92908200
Cl	0.20231000	-1.24098600	-1.15999700

ts2-a

E = -4060.411555273425 Hartree

Sb	-0.18489700	0.28587400	1.09501600
C	0.38831900	4.13300400	1.09413500
Cl	1.83603900	3.82006200	0.33081000
Cl	-0.81009900	4.93598000	0.24476100
Cl	0.34208500	4.16560700	2.76188000
F	-0.48940000	2.30794600	0.83850200
Cl	-1.54055800	0.52168500	3.03753300
Cl	1.73101400	0.88592900	2.40443900
Cl	0.15489400	-2.03358900	1.37686200
Cl	1.16896700	0.42989000	-0.86639000
Cl	-2.12343200	0.03951300	-0.25166000

int-a

E = -4060.413298349984 Hartree

Sb	1.11358600	0.00398700	0.04957200
C	-2.98485500	-0.00174300	0.02986500
Cl	-2.67531700	-0.97435300	-1.25872600
Cl	-3.44077100	-0.66837100	1.47765900
Cl	-2.98385800	1.64074500	-0.15135800
F	-0.70202600	-0.00759800	0.84256600

Cl	1.47206200	2.07584800	1.16412400
Cl	0.12414800	1.19138500	-1.80354300
Cl	3.25765000	-0.00028200	-0.96999600
Cl	0.48637300	-2.06449900	-1.02177700
Cl	1.84409400	-1.20779900	1.95829600

ts1-b

E = -3700.056312908652 Hartree

Sb	-0.11756000	-0.14904600	0.95528600
F	-0.40960500	0.87522000	2.56620700
Cl	-0.51854100	2.01482900	-0.20506300
C	0.19330300	3.94378500	1.62335800
Cl	1.60236900	3.23667000	2.11987900
Cl	0.24688000	5.12735400	0.43990200
Cl	-1.17373900	3.80695700	2.55724200
F	1.71057600	0.45194000	1.06204900
Cl	0.40205700	-2.06048200	2.21682600
Cl	-2.44086700	-0.60717600	0.85927600
Cl	0.33078100	-1.14870500	-1.14087400

ts2-b

E = -3700.058820847599 Hartree

Sb	-0.22120400	0.32676100	1.02575600
C	0.39294700	4.01383600	1.16206900
Cl	1.86271400	3.70406900	0.43213700
Cl	-0.69879200	5.00746200	0.36094800
Cl	0.27752900	3.88811600	2.82372800
F	1.31150600	1.00234400	1.97673500
F	-0.56755900	2.32918900	0.65820800
Cl	-1.46867400	0.66640200	3.01298700
Cl	-2.18794400	-0.07539400	-0.22719300
Cl	0.28169700	-1.91575200	1.51227000
Cl	1.10582500	0.38693400	-0.93790900

int-b

E = -3700.060986759017 Hartree

Sb	-1.06054500	0.01208800	-0.00429300
C	2.86692100	0.00805500	-0.10643700
Cl	2.65802800	1.42442600	-0.92586400
Cl	3.52095400	0.03139000	1.41807900
Cl	2.57765900	-1.43246000	-0.84869000
F	0.01654800	0.08738700	-1.61384300
F	0.67120900	0.09682200	0.94018100
Cl	-0.73171100	-2.35543300	-0.05903600

Cl	-2.14987100	-0.09287200	2.09848000
Cl	-3.04763000	-0.10158100	-1.28059800
Cl	-1.02175500	2.38990000	0.00471800

ts1-c

E = -3339.701309790460 Hartree

Sb	-0.10901100	-0.12752400	0.96177700
F	-0.37733500	0.85119100	2.59065700
F	0.28054700	-1.70242100	1.94543400
Cl	-0.47907000	2.07641100	-0.17332000
C	0.16732600	3.92312800	1.57453500
Cl	1.59865700	3.27029100	2.10710500
Cl	0.22009100	5.14315300	0.41858200
Cl	-1.19116300	3.80344700	2.53565200
F	1.72307000	0.41700600	1.08582900
Cl	0.32749300	-1.12571800	-1.12126000
Cl	-2.41795100	-0.58431500	0.88757100

ts2-c

E = -3339.705017116761 Hartree

Sb	-0.27250900	0.33972400	1.11083300
F	0.84732600	0.57186200	-0.42286600
C	0.43280900	3.98563800	1.08738000
Cl	1.80181600	3.52707300	0.25085900
Cl	-0.67497800	4.98556800	0.31573900
Cl	0.47467800	3.99654200	2.75968400
F	1.20640700	1.00979300	2.13263600
F	-0.66805300	2.33467100	0.83594100
Cl	-1.61162300	0.48136400	3.05096200
Cl	0.37114700	-1.89036300	1.39497600
Cl	-2.11055400	-0.05992400	-0.30381000

int-c

E = -3339.706917028243 Hartree

Sb	1.06911000	-0.04796000	-0.04840800
F	0.44750800	-1.56189400	-1.06385300
C	-2.83489000	0.00066600	-0.12219700
Cl	-2.46095600	-0.92470700	-1.42966400
Cl	-3.47201700	-0.70840900	1.23607300
Cl	-2.74232000	1.64643000	-0.21644600
F	0.05111400	1.02530600	-1.28920900
F	-0.64478600	-0.20957000	0.90611000
Cl	1.51478200	1.89906300	1.22353300
Cl	2.99322900	0.13377100	-1.39374600

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Cl	2.03788400	-1.50747800	1.53463600

ts1-d

E = -2979.345756805519 Hartree

Sb	1.41685200	-0.21602500	-0.01243500
F	0.17685700	-1.66386400	-0.10740100
F	2.80172000	-1.40124100	0.48467000
Cl	-0.52674500	1.21811500	-0.63690500
C	-2.65788700	-0.04213200	0.08311600
Cl	-2.19383400	-0.48845700	1.61925900
Cl	-3.65804800	1.30216500	-0.08815500
Cl	-2.67468600	-1.19435200	-1.12646300
F	0.86782100	0.01777100	1.80592800
F	1.75107800	-0.45550500	-1.87115700
Cl	2.77746600	1.67991800	0.07503700

ts2-d

E = -2979.349048678541 Hartree

Sb	-0.23096200	0.34034500	1.14300300
F	0.84947100	0.58040200	-0.40469200
C	0.41247500	3.96526000	1.07436500
Cl	1.79816900	3.53197000	0.24326300
Cl	-0.70171700	4.95436100	0.29112000
Cl	0.47018700	4.02299400	2.75019200
F	1.24943100	0.99449200	2.16981000
F	-1.72973900	0.07049500	0.00184000
F	-0.63827300	2.33612300	0.86921400
Cl	-1.61816400	0.46691900	3.02788400
Cl	0.33240500	-1.90529800	1.35043400

int-d

E = -2979.351751558531 Hartree

Sb	-0.26486900	-1.08050200	-0.07267100
F	0.83854200	-0.74080800	-1.60413000
C	0.65481900	2.71359500	-0.15821600
Cl	1.87838100	2.01281500	-1.00393400
Cl	-0.50086600	3.59398700	-0.95730400
Cl	0.65523800	2.67433900	1.49245200
F	1.16045800	-0.32657400	0.99154500
F	-1.68266000	-1.59851000	-1.23923000
F	-0.84759800	0.77266500	-0.30368200
Cl	-1.65043700	-1.21648000	1.82618400
Cl	0.58424800	-3.25553500	0.11965200

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ts1-e

E = -2618.990111535388 Hartree

Sb	-0.05694800	-0.11687300	1.03170900
F	-0.33642300	0.81721300	2.66855500
F	0.20730200	-0.84064300	-0.69596000
F	0.24290500	-1.75455000	1.90428700
Cl	-0.42972200	2.07185600	-0.10244200
C	0.13329100	3.87672500	1.51598200
Cl	1.59475700	3.31494700	2.10376800
Cl	0.17200900	5.10902900	0.35988500
Cl	-1.21466800	3.78809100	2.51032100
F	1.78010800	0.36569400	1.12348300
F	-1.92164500	-0.41305200	0.89406100

ts2-e

E = -2618.993196895054 Hartree

Sb	1.31676700	-0.20723500	0.03825000
F	0.78807100	-2.02384300	0.05243500
F	3.03468400	-0.63122200	-0.61521600
C	-2.33102300	0.03493100	-0.03755600
Cl	-2.27343400	-1.49214500	-0.73174400
Cl	-3.17725100	0.20420300	1.41289200
Cl	-2.26579400	1.37037800	-1.05960300
F	0.52469800	-0.07359700	-1.69036900
F	1.78003400	-0.37131600	1.86767800
F	-0.60271800	0.14167600	0.73473500
Cl	1.66401400	2.09310100	0.09205500

int-e

E = -2618.996888679643 Hartree

Sb	1.30133600	-0.20862300	0.03945200
F	0.55827500	-1.96688900	-0.03466100
F	2.82625400	-0.80899100	-0.91723100
C	-2.60332800	0.05690400	-0.08752200
Cl	-2.30214200	-1.44397900	-0.68638200
Cl	-3.23592300	0.22736400	1.43468000
Cl	-2.40223400	1.38748900	-1.04273100
F	0.35430100	0.15059900	-1.59532300
F	2.07087400	-0.63840900	1.72266900
F	-0.34998600	0.30555000	0.94833700
Cl	2.06467400	2.00098400	0.14143000

ts3-a

E = -2258.633939687900 Hartree

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Sb	-1.29255200	0.07778700	-0.04971800
F	0.13400500	0.36063700	-1.32317900
F	-2.65219300	-0.16203100	1.25199400
F	-2.16408000	1.61253700	-0.73192100
Cl	-0.07807800	-1.79001600	0.78722300
C	2.70959800	0.04065000	0.21606000
Cl	2.43560800	1.64391100	0.21080100
Cl	2.84148700	-0.87429300	-1.13000500
F	-0.29770600	1.20399100	1.15390400
F	-2.19676500	-1.02607500	-1.30348700
F	2.87443700	-0.52953300	1.33968500

ts3-b

E = -1898.275490870944 Hartree

Sb	-1.09909551	0.06166388	-0.03747359
F	0.27224449	0.74230388	-1.21614959
F	-2.38340151	-0.61847812	1.18011141
F	-2.15948751	1.58188088	-0.39999659
Cl	0.37066849	-1.77505412	0.41073341
C	2.71620849	0.36332488	0.33577541
F	-0.21090951	1.00932988	1.37640641
F	-1.87922351	-0.88103112	-1.48801359
F	2.94608749	-0.25241912	1.40379541
F	2.27917449	1.52444388	0.46089241
Cl	3.11424149	-0.25031712	-1.11193959

ts3-c

E = -1537.917497023271 Hartree

Sb	-0.92156944	-0.06932024	-0.00095524
F	0.30251356	-0.83978024	1.27859676
F	-2.02271144	0.71418676	-1.32748024
F	-1.94198044	-1.65529924	0.00694576
Cl	0.54382656	1.82822476	-0.00522624
C	2.77018756	-0.26271424	0.00387176
F	0.23361356	-0.80628424	-1.35661224
F	-1.95370344	0.67641476	1.40113776
F	3.05622856	0.37474576	-1.02076824
F	2.97067556	0.23414176	1.12084276
F	2.46941556	-1.45610824	-0.08940924

S2. Linear free energy relationship between the charges on carbon atoms with the barriers of reaction

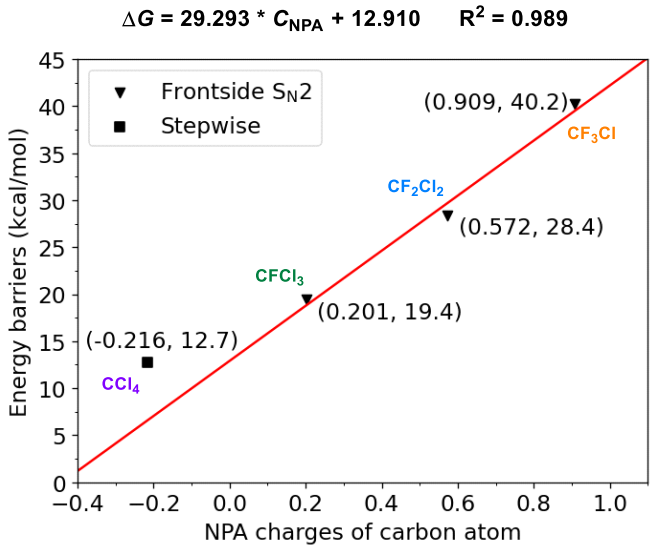

Figure S1. Correlation between the NPA charges of carbon atom (C_{NPA}) in $CF_yCl_{(4-x)}$ and the free energy of activation (ΔG) for the Swarts reaction. CCl_4 deviates from the linear trend due to its distinct mechanism. Excluding CCl_4, regression analysis was carried out for only three data points with a R^2 equal 0.989.

S3. Strategies for Distortion/interaction activation strain analysis

Intrinsic reaction coordinate (IRC) calculations were performed for **ts3-a**, **ts3-b** and **ts3-c** at the level of B3LYP-D3(BJ)/def2-TZVPP [1-4] via Gaussian 16 program [5]. The solvation model density (SMD) [6] was used in the calculations with carbon tetrachloride as a solvent. Gradient magnitude for Damped-Velocity Verlet (DVV) stopping criteria were turn off and fifty points were set along the reaction path in each direction. Electronic energies were calculated for all points. The strain and interaction energy at point ζ are given by [7]:

$$\Delta E_{\text{strain}}(\zeta) = \big(E_1(\zeta) - E_1(\text{free})\big) + \big(E_2(\zeta) - E_2(\text{free})\big)$$

$$\Delta E_{\text{int}}(\zeta) = E_{\text{total}}(\zeta) - E_1(\zeta) - E_2(\zeta)$$

where $E_1(\zeta)$ and $E_2(\zeta)$ indicate the electronic energies of fragment 1 and 2 at point ζ, E_1(free) and E_2(free) indicate the electronic energies of fragment 1 and 2 at free energy state and $E_{\text{total}}(\zeta)$ indicate the total electronic energy at point ζ.

Then, the total energy change at point ζ equals $\Delta E_{\text{strain}}(\zeta)$ plus $\Delta E_{\text{int}}(\zeta)$:

$$\Delta E(\zeta) = \Delta E_{\text{strain}}(\zeta) + \Delta E_{\text{int}}(\zeta)$$

S4. Bond variation and energy evolution for the reaction of CF_2Cl_2 and CF_3Cl with SbF_5

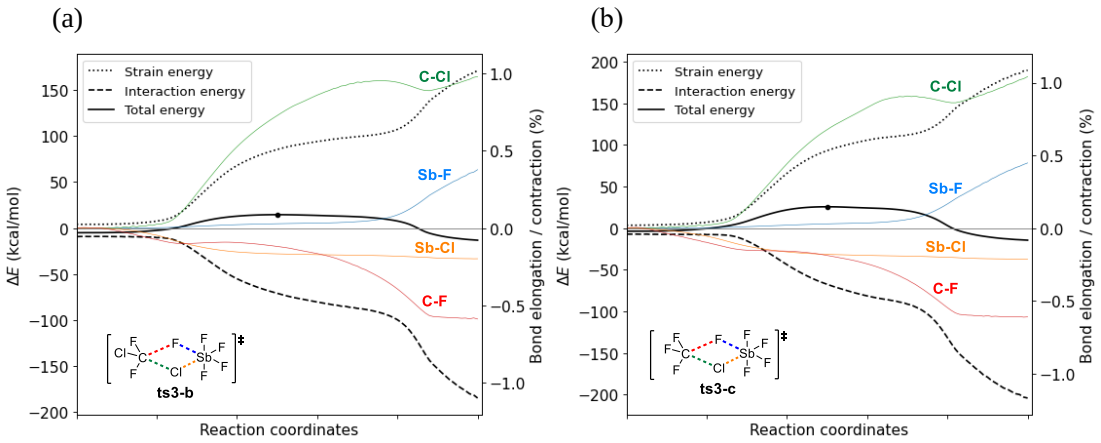

Figure S2. Activation strain analysis of the SbF_5 + CF_2Cl_2 (a) / CF_3Cl (b) reaction along the IRC. The left y-axis shows the change of each energy composition, and the right y-axis shows the change in C-Cl, Sb-F, Sb-Cl and C-F bond length relative to the first step. The transition state **ts3-a** is indicated with a thick dot and the zero line is show in grey.

References

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