Supplementary Information

"High Level *ab initio* Investigation of the Catalytic Effect of Water on Formic Acid Decomposition and Isomerization"

1. Cartesian Coordinates of each stationary point (Bohr) / harmonic vibrational frequencies in cm^{-1}
For structures that are *Cs* symmetry, A'' modes are **bold.**

2. NBO Results for Transition States.

3. 200 K Gibbs Free Energy Diagram. Additive Gibbs Free Energy corrections were obtained from harmonic vibrational frequency computations in CFOUR2.0. The PES is the sum of the Gibbs corrections and the CCSDT(Q)/CBS energies.

Section 1.
Monomers/Products:

CO

O	-0.00000000	0.00000000	0.92016058
C	0.00000000	0.00000000	-1.22649083

Frequencies:
2144

CO_2

O	-0.00000000	-0.00000000	2.20523758
C	-0.00000000	-0.00000000	-0.00000000
O	0.00000000	0.00000000	-2.20523758

Frequencies:
664
664
1341
2373

H_2

H	-0.00000000	0.00000000	0.70201448
H	0.00000000	0.00000000	-0.70201448

Frequencies:
4401

H_2O

O	0.00000000	0.00000000	0.12495140
H	0.00000000	-1.43366380	-0.99153466
H	0.00000000	1.43366380	-0.99153466

Frequencies:

1646
3811
3920

FA-*cis*

H	-0.05631403	2.83518096	-0.00000000
O	2.08042249	-0.42090329	-0.00000000
H	3.40193501	0.83571081	-0.00000000
O	-2.14702001	-0.38010153	0.00000000
C	-0.19221491	0.75936559	-0.00000000

Frequencies:

513
655
1029
1114
1288
1415
1843
3006
3805

FA-*trans*

H	0.05864415	2.84797879	0.00000000
O	-2.14916597	-0.23068232	0.00000000
H	-1.93011433	-2.05066427	0.00000000
O	2.12630969	-0.40726313	0.00000000
C	0.18764156	0.78336079	0.00000000

Frequencies:

627
665
1051
1132
1311
1405
1803

3088
3742

Complexes:

T1

H	-4.2611702600	-0.2470350100	0.0215261800
O	-1.0015278500	-2.1682927800	-0.0135354700
H	0.8270078300	-1.8100956200	-0.0319083300
O	-1.2258473600	2.1095698900	-0.0082012200
C	-2.2120652400	0.0355844900	0.0008788200
H	4.8563689600	0.2474248100	-1.2336638500
O	3.6381172300	0.0510014600	0.1002974300
H	2.5269758400	1.5085520600	-0.0132339400

Frequencies:
173
185
219
266
358
603
693
908
1070
1211
1389
1458
1644
1769
3087
3427
3683
3882

T2

H	-0.08064623	2.08848197	-0.00000000
O	-3.67321995	0.84018190	-0.00000000
H	-4.53972292	-0.77576277	0.00000000
O	-0.28994159	-1.75893418	0.00000000
C	-1.18822221	0.34384166	-0.00000000
O	4.54178634	0.63404925	-0.00000000
H	3.38591013	-0.78238223	0.00000000
H	6.19922174	-0.10595700	0.00000000

Frequencies:
60
78

79
171
352
475
636
676
1068
1149
1325
1412
1654
1781
3112
3737
3741
3899

T3

H	-0.06218989	1.96622749	-0.00000000
O	0.33780693	-1.81214972	-0.00000000
H	1.71444367	-3.02165594	0.00000000
O	3.65558029	0.88257032	0.00000000
C	1.41177652	0.51855906	0.00000000
H	-3.69775762	-0.97087741	-0.00000000
O	-4.52650453	0.65087060	-0.00000000
H	-6.30331866	0.27522267	-0.00000000

Frequencies:

45
74
88
134
273
317
626
648
1058
1114
1294
1411
1645
1804
3116
3746
3795
3911

C1

H	-0.78145276	2.42672801	-0.00000006
O	-0.18254495	-1.39946904	0.00000001
H	1.55364735	-0.78188333	0.00000001
O	-4.02414490	0.38120447	0.00000001
C	-1.76206602	0.58992376	-0.00000002
O	4.74985715	0.46024078	-0.00000001
H	5.79398234	0.09363822	-1.44350312
H	5.79398224	0.09363852	1.44350326

Frequencies:

69
87
109
191
250
278
680
856
1042
1163
1384
1416
1650
1829
2995
3608
3806
3910

C2

H	0.03494843	2.02931083	-0.00000000
O	3.69580356	0.66660928	-0.00000000
H	4.03015760	2.45977065	-0.00000000
O	0.27427950	-1.79372510	0.00000000
C	1.17592424	0.29431119	-0.00000000
O	-4.50635451	0.67384109	-0.00000000
H	-6.17781679	-0.03383631	0.00000000
H	-3.37780062	-0.76575911	0.00000000

Frequencies:

75
83
88
173

363
487
534
664
1049
1136
1296
1430
1656
1821
3041
3730
3803
3898

C3

H	-5.7935348600	0.7665493599	0.0000000000
O	-4.6192667200	-0.6186046500	0.0000000000
H	-2.9804149500	0.1884808200	0.0000000000
O	0.4223797499	1.8831154100	0.0000000000
C	2.3753004801	0.7234285700	0.0000000000
O	2.4374498600	-1.8198352600	0.0000000000
H	4.1713736501	-2.3862179600	0.0000000000
H	4.2438240700	1.6308505500	0.0000000000

Frequencies:
32
51
75
147
281
493
529
663
1037
1136
1291
1417
1669
1829
3028
3754
3804
3892

C4

H	4.38323432	1.10152586	-0.00000000
O	1.96841802	-1.95933521	-0.00000000
H	3.56868244	-2.83490470	-0.00000000
O	0.67074668	2.05381401	0.00000000
C	2.37830291	0.56016431	-0.00000000
O	-4.49128436	-0.31504823	0.00000000
H	-2.92005405	0.61501151	0.00000000
H	-3.95542495	-2.05081615	-0.00000000

Frequencies:

27
37
121
143
255
474
522
663
1034
1125
1290
1414
1671
1831
3031
3765
3803
3889

Transition States

Inter

H	-0.16614516	2.84663993	-0.03428326
C	-0.22468884	0.77231950	-0.02319657
O	2.14527457	-0.30137726	0.12188302
H	2.82440743	-0.55659622	-1.54962156
O	-2.14419905	-0.42234010	-0.00467967

Frequencies:

599i
670
915
1090
1208
1392
1806
3039

3827

Cis-TS

H	0.24957415	3.02979821	0.00000001
O	2.17294998	-0.36557240	0.00000000
H	1.94687418	2.11422778	-0.00000001
O	-2.23820209	-0.22955634	-0.00000000
C	-0.09749447	0.36122961	-0.00000000

Frequencies:

2264i
616
721
886
1038
1321
1759
2086
2089

Trans-TS

H	-2.97293106	-1.34018340	1.29723903
O	-2.64222309	-0.22148459	-0.11397953
C	0.70139796	0.89378299	0.03950093
O	2.37684005	-0.48877327	-0.02142037
H	-1.16667284	1.97037019	0.38132476

Frequencies:

1680i
315
337
577
740
1046
1911
2614
3764

T1-TS

H	-2.2897195800	-1.7805179801	1.5570974700
O	-0.6610553599	-2.6520903700	-0.3070310099
H	1.0956378100	-2.1597244200	-0.0513596600
O	-1.8473214600	2.1126201799	-0.3425455901

C	-2.3560923899	0.1981956101	0.5886182800
H	5.5341480000	0.3760734600	-0.3685536500
O	3.8098362099	0.5042783701	0.1922890801
H	3.0584172100	1.7628075800	-0.8882762700

Frequencies:

1749i
63
92
152
163
198
250
358
572
708
871
1068
1643
1867
2562
3665
3797
3907

T2-TS

H	6.24947892	1.73219204	-0.02433980
O	4.64706904	0.87638792	-0.08255629
H	5.07295335	-0.88890236	0.01568524
O	-0.25839906	-2.15526007	-0.08749649
C	-0.78563627	-0.10087811	0.37461523
H	-1.57430801	1.92113121	0.45948604
O	-4.12148736	1.11887838	-0.02735329
H	-4.63406988	0.97593475	-1.77833343

Frequencies:

1644i
32i
47
95
119
136
142
312
335
556
722

1044
1646
1920
2648
3768
3805
3914

T3-TSa

C	1.24650718	-0.77961143	-0.09089814
O	3.41982783	-0.65566808	0.06091185
O	-0.46140764	2.22892201	-0.09756258
H	-1.13454566	-1.68121725	-0.10965829
O	-3.40739697	-1.05090608	-0.06806220
H	-2.47835153	0.88400354	0.14596715
H	-4.21930974	-1.55124686	1.48284003
H	0.11584688	3.34112082	1.22503001

Frequencies:

1702i
203
293
379
501
535
597
641
665
764
1110
1360
1503
1641
1974
2053
3825
3841

T3-TSb

H	-0.3635076200	-0.5216239500	0.4539301600
O	-0.3306174500	2.2295083900	-0.1110815200
H	0.1774106600	3.3573224900	1.2350401500
O	3.9046181000	-0.7311457900	-0.0682397000
C	1.7534034900	-0.8362851400	0.1014930400
H	-3.6792357300	0.6926197900	-0.2132388300
O	-4.3094266000	-1.0042132100	0.0948654100
H	-5.3403986000	-1.4133239600	-1.3438166200

Frequencies:

1556i
75
87
201
214
274
320
369
567
623
698
1058
1641
1952
2627
3665
3782
3883

C1-TS

H	0.1243125001	2.2659889299	0.0468542001
O	-0.0071217501	-1.7932995600	0.0063173099
H	2.7545923300	-0.8809597801	-0.0448151300
O	-3.5057677200	0.8054247000	0.0012353600
C	-1.3670720700	0.1004771800	0.0097048101
O	3.9302141601	0.6562718701	-0.1097438700
H	1.9853864099	1.9211518300	0.0053361899
H	4.7899559200	0.7602345401	1.4989196300

Frequencies:
1514i
169
372
459
488
598
786
844
896
1265
1360
1397
1611
1658
1890
1998
2873
3807

C2-TS

H	-6.2568252400	-0.4229615501	0.0474993300
O	-4.4660054900	-0.7179905200	-0.0236722101
H	-3.7108853701	0.9400910499	-0.0361174399
O	0.3276855801	1.9570565000	0.0041536801
C	1.4360172200	0.0103705900	0.0454930201
O	3.5972258000	-0.9900196401	-0.0451374101
H	1.6317385100	-2.5936615799	0.1912436300
H	-0.1748826500	-1.9994948700	0.2818334401

Frequencies:

2176i
55
76
101
142
260
340
609
728
986
1020
1344
1639
1810
2055
2180
3791
3907

C3-TS

O	0.1309615300	1.2623146600	0.0000000000
H	-3.7069287800	-0.0118321000	0.0000000000
O	-5.4264038300	-0.6089752500	0.0000000000
H	-6.4236440000	0.9092322200	0.0000000000
C	2.2410269700	0.5452323900	0.0000000000
H	3.9786324300	2.5628224400	0.0000000000
O	3.6937653400	-1.3354902000	0.0000000000
H	4.8881918200	0.8740169300	0.0000000000

Frequencies:

2246i
15i
19
43
110
192

330
612
725
914
1023
1334
1656
1773
2077
2112
3803
3909

Inter2

H	-4.33664548	1.02985078	1.62882979
O	-3.74794989	0.73548250	-0.07068364
C	-1.18932402	0.31034084	-0.08126743
H	-0.05359014	2.02928752	-0.30727653
O	-0.27710565	-1.76732267	0.01708055
H	3.45156368	-0.77559061	-0.00662672
O	4.58415200	0.65667267	0.05159065
H	6.22648265	-0.02454245	-0.31535026

Frequencies:
618i
70
76
88
164
331
466
679
926
1108
1215
1405
1652
1785
3067
3750
3826
3898

Inter1

H	-2.38591844	0.82301608	2.69325643
O	-0.25332501	1.77768437	-0.42454006
H	1.43644320	1.09393137	-0.12925205
O	-3.16852422	-1.36073186	-0.33268340

C	-2.02078941	0.29416525	0.71594273
H	5.26083865	-1.09789942	1.53213209
O	4.38902153	-0.56263466	0.02963215
H	4.40010366	-2.00954171	-1.07334164

Frequencies:
379i
58
76
168
207
225
547
689
975
1136
1284
1398
1647
1790
3012
3572
3807
3913

Section 2: NBO output for Minima:
Results show the primary donor and acceptor interactions for each minima in kcal mol^{-1}.

T1

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	1.67	0.92	0.035
5. LP (1) O 2	22. BD*(2) O 4- C 5	8.13	1.14	0.086
5. LP (1) O 2	77. RY (1) C 5	1.27	1.18	0.035
5. LP (1) O 2	80. RY (4) C 5	0.82	2.06	0.037
6. LP (2) O 2	21. BD*(1) O 4- C 5	56.09	0.32	0.120
6. LP (2) O 2	79. RY (3) C 5	1.60	2.04	0.051
7. LP (1) O 4	18. BD*(1) H 1- C 5	0.76	0.98	0.024
7. LP (1) O 4	20. BD*(1) O 2- C 5	1.39	0.97	0.033
7. LP (1) O 4	77. RY (1) C 5	5.72	1.24	0.075
7. LP (1) O 4	78. RY (2) C 5	0.53	2.10	0.030
8. LP (2) O 4	18. BD*(1) H 1- C 5	20.31	0.67	0.104
8. LP (2) O 4	20. BD*(1) O 2- C 5	29.94	0.67	0.126
8. LP (2) O 4	68. RY (10) O 4	0.53	1.91	0.029
8. LP (2) O 4	78. RY (2) C 5	2.20	1.79	0.056
8. LP (2) O 4	80. RY (4) C 5	0.53	1.82	0.028
11. BD (1) H 1- C 5	19. BD*(1) O 2- H 3	3.38	0.95	0.051
11. BD (1) H 1- C 5	59. RY (1) O 4	1.06	1.59	0.037
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	3.49	1.10	0.055
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	1.34	1.32	0.038
12. BD (1) O 2- H 3	77. RY (1) C 5	1.27	1.36	0.037
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	1.04	0.38	0.018
14. BD (1) O 4- C 5	34. RY (2) O 2	0.67	1.14	0.025
from unit 1 to unit 2				
7. LP (1) O 4	24. BD*(1) O 7- H 8	1.77	1.05	0.038
8. LP (2) O 4	23. BD*(1) H 6- O 7	0.08	0.74	0.007
8. LP (2) O 4	24. BD*(1) O 7- H 8	5.61	0.74	0.058
8. LP (2) O 4	103. RY (1) O 7	0.06	1.55	0.009
12. BD (1) O 2- H 3	23. BD*(1) H 6- O 7	0.19	1.17	0.013
12. BD (1) O 2- H 3	103. RY (1) O 7	0.10	1.98	0.012
12. BD (1) O 2- H 3	104. RY (2) O 7	0.18	1.96	0.017
from unit 2 to unit 1				
9. LP (1) O 7	19. BD*(1) O 2- H 3	0.39	0.87	0.016
10. LP (2) O 7	19. BD*(1) O 2- H 3	18.50	0.84	0.111
10. LP (2) O 7	35. RY (3) O 2	0.07	1.50	0.009
10. LP (2) O 7	51. RY (1) H 3	0.19	1.56	0.015
10. LP (2) O 7	52. RY (2) H 3	0.08	1.27	0.009
10. LP (2) O 7	53. RY (3) H 3	0.06	1.17	0.007
10. LP (2) O 7	56. RY (6) H 3	0.11	1.72	0.012
16. BD (1) H 6- O 7	52. RY (2) H 3	0.10	1.54	0.011
16. BD (1) H 6- O 7	53. RY (3) H 3	0.10	1.44	0.010
17. BD (1) O 7- H 8	19. BD*(1) O 2- H 3	1.14	1.12	0.032
17. BD (1) O 7- H 8	51. RY (1) H 3	0.11	1.83	0.013
17. BD (1) O 7- H 8	52. RY (2) H 3	0.15	1.55	0.014
17. BD (1) O 7- H 8	53. RY (3) H 3	0.09	1.45	0.010
17. BD (1) O 7- H 8	59. RY (1) O 4	0.14	1.76	0.014
17. BD (1) O 7- H 8	62. RY (4) O 4	0.12	1.92	0.014
within unit 2				
9. LP (1) O 7	95. RY (1) H 6	0.70	1.55	0.029
9. LP (1) O 7	122. RY (2) H 8	0.62	1.48	0.027
10. LP (2) O 7	95. RY (1) H 6	0.70	1.52	0.029
10. LP (2) O 7	124. RY (4) H 8	0.63	1.66	0.029

T2

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	1.21	0.96	0.030
5. LP (1) O 2	22. BD*(2) O 4- C 5	6.91	1.18	0.080
5. LP (1) O 2	77. RY (1) C 5	1.08	1.26	0.033
5. LP (1) O 2	80. RY (4) C 5	0.85	1.98	0.037
6. LP (2) O 2	21. BD*(1) O 4- C 5	50.08	0.34	0.116
6. LP (2) O 2	52. RY (2) H 3	1.20	1.50	0.038
6. LP (2) O 2	79. RY (3) C 5	1.60	2.06	0.051
6. LP (2) O 2	89. RY (13) C 5	0.59	0.98	0.021
7. LP (1) O 4	18. BD*(1) H 1- C 5	1.60	0.99	0.035
7. LP (1) O 4	77. RY (1) C 5	5.05	1.29	0.072
7. LP (1) O 4	78. RY (2) C 5	0.98	2.04	0.040
8. LP (2) O 4	18. BD*(1) H 1- C 5	19.09	0.68	0.102
8. LP (2) O 4	20. BD*(1) O 2- C 5	33.01	0.65	0.131
8. LP (2) O 4	66. RY (8) O 4	0.77	1.65	0.032
8. LP (2) O 4	78. RY (2) C 5	1.85	1.73	0.051
8. LP (2) O 4	80. RY (4) C 5	0.99	1.71	0.037
11. BD (1) H 1- C 5	19. BD*(1) O 2- H 3	3.72	0.94	0.053
11. BD (1) H 1- C 5	59. RY (1) O 4	1.33	1.40	0.039
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	3.50	1.11	0.056
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	1.69	1.33	0.042
12. BD (1) O 2- H 3	77. RY (1) C 5	1.13	1.41	0.036
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	0.89	0.39	0.017
14. BD (1) O 4- C 5	34. RY (2) O 2	0.68	1.17	0.025
from unit 1 to unit 2				
7. LP (1) O 4	23. BD*(1) O 6- H 7	1.09	1.09	0.031
8. LP (2) O 4	23. BD*(1) O 6- H 7	5.35	0.79	0.058
8. LP (2) O 4	114. RY (2) H 7	0.10	1.35	0.010
11. BD (1) H 1- C 5	24. BD*(1) O 6- H 8	0.13	1.04	0.010
from unit 2 to unit 1				
9. LP (1) O 6	18. BD*(1) H 1- C 5	0.50	0.92	0.019
9. LP (1) O 6	20. BD*(1) O 2- C 5	0.09	0.89	0.008
9. LP (1) O 6	77. RY (1) C 5	0.06	1.22	0.007
16. BD (1) O 6- H 7	18. BD*(1) H 1- C 5	0.11	1.07	0.010
16. BD (1) O 6- H 7	20. BD*(1) O 2- C 5	0.16	1.03	0.011
16. BD (1) O 6- H 7	22. BD*(2) O 4- C 5	0.06	1.29	0.008
16. BD (1) O 6- H 7	26. RY (2) H 1	0.10	1.18	0.010
16. BD (1) O 6- H 7	62. RY (4) O 4	0.09	1.74	0.011
16. BD (1) O 6- H 7	82. RY (6) C 5	0.06	1.91	0.010
17. BD (1) O 6- H 8	20. BD*(1) O 2- C 5	0.08	1.03	0.008
17. BD (1) O 6- H 8	22. BD*(2) O 4- C 5	0.06	1.28	0.008
17. BD (1) O 6- H 8	25. RY (1) H 1	0.35	1.16	0.018
17. BD (1) O 6- H 8	26. RY (2) H 1	0.33	1.17	0.018
within unit 2				
9. LP (1) O 6	122. RY (2) H 8	0.74	1.77	0.032
10. LP (2) O 6	113. RY (1) H 7	1.30	1.46	0.039
10. LP (2) O 6	121. RY (1) H 8	1.68	1.37	0.043
17. BD (1) O 6- H 8	115. RY (3) H 7	0.75	1.83	0.033

T3

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	1.09	0.97	0.029
5. LP (1) O 2	22. BD*(2) O 4- C 5	6.04	1.21	0.076
5. LP (1) O 2	77. RY (1) C 5	0.95	1.23	0.030
5. LP (1) O 2	80. RY (4) C 5	0.82	2.07	0.037
6. LP (2) O 2	21. BD*(1) O 4- C 5	44.13	0.35	0.111
6. LP (2) O 2	52. RY (2) H 3	1.20	1.54	0.038
6. LP (2) O 2	79. RY (3) C 5	1.46	2.05	0.049
6. LP (2) O 2	83. RY (7) C 5	0.68	1.11	0.025
7. LP (1) O 4	18. BD*(1) H 1- C 5	1.37	0.98	0.033
7. LP (1) O 4	20. BD*(1) O 2- C 5	0.78	0.92	0.024
7. LP (1) O 4	77. RY (1) C 5	6.25	1.24	0.078
7. LP (1) O 4	78. RY (2) C 5	0.58	2.10	0.031
8. LP (2) O 4	18. BD*(1) H 1- C 5	19.91	0.68	0.104
8. LP (2) O 4	20. BD*(1) O 2- C 5	36.41	0.62	0.134
8. LP (2) O 4	67. RY (9) O 4	0.57	1.48	0.026
8. LP (2) O 4	78. RY (2) C 5	2.30	1.79	0.057
8. LP (2) O 4	80. RY (4) C 5	0.96	1.77	0.037
11. BD (1) H 1- C 5	19. BD*(1) O 2- H 3	3.46	0.94	0.051
11. BD (1) H 1- C 5	59. RY (1) O 4	1.43	1.34	0.039
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	3.13	1.12	0.053
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	1.58	1.36	0.041
12. BD (1) O 2- H 3	77. RY (1) C 5	0.99	1.38	0.033
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	0.75	0.39	0.015
14. BD (1) O 4- C 5	34. RY (2) O 2	0.64	1.17	0.024
from unit 1 to unit 2				
5. LP (1) O 2	23. BD*(1) H 6- O 7	1.73	1.05	0.038
5. LP (1) O 2	24. BD*(1) O 7- H 8	0.06	1.05	0.007
11. BD (1) H 1- C 5	24. BD*(1) O 7- H 8	0.14	1.03	0.011
12. BD (1) O 2- H 3	23. BD*(1) H 6- O 7	0.06	1.21	0.008
12. BD (1) O 2- H 3	97. RY (3) H 6	0.08	1.59	0.010
from unit 2 to unit 1				
10. LP (2) O 7	18. BD*(1) H 1- C 5	1.20	0.95	0.030
10. LP (2) O 7	22. BD*(2) O 4- C 5	0.09	1.19	0.009
10. LP (2) O 7	77. RY (1) C 5	0.05	1.21	0.007
16. BD (1) H 6- O 7	18. BD*(1) H 1- C 5	0.18	1.09	0.012
16. BD (1) H 6- O 7	19. BD*(1) O 2- H 3	0.19	1.09	0.013
16. BD (1) H 6- O 7	25. RY (1) H 1	0.12	1.30	0.011
16. BD (1) H 6- O 7	35. RY (3) O 2	0.11	1.30	0.011
17. BD (1) O 7- H 8	22. BD*(2) O 4- C 5	0.06	1.32	0.008
17. BD (1) O 7- H 8	25. RY (1) H 1	0.76	1.29	0.028
17. BD (1) O 7- H 8	77. RY (1) C 5	0.05	1.34	0.008
within unit 2				
9. LP (1) O 7	95. RY (1) H 6	1.48	1.43	0.041
9. LP (1) O 7	121. RY (1) H 8	1.69	1.38	0.043
10. LP (2) O 7	122. RY (2) H 8	0.79	1.67	0.032
17. BD (1) O 7- H 8	96. RY (2) H 6	0.51	1.76	0.027

C1

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	4.65	0.91	0.058
5. LP (1) O 2	22. BD*(2) O 4- C 5	2.31	1.18	0.047
5. LP (1) O 2	78. RY (2) C 5	0.70	2.03	0.034
5. LP (1) O 2	81. RY (5) C 5	0.68	2.13	0.034
6. LP (2) O 2	21. BD*(1) O 4- C 5	49.41	0.34	0.115
6. LP (2) O 2	51. RY (1) H 3	0.96	1.03	0.028
6. LP (2) O 2	56. RY (6) H 3	0.57	2.09	0.031
6. LP (2) O 2	79. RY (3) C 5	1.43	2.01	0.048
6. LP (2) O 2	93. RY (17) C 5	0.88	0.90	0.025
7. LP (1) O 4	18. BD*(1) H 1- C 5	1.35	0.94	0.032
7. LP (1) O 4	20. BD*(1) O 2- C 5	0.69	0.94	0.023
7. LP (1) O 4	77. RY (1) C 5	6.89	1.26	0.083
8. LP (2) O 4	18. BD*(1) H 1- C 5	21.52	0.64	0.105
8. LP (2) O 4	20. BD*(1) O 2- C 5	34.61	0.64	0.132
8. LP (2) O 4	65. RY (7) O 4	0.95	1.73	0.036
8. LP (2) O 4	78. RY (2) C 5	2.08	1.76	0.054
8. LP (2) O 4	81. RY (5) C 5	0.52	1.86	0.028
8. LP (2) O 4	82. RY (6) C 5	0.51	1.70	0.026
11. BD (1) H 1- C 5	20. BD*(1) O 2- C 5	0.51	0.92	0.019
11. BD (1) H 1- C 5	33. RY (1) O 2	0.50	1.12	0.021
11. BD (1) H 1- C 5	59. RY (1) O 4	1.47	1.30	0.039
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	0.62	1.09	0.023
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	5.27	1.36	0.076
12. BD (1) O 2- H 3	80. RY (4) C 5	1.56	1.76	0.047
13. BD (1) O 2- C 5	18. BD*(1) H 1- C 5	0.53	1.20	0.023
13. BD (1) O 2- C 5	59. RY (1) O 4	0.61	1.58	0.028
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	0.89	0.39	0.017
14. BD (1) O 4- C 5	34. RY (2) O 2	0.67	1.39	0.027
15. BD (2) O 4- C 5	19. BD*(1) O 2- H 3	0.94	1.35	0.032
15. BD (2) O 4- C 5	33. RY (1) O 2	0.59	1.50	0.027
from unit 1 to unit 2				
12. BD (1) O 2- H 3	23. BD*(1) O 6- H 7	0.06	1.14	0.008
12. BD (1) O 2- H 3	24. BD*(1) O 6- H 8	0.06	1.14	0.008
12. BD (1) O 2- H 3	96. RY (2) O 6	0.26	2.07	0.021
from unit 2 to unit 1				
9. LP (1) O 6	18. BD*(1) H 1- C 5	0.08	0.83	0.007
9. LP (1) O 6	19. BD*(1) O 2- H 3	0.22	0.88	0.012
10. LP (2) O 6	19. BD*(1) O 2- H 3	16.44	0.96	0.112
10. LP (2) O 6	33. RY (1) O 2	0.14	1.11	0.011
10. LP (2) O 6	53. RY (3) H 3	0.18	1.11	0.013
10. LP (2) O 6	55. RY (5) H 3	0.14	1.99	0.015
10. LP (2) O 6	57. RY (7) H 3	0.31	2.13	0.023
16. BD (1) O 6- H 7	19. BD*(1) O 2- H 3	0.07	1.17	0.008
16. BD (1) O 6- H 7	51. RY (1) H 3	0.15	1.44	0.013
16. BD (1) O 6- H 7	54. RY (4) H 3	0.06	1.73	0.009
17. BD (1) O 6- H 8	19. BD*(1) O 2- H 3	0.07	1.17	0.008
17. BD (1) O 6- H 8	51. RY (1) H 3	0.15	1.44	0.013
17. BD (1) O 6- H 8	54. RY (4) H 3	0.06	1.73	0.009
within unit 2				
9. LP (1) O 6	113. RY (1) H 7	1.17	1.56	0.038
9. LP (1) O 6	121. RY (1) H 8	1.17	1.56	0.038
10. LP (2) O 6	114. RY (2) H 7	0.61	1.64	0.028
10. LP (2) O 6	122. RY (2) H 8	0.61	1.64	0.028

C2

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	4.07	0.94	0.055
5. LP (1) O 2	22. BD*(2) O 4- C 5	2.05	1.19	0.044
5. LP (1) O 2	78. RY (2) C 5	0.86	1.90	0.036
5. LP (1) O 2	81. RY (5) C 5	0.56	2.30	0.032
6. LP (2) O 2	21. BD*(1) O 4- C 5	47.63	0.34	0.114
6. LP (2) O 2	51. RY (1) H 3	1.50	1.15	0.037
6. LP (2) O 2	79. RY (3) C 5	1.52	2.02	0.049
6. LP (2) O 2	90. RY (14) C 5	0.53	1.01	0.021
7. LP (1) O 4	18. BD*(1) H 1- C 5	1.72	0.96	0.036
7. LP (1) O 4	77. RY (1) C 5	5.32	1.34	0.075
7. LP (1) O 4	78. RY (2) C 5	0.84	1.91	0.036
8. LP (2) O 4	18. BD*(1) H 1- C 5	19.55	0.66	0.102
8. LP (2) O 4	20. BD*(1) O 2- C 5	34.30	0.64	0.132
8. LP (2) O 4	77. RY (1) C 5	0.68	1.04	0.024
8. LP (2) O 4	78. RY (2) C 5	1.66	1.61	0.046
8. LP (2) O 4	80. RY (4) C 5	0.99	1.33	0.032
11. BD (1) H 1- C 5	20. BD*(1) O 2- C 5	0.50	0.91	0.019
11. BD (1) H 1- C 5	59. RY (1) O 4	1.45	1.39	0.040
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	0.60	1.10	0.023
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	5.49	1.35	0.077
12. BD (1) O 2- H 3	80. RY (4) C 5	1.35	1.77	0.044
13. BD (1) O 2- C 5	18. BD*(1) H 1- C 5	0.50	1.23	0.022
13. BD (1) O 2- C 5	59. RY (1) O 4	0.54	1.68	0.027
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	0.84	0.39	0.016
14. BD (1) O 4- C 5	34. RY (2) O 2	0.69	1.38	0.027
15. BD (2) O 4- C 5	19. BD*(1) O 2- H 3	0.90	1.33	0.031
15. BD (2) O 4- C 5	33. RY (1) O 2	0.59	1.67	0.028
from unit 1 to unit 2				
7. LP (1) O 4	24. BD*(1) O 6- H 8	1.06	1.08	0.030
8. LP (2) O 4	23. BD*(1) O 6- H 7	0.05	0.78	0.006
8. LP (2) O 4	24. BD*(1) O 6- H 8	5.62	0.78	0.059
8. LP (2) O 4	97. RY (3) O 6	0.06	1.61	0.009
11. BD (1) H 1- C 5	23. BD*(1) O 6- H 7	0.14	1.05	0.011
from unit 2 to unit 1				
10. LP (2) O 6	18. BD*(1) H 1- C 5	0.65	0.91	0.022
10. LP (2) O 6	20. BD*(1) O 2- C 5	0.10	0.88	0.009
16. BD (1) O 6- H 7	20. BD*(1) O 2- C 5	0.08	1.02	0.008
16. BD (1) O 6- H 7	22. BD*(2) O 4- C 5	0.06	1.30	0.008
16. BD (1) O 6- H 7	25. RY (1) H 1	0.41	1.13	0.019
16. BD (1) O 6- H 7	26. RY (2) H 1	0.27	1.21	0.016
16. BD (1) O 6- H 7	80. RY (4) C 5	0.05	1.72	0.009
17. BD (1) O 6- H 8	18. BD*(1) H 1- C 5	0.14	1.05	0.011
17. BD (1) O 6- H 8	20. BD*(1) O 2- C 5	0.18	1.03	0.012
17. BD (1) O 6- H 8	22. BD*(2) O 4- C 5	0.07	1.30	0.009
17. BD (1) O 6- H 8	26. RY (2) H 1	0.07	1.22	0.008
17. BD (1) O 6- H 8	59. RY (1) O 4	0.06	1.51	0.009
17. BD (1) O 6- H 8	61. RY (3) O 4	0.06	1.75	0.009
17. BD (1) O 6- H 8	80. RY (4) C 5	0.07	1.72	0.010
within unit 2				
9. LP (1) O 6	113. RY (1) H 7	1.67	1.37	0.043
9. LP (1) O 6	121. RY (1) H 8	1.28	1.46	0.039
10. LP (2) O 6	114. RY (2) H 7	0.72	1.79	0.032
16. BD (1) O 6- H 7	123. RY (3) H 8	0.73	1.86	0.033

C3

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	26. RY (2) H 1	0.84	1.72	0.034
5. LP (1) O 2	54. RY (4) H 3	0.55	1.91	0.029
6. LP (2) O 2	25. RY (1) H 1	1.82	1.36	0.044
6. LP (2) O 2	52. RY (2) H 3	1.35	1.55	0.041
11. BD (1) H 1- O 2	53. RY (3) H 3	0.88	1.85	0.036
from unit 1 to unit 2				
5. LP (1) O 2	21. BD*(2) O 4- C 5	0.09	1.13	0.009
12. BD (1) O 2- H 3	59. RY (1) O 4	0.13	1.67	0.013
12. BD (1) O 2- H 3	62. RY (4) O 4	0.07	2.10	0.011
from unit 2 to unit 1				
7. LP (1) O 4	19. BD*(1) O 2- H 3	2.53	1.12	0.048
8. LP (2) O 4	19. BD*(1) O 2- H 3	4.08	0.82	0.052
16. BD (1) C 5- H 8	19. BD*(1) O 2- H 3	0.07	1.10	0.008
16. BD (1) C 5- H 8	51. RY (1) H 3	0.07	1.53	0.009
within unit 2				
7. LP (1) O 4	22. BD*(1) C 5- O 6	0.91	0.94	0.026
7. LP (1) O 4	23. BD*(1) C 5- H 8	0.96	0.95	0.027
7. LP (1) O 4	77. RY (1) C 5	6.89	1.25	0.083
8. LP (2) O 4	22. BD*(1) C 5- O 6	34.02	0.63	0.131
8. LP (2) O 4	23. BD*(1) C 5- H 8	21.32	0.65	0.105
8. LP (2) O 4	64. RY (6) O 4	0.82	1.41	0.030
8. LP (2) O 4	78. RY (2) C 5	2.23	1.73	0.055
8. LP (2) O 4	80. RY (4) C 5	0.64	1.37	0.027
9. LP (1) O 6	21. BD*(2) O 4- C 5	2.12	1.19	0.045
9. LP (1) O 6	23. BD*(1) C 5- H 8	4.21	0.93	0.056
9. LP (1) O 6	78. RY (2) C 5	0.70	2.01	0.034
9. LP (1) O 6	81. RY (5) C 5	0.63	2.18	0.033
10. LP (2) O 6	20. BD*(1) O 4- C 5	48.32	0.34	0.114
10. LP (2) O 6	79. RY (3) C 5	1.53	2.02	0.050
10. LP (2) O 6	113. RY (1) H 7	1.49	1.18	0.037
13. BD (1) O 4- C 5	20. BD*(1) O 4- C 5	0.86	0.39	0.016
13. BD (1) O 4- C 5	96. RY (2) O 6	0.67	1.35	0.027
14. BD (2) O 4- C 5	24. BD*(1) O 6- H 7	0.90	1.34	0.031
14. BD (2) O 4- C 5	95. RY (1) O 6	0.58	1.68	0.028
15. BD (1) C 5- O 6	23. BD*(1) C 5- H 8	0.52	1.21	0.022
15. BD (1) C 5- O 6	59. RY (1) O 4	0.63	1.87	0.031
16. BD (1) C 5- H 8	22. BD*(1) C 5- O 6	0.58	0.91	0.020
16. BD (1) C 5- H 8	59. RY (1) O 4	1.23	1.58	0.039
17. BD (1) O 6- H 7	21. BD*(2) O 4- C 5	5.39	1.36	0.076
17. BD (1) O 6- H 7	23. BD*(1) C 5- H 8	0.64	1.09	0.024
17. BD (1) O 6- H 7	80. RY (4) C 5	1.49	1.82	0.046

C4

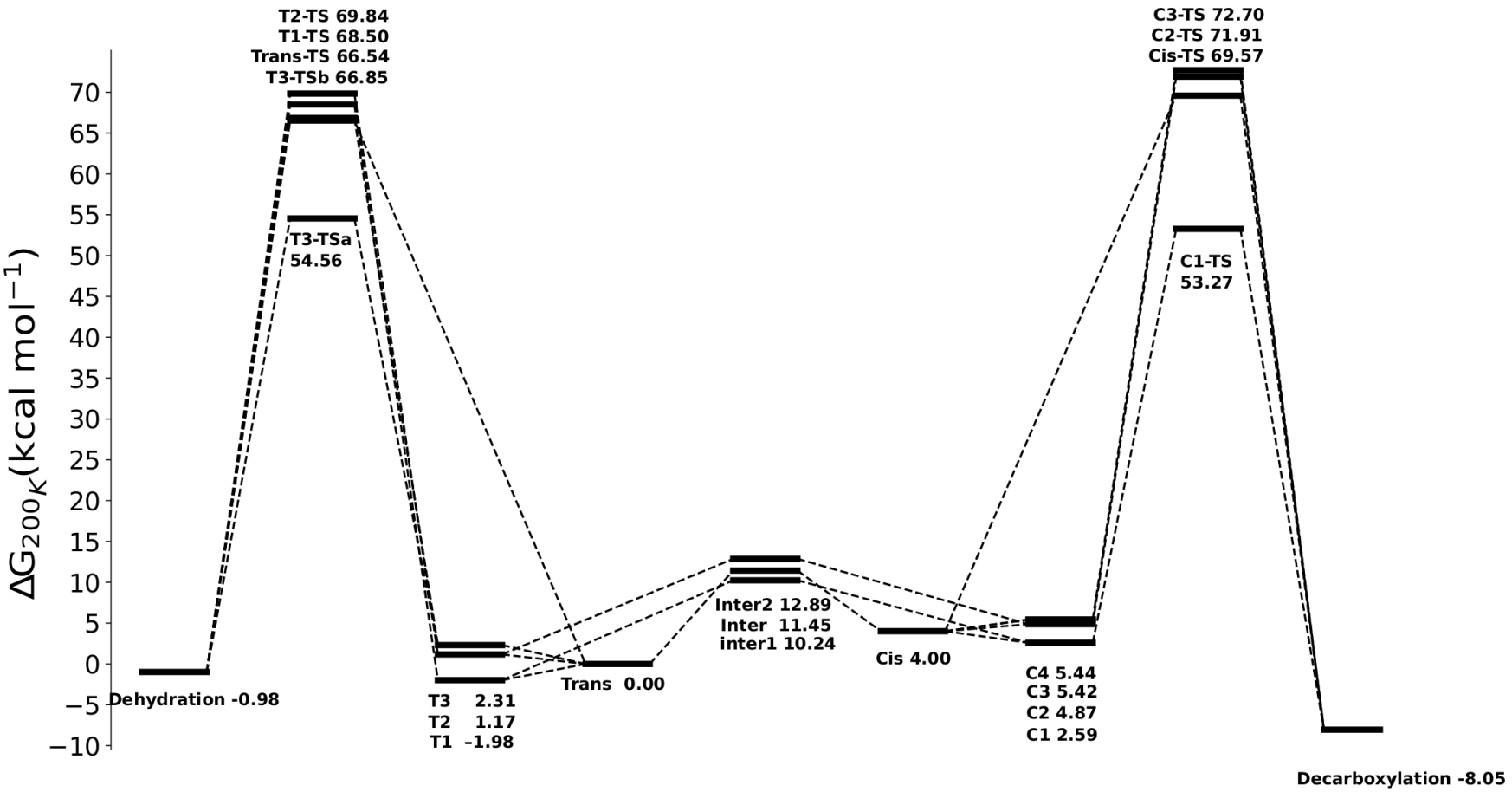
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
5. LP (1) O 2	18. BD*(1) H 1- C 5	4.10	0.93	0.055
5. LP (1) O 2	22. BD*(2) O 4- C 5	2.08	1.20	0.045
5. LP (1) O 2	78. RY (2) C 5	0.71	2.01	0.034
5. LP (1) O 2	81. RY (5) C 5	0.62	2.19	0.033
6. LP (2) O 2	21. BD*(1) O 4- C 5	46.60	0.34	0.113
6. LP (2) O 2	51. RY (1) H 3	1.47	1.18	0.037
6. LP (2) O 2	79. RY (3) C 5	1.50	2.02	0.049
6. LP (2) O 2	91. RY (15) C 5	0.89	0.90	0.025
7. LP (1) O 4	18. BD*(1) H 1- C 5	1.03	0.95	0.028
7. LP (1) O 4	20. BD*(1) O 2- C 5	0.87	0.93	0.025
7. LP (1) O 4	77. RY (1) C 5	7.05	1.25	0.084
8. LP (2) O 4	18. BD*(1) H 1- C 5	21.46	0.65	0.105
8. LP (2) O 4	20. BD*(1) O 2- C 5	34.87	0.63	0.132
8. LP (2) O 4	66. RY (8) O 4	0.52	1.80	0.027
8. LP (2) O 4	78. RY (2) C 5	2.27	1.72	0.056
8. LP (2) O 4	80. RY (4) C 5	0.67	1.37	0.027
8. LP (2) O 4	85. RY (9) C 5	0.62	1.38	0.026
11. BD (1) H 1- C 5	20. BD*(1) O 2- C 5	0.59	0.91	0.021
11. BD (1) H 1- C 5	59. RY (1) O 4	1.20	1.59	0.039
12. BD (1) O 2- H 3	18. BD*(1) H 1- C 5	0.63	1.09	0.023
12. BD (1) O 2- H 3	22. BD*(2) O 4- C 5	5.24	1.36	0.075
12. BD (1) O 2- H 3	80. RY (4) C 5	1.45	1.82	0.046
13. BD (1) O 2- C 5	18. BD*(1) H 1- C 5	0.54	1.21	0.023
13. BD (1) O 2- C 5	59. RY (1) O 4	0.62	1.88	0.030
14. BD (1) O 4- C 5	21. BD*(1) O 4- C 5	0.82	0.39	0.016
14. BD (1) O 4- C 5	34. RY (2) O 2	0.65	1.32	0.026
15. BD (2) O 4- C 5	19. BD*(1) O 2- H 3	0.89	1.34	0.031
15. BD (2) O 4- C 5	33. RY (1) O 2	0.56	1.69	0.027
from unit 1 to unit 2				
7. LP (1) O 4	23. BD*(1) O 6- H 7	1.91	1.12	0.041
8. LP (2) O 4	23. BD*(1) O 6- H 7	3.98	0.82	0.051
11. BD (1) H 1- C 5	23. BD*(1) O 6- H 7	0.06	1.10	0.007
11. BD (1) H 1- C 5	113. RY (1) H 7	0.07	1.47	0.009
from unit 2 to unit 1				
9. LP (1) O 6	22. BD*(2) O 4- C 5	0.05	1.13	0.007
16. BD (1) O 6- H 7	59. RY (1) O 4	0.09	1.67	0.011
16. BD (1) O 6- H 7	63. RY (5) O 4	0.06	2.00	0.010
within unit 2				
9. LP (1) O 6	116. RY (4) H 7	0.58	1.85	0.029
9. LP (1) O 6	122. RY (2) H 8	0.82	1.67	0.033
10. LP (2) O 6	114. RY (2) H 7	1.37	1.53	0.041
10. LP (2) O 6	121. RY (1) H 8	1.80	1.34	0.044
17. BD (1) O 6- H 8	115. RY (3) H 7	1.12	1.78	0.040

Section 3

Figure 1


T2-TS 69.84
T1-TS 68.50
Trans-TS 66.54
T3-TSb 66.85
T3-TSa
54.56
C3-TS 72.70
C2-TS 71.91
Cis-TS 69.57
C1-TS
53.27
Inter2 12.89
Inter 11.45
inter1 10.24
Cis 4.00
C4 5.44
C3 5.42
C2 4.87
C1 2.59
Dehydration -0.98
T3 2.31
T2 1.17
T1 -1.98
Trans 0.00
Decarboxylation -8.05
ΔG_{200_K}(kcal mol^{-1})
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10