

Theoretical Study on the Origin of Abnormal Regioselectivity in Ring-opening Reaction of Hexafluoropropylene Oxide

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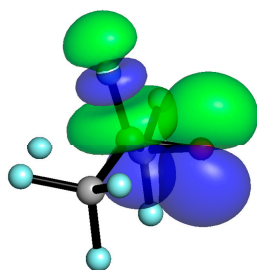
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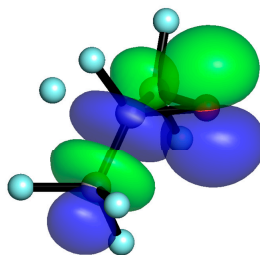
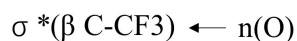
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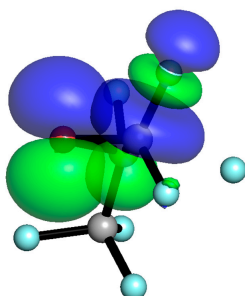
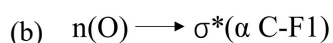
Part 1. Negative hyperconjugation in TS1 α and TS1 β .



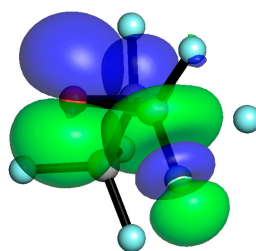
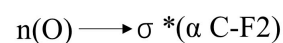
$$E(2) = 30.5 \text{ kcal/mol}$$



$$E(2) = 13.6 \text{ kcal/mol}$$



$$E(2) = 27.0 \text{ kcal/mol}$$

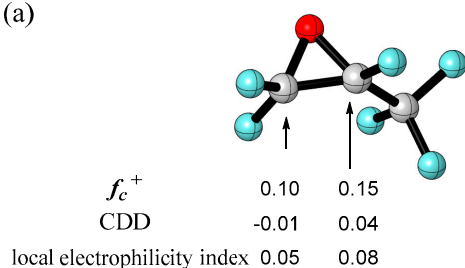


$$E(2) = 24.0 \text{ kcal/mol}$$

Figure S1. The key donor-acceptor orbital interactions in TS1 α (a) and TS1 β (b) by NBO analysis at the ω B97X-D/6-31+G(d,p)-SMD-(ethyl ether) level.

Part 2. The reactivity descriptors of epoxide carbon atoms of 1 and 2.

(a)



(b)

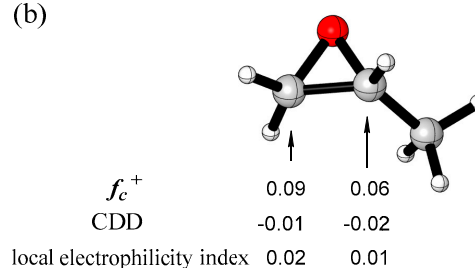


Figure S2. The reactivity descriptors of epoxide carbon atoms of 1(a) and 2(b), respectively.

To investigate the influence of electrophilicity on the regioselectivity, we conducted conceptual density functional theory (CDFT) [1-4] calculation (Figure S2). Interestingly, condensed Fukui function f_c^+ [5,6], condensed dual descriptors CDD [7], and condensed local electrophilicity index [8] all indicate that β -C should be more inclined to be attacked. These results remind us to visualize the lowest unoccupied molecular orbital and key Natural Bond Orbitals (NBOs) of 1 and 2.

Part 3. Key NBOs of 1 and 2.

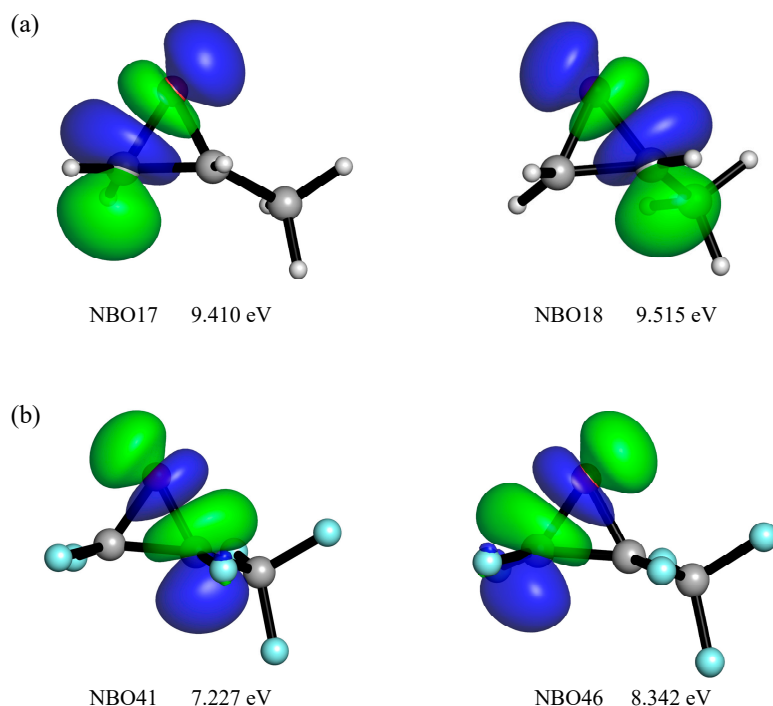


Figure S3. The key NBOs isosurfaces of **2(a)** and **1(b)** obtained at the ω B97X-D/6-31G(d,p)-SMD-(ethyl ether). Orbital energies are provided below the isosurfaces

NBO analysis shows that the energy of $\sigma^*_{\text{C}(\beta)\text{-O}}$ is lower than that of $\sigma^*_{\text{C}(\alpha)\text{-O}}$ for **1**, while the opposite trend was observed for **2** (Figure S2). These results indicate that charge-transfer or donor-acceptor orbital interactions between the incoming fluoride and the antibonding orbital of C-O bond in **1/2** may contribute to both the reactivity and regioselectivity.

Part 4. Reference.

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Part 5. ω B97X-D/6-31+G(d,p)-SMD-(ethyl ether) Calculated Cartesian Coordinates and Single Points Energy Calculated Using the ω B97X-D/6-311++G(2df,2p)-SMD-(ethyl ether).

1

C	1.40388	0.17884	0.00822
C	0.11485	-0.49349	0.07616
O	0.87325	-0.17061	1.22632
F	1.56207	1.47411	-0.22893
C	-1.26128	0.16294	-0.05531
F	0.04058	-1.79959	-0.2125
F	-1.69058	0.06395	-1.31633
F	-1.21135	1.44976	0.28355
F	-2.13735	-0.4545	0.74261
F	2.48878	-0.48094	-0.37785
Zero-point correction=			0.038925 (Hartree/Particle)
Thermal correction to Energy=			0.047239
Thermal correction to Enthalpy=			0.048183
Thermal correction to Gibbs Free Energy=			0.004663
SCF Done: E(RwB97XD) = -788.611652881			

2

C	1.0376	0.61743	-0.05631
C	-0.15168	-0.04215	0.48702
O	0.82787	-0.78509	-0.24634
C	-1.50612	0.09917	-0.14851
H	1.86718	0.87513	0.59986
H	-0.15264	-0.27027	1.5534
H	-2.07022	0.89959	0.34203
H	-2.07678	-0.82967	-0.04766
H	-1.41436	0.33741	-1.21233
H	0.94507	1.22184	-0.95786
Zero-point correction=			0.086283 (Hartree/Particle)
Thermal correction to Energy=			0.090652
Thermal correction to Enthalpy=			0.091597
Thermal correction to Gibbs Free Energy=			0.059939
SCF Done: E(RwB97XD) = -193.120552207			

Int1a

C	1.30219	-0.19929	-0.00229
C	0.0001	0.64047	-0.25307
O	0.00173	1.2995	-1.31618
F	2.38414	0.59623	-0.03643
F	1.34367	-0.86685	1.17172
C	-1.30277	-0.19878	-0.00261
F	1.46858	-1.1286	-0.97003
F	-1.42516	-1.18031	-0.9263
F	-1.38239	-0.80311	1.20204
F	-2.38909	0.58258	-0.11774
F	-0.00097	1.48335	1.01866
Zero-point correction=			0.040002 (Hartree/Particle)
Thermal correction to Energy=			0.049801

Thermal correction to Enthalpy= 0.050745
 Thermal correction to Gibbs Free Energy= 0.003517
 SCF Done: E(RwB97XD) = -888.652430169

Int1 β

C	0.05136	0.5408	-0.00325
C	1.32133	-0.35267	0.18258
O	1.36119	-1.09981	1.1584
C	-1.29829	-0.22337	0.00624
F	-1.32711	-1.18908	-0.91772
F	0.07662	1.25945	-1.15801
F	1.47255	-0.99817	-1.11454
F	2.39685	0.63025	0.0898
F	-1.55435	-0.7684	1.197
F	-2.30416	0.62993	-0.26941
F	-0.01995	1.43712	1.01947

Zero-point correction= 0.040180 (Hartree/Particle)
 Thermal correction to Energy= 0.049851
 Thermal correction to Enthalpy= 0.050795
 Thermal correction to Gibbs Free Energy= 0.004763
 SCF Done: E(RwB97XD) = -888.657861420

Int2 α

C	-0.77042	-0.61991	0.25361
C	0.55753	-0.12251	-0.32972
O	1.52689	-0.99047	0.03806
F	-1.90534	0.17979	-0.12362
C	0.81115	1.33177	0.12237
H	-0.73877	-0.60234	1.34906
H	-0.9847	-1.6321	-0.10074
H	0.91345	1.36618	1.21596
H	0.39362	-0.0685	-1.44281
H	0.00722	2.01918	-0.17755
H	1.75261	1.68709	-0.31333

Zero-point correction= 0.087433 (Hartree/Particle)
 Thermal correction to Energy= 0.093003
 Thermal correction to Enthalpy= 0.093947
 Thermal correction to Gibbs Free Energy= 0.058764
 SCF Done: E(RwB97XD) = -293.079702585

Int2 β

C	-0.39466	-0.04831	-0.34087
C	0.93175	-0.55416	0.25468
O	1.98812	0.18294	-0.14124
C	-0.79184	1.33018	0.12517
F	-1.4604	-0.94947	0.0284
H	-0.34681	-0.0995	-1.43483
H	0.98026	-1.64109	-0.03411
H	0.76184	-0.57425	1.37003
H	0.0072	2.02752	-0.1418
H	-1.72888	1.66194	-0.33482
H	-0.90649	1.3408	1.21594

Zero-point correction= 0.087079 (Hartree/Particle)
 Thermal correction to Energy= 0.092672
 Thermal correction to Enthalpy= 0.093616
 Thermal correction to Gibbs Free Energy= 0.058370
 SCF Done: E(RwB97XD) = -293.080411305

P1 α

C	-1.32702	-0.09815	-0.00399
C	-0.00001	0.71231	-0.00008
O	-0.00002	1.90592	-0.00001
F	-2.32897	0.66662	-0.42043
F	-1.23493	-1.1661	-0.80416
C	1.32705	-0.09808	0.00393
F	-1.59497	-0.51959	1.23871
F	1.23518	-1.16546	0.80504
F	1.59452	-0.5206	-1.23846
F	2.32917	0.66692	0.4194

Zero-point correction= 0.038593 (Hartree/Particle)
 Thermal correction to Energy= 0.047442
 Thermal correction to Enthalpy= 0.048386
 Thermal correction to Gibbs Free Energy= 0.003142
 SCF Done: E(RwB97XD) = -788.641983264

P1 β

C	0.168	0.49094	-0.33066
C	1.4986	-0.0975	0.1941
O	2.1452	0.34282	1.07826
C	-1.08845	-0.25548	0.20454
F	-1.09665	-1.51744	-0.22515
F	0.14979	0.44284	-1.6765
F	1.83024	-1.19221	-0.48787
F	-1.07416	-0.25466	1.53943
F	-2.19102	0.35466	-0.21922
F	0.08953	1.77011	0.06553

Zero-point correction= 0.038748 (Hartree/Particle)
 Thermal correction to Energy= 0.047580
 Thermal correction to Enthalpy= 0.048524
 Thermal correction to Gibbs Free Energy= 0.003528
 SCF Done: E(RwB97XD) = -788.651092777

ts1 α

C	1.26191	0.04834	0.25973
C	-0.03973	0.59714	-0.04394
O	0.39061	1.20642	1.07646
F	1.47925	-0.89969	1.13741
F	1.4049	-1.2998	-1.24406
F	2.35624	0.64936	-0.13749
C	-1.3605	-0.18505	0.04772
F	-2.34395	0.66415	0.40868
F	-1.71467	-0.74316	-1.11165
F	-1.2994	-1.14637	0.97637
F	-0.13736	1.39617	-1.16179

Zero-point correction=	0.038582 (Hartree/Particle)
Thermal correction to Energy=	0.048337
Thermal correction to Enthalpy=	0.049281
Thermal correction to Gibbs Free Energy=	0.002888
SCF Done: E(RwB97XD) =	-888.571642171

ts1 β

C	-0.12305	0.29547	-0.35667
C	-1.39163	-0.31221	-0.02996
O	-0.89216	-0.95456	-1.08226
C	1.27142	-0.22996	0.02768
F	1.26835	-0.85591	1.20391
F	0.00587	1.60717	1.2191
F	-1.58515	-1.03624	1.0945
F	-2.53061	0.39372	-0.2286
F	1.70356	-1.12148	-0.89204
F	2.17921	0.74483	0.04429
F	-0.08603	1.28088	-1.23986
Zero-point correction=	0.038559 (Hartree/Particle)		
Thermal correction to Energy=	0.048248		
Thermal correction to Enthalpy=	0.049192		
Thermal correction to Gibbs Free Energy=	0.003092		
SCF Done: E(RwB97XD) =	-888.577972634		

ts2 α

C	-0.54487	-0.68452	0.1854
C	0.61662	-0.03415	-0.41703
O	1.27573	-1.13961	0.09282
F	-2.13719	0.30156	-0.04825
C	1.03209	1.31767	0.13766
H	-0.63694	-0.62602	1.2607
H	-0.96192	-1.54193	-0.322
H	1.01422	1.30053	1.23371
H	0.58002	0.00853	-1.5207
H	0.35795	2.1092	-0.21152
H	2.05246	1.55856	-0.18469
Zero-point correction=	0.085834 (Hartree/Particle)		
Thermal correction to Energy=	0.091537		
Thermal correction to Enthalpy=	0.092482		
Thermal correction to Gibbs Free Energy=	0.056866		
SCF Done: E(RwB97XD) =	-293.056455571		

ts2 β

C	-0.08624	0.04428	-0.33405
C	0.88842	-0.78284	0.36831
O	1.82251	0.03525	-0.24135
C	-0.46494	1.40167	0.17534
F	-1.83011	-0.75343	-0.04282
H	-0.17843	-0.14667	-1.3945
H	0.9032	-1.84651	0.07278
H	0.83468	-0.71859	1.47074
H	0.26096	2.1505	-0.15057

H	-1.44915	1.67672	-0.20923
H	-0.50383	1.40474	1.26936
Zero-point correction=			0.085744 (Hartree/Particle)
Thermal correction to Energy=			0.091572
Thermal correction to Enthalpy=			0.092516
Thermal correction to Gibbs Free Energy=			0.056612
SCF Done: E(RwB97XD) =	-293.051506522		

Part 6. ωB97X-D/6-31G(d,p)-SMD-(ethyl ether) Calculated Cartesian Coordinates.

1

C	1.39450800	0.17849400	-0.00914100
C	0.11298500	-0.50077200	-0.07484000
O	0.86780100	-0.17256600	-1.22990700
F	2.48054700	-0.47357900	0.37730000
F	1.53582600	1.47261900	0.23091400
F	0.04072100	-1.80337900	0.21547900
C	-1.25267600	0.16244000	0.05467300
F	-1.18743200	1.44686400	-0.28381000
F	-1.67984000	0.06601700	1.31436600
F	-2.13107900	-0.44859200	-0.74146000
Zero-point correction=			0.039654 (Hartree/Particle)
Thermal correction to Energy=			0.047903
Thermal correction to Enthalpy=			0.048848
Thermal correction to Gibbs Free Energy=			0.005484

2

C	1.03800900	0.61429900	-0.05658000
C	-0.15028200	-0.04521300	0.48789000
O	0.82516200	-0.78312200	-0.24777400
C	-1.50442100	0.10056200	-0.14787800
H	1.86604000	0.87652200	0.60097800
H	-0.15342700	-0.26897800	1.55596100
H	-2.07054200	0.90015100	0.34045000
H	-2.07751700	-0.82683100	-0.05200800
H	-1.40882900	0.33900600	-1.21090400
H	0.94314400	1.22721700	-0.95287700
Zero-point correction=			0.086484 (Hartree/Particle)
Thermal correction to Energy=			0.090846
Thermal correction to Enthalpy=			0.091790
Thermal correction to Gibbs Free Energy=			0.060143