Electronic Supplementary Information for Dalton Transactions

Why does the enzyme SyrB2 chlorinate, but does not hydroxylate, saturated hydrocarbons? A density functional theory (DFT) study

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Coordinates (Å) for the optimized structures at the B3LYP/B1 level and free energies (hartrees) at the B3LYP/B2/CPCM//B3LYP/B1 level.

1. Reac (-2560.072190)

C	-1.24952300	2.96189800	0.17701200
N	-0.82725700	1.90629600	-0.49593100
C	-1.11754100	2.12667000	-1.82630600
C	-1.73702700	3.33942200	-1.95293100
N	-1.81302700	3.85432200	-0.67193500
Fe	0.33310200	0.32616500	0.30751200
Cl	0.21653900	0.98771300	2.54134100
N	-1.50395100	-0.72791300	0.62308500
C	-1.98395400	-1.13660200	1.78626900
N	-3.12675100	-1.83705700	1.60042700
C	-3.39265200	-1.87944300	0.24434400
C	-2.37429100	-1.18731900	-0.34848800
O	1.16618700	-1.54026200	0.07567100
C	0.87401100	-1.59155600	-1.16470500
C	1.34644000	-2.75945500	-1.99250100
O	0.21306500	-0.64358100	-1.68404000
O	1.70973800	1.08897800	-0.01438500
C	4.85175700	-1.22058000	-0.21476800
C	5.03803400	-0.03308800	0.73171400
H	0.74322000	-2.86001200	-2.89590100
H	2.38681200	-2.57894600	-2.28269000
H	1.31882700	-3.67940000	-1.40508200
H	-3.67870800	-2.25628300	2.33277500
H	-4.25529500	-2.38391300	-0.15996300
H	-1.53608100	-0.92366200	2.74442900
H	-2.18442300	-1.00267700	-1.39267200
H	-1.14430000	3.09602600	1.24312500
H	-2.20132800	4.74699000	-0.40888200
H	-2.11569400	3.87096700	-2.81090500
H	-0.84590800	1.40130300	-2.57655600
H	3.89584600	-1.71743700	-0.02321600
H	5.65149300	-1.96186400	-0.10124300
H	4.85200800	-0.89413200	-1.26132900
H	5.97051200	0.50479600	0.52516000
H	4.20611800	0.67031000	0.63443700
H	5.07047300	-0.36172400	1.77615000

2. TS-H (-2560.051722)

C	4.552441	2.324087	-1.029078
N	5.040026	1.032623	-0.938955
C	3.251705	2.256039	-0.612194
C	4.043329	0.236108	-0.483029
N	2.953617	0.952604	-0.273355
C	2.717545	0.639703	4.420609
N	1.710917	1.587241	4.423673
C	2.687690	0.084735	3.170609
C	1.119137	1.574236	3.202729
N	1.688737	0.674954	2.421229
Fe	1.054608	0.139331	0.267517
Cl	-0.200070	2.125343	0.328643
O	0.035933	-1.426854	1.208693
O	2.171694	-1.696281	0.773878
O	0.686894	-0.372050	-1.340638
H	-0.824901	0.614612	-3.672136
H	4.124298	-0.826513	-0.314616
H	5.969449	0.727514	-1.183219

H	5.159151	3.146030	-1.373022
H	2.504422	3.030486	-0.533573
H	3.293593	-0.704316	2.755263
H	0.303606	2.216091	2.905842
H	1.451844	2.183125	5.194566
H	3.339080	0.455541	5.282313
C	1.069331	-2.165838	1.200274
C	0.974779	-3.599646	1.660989
H	1.929129	-3.934370	2.072087
H	0.176579	-3.714301	2.396144
H	0.736954	-4.228553	0.796212
H	-0.982520	-1.184841	-3.652672
C	-1.102475	-0.261205	-3.080861
C	-2.406482	-0.132676	-2.329803
H	-0.186312	-0.320265	-2.218088
H	-2.407913	0.756651	-1.693677
H	-2.588812	-1.004668	-1.694302
H	-3.251449	-0.050383	-3.029288

3. Int1 (-2560.070701)

C	4.901847	2.153954	-1.023203
N	5.299362	0.833653	-0.910724
C	3.581323	2.171387	-0.668479
C	4.232630	0.105115	-0.503060
N	3.182810	0.891279	-0.344107
C	2.508466	0.685546	4.343471
N	1.562027	1.687099	4.235062
C	2.560913	0.102455	3.106793
C	1.084721	1.676723	2.964769
N	1.670270	0.728558	2.256567
Fe	1.200034	0.174365	0.035946
Cl	-0.011241	2.170327	-0.032226
O	0.001005	-1.306600	0.919045
O	2.151493	-1.696935	0.699221
O	0.931356	-0.386739	-1.665790
H	0.064780	-0.250636	-2.089403
H	4.235849	-0.960856	-0.335053
H	6.216829	0.467631	-1.112912
H	5.576228	2.933355	-1.338856
H	2.883573	2.993567	-0.629570
H	3.156872	-0.728297	2.764170
H	0.334218	2.352443	2.583722
H	1.268068	2.314712	4.967196
H	3.036624	0.488424	5.262647
C	0.991864	-2.097631	1.031174
C	0.788765	-3.481880	1.595393
H	0.854077	-3.431922	2.688072
H	-0.202512	-3.855805	1.333700
H	1.563365	-4.160267	1.233942
H	-2.039012	0.706044	-1.834034
C	-2.114963	-0.194278	-2.436611
C	-2.444310	-1.500426	-1.799570
H	-2.188562	-0.069546	-3.513156
H	-2.199408	-2.345952	-2.451576
H	-3.522615	-1.577623	-1.573515
H	-1.912753	-1.627524	-0.850462

4. TS-Cl (-2560.060889)

C	4.518184	2.165896	-1.287297
N	4.940189	0.849586	-1.241703
C	3.278577	2.171817	-0.709258
C	3.965285	0.114074	-0.653430
N	2.951320	0.890948	-0.317341
C	2.961401	0.682109	4.337027
N	1.971030	1.643496	4.419060
C	2.827698	0.128014	3.093999
C	1.285170	1.638056	3.248662
N	1.779930	0.732577	2.424588
Fe	1.058663	0.112174	0.362834
Cl	-0.444900	2.106930	0.558403
O	0.163690	-1.481511	1.314336
O	2.294441	-1.859552	0.858179
O	0.462151	-0.201122	-1.336799
H	-0.464694	-0.008802	-1.523446
H	4.005270	-0.950862	-0.481517
H	5.811594	0.489947	-1.599194
H	5.121078	2.949661	-1.716642
H	2.596447	2.993498	-0.553886
H	3.379868	-0.675674	2.633988
H	0.451587	2.284946	3.023569
H	1.779434	2.239630	5.209155
H	3.643941	0.487078	5.148627
C	1.174038	-2.264700	1.276955
C	0.984249	-3.699046	1.719902
H	0.368733	-3.739259	2.621825
H	0.450285	-4.242643	0.933306
H	1.947378	-4.181892	1.891951
H	-2.401299	3.780438	1.424336
C	-1.800751	4.030875	0.555200
C	-2.468148	4.034428	-0.780570
H	-1.020559	4.763823	0.738198
H	-1.736568	4.081481	-1.592942
H	-3.136554	4.904792	-0.889668
H	-3.076746	3.136569	-0.923319

5. TS-OH (-2560.063287)

C	4.612395	1.700424	-1.468814
N	5.044730	0.421386	-1.168538
C	3.305752	1.750066	-1.066747
C	4.010347	-0.251732	-0.607057
N	2.947653	0.529910	-0.531244
C	2.525976	0.940074	4.209885
N	1.578718	1.928446	4.018304
C	2.509805	0.196220	3.061699
C	1.032941	1.753327	2.788179
N	1.576825	0.712670	2.184399
Fe	1.004894	-0.124831	0.129520
Cl	-0.201854	1.867965	-0.217208
O	-0.098212	-1.531183	1.295227
O	2.022440	-1.906714	0.850759
O	0.493210	-0.918973	-1.469277
H	-0.311114	-0.535933	-1.844807
H	4.047093	-1.275053	-0.266020
H	5.964596	0.046606	-1.342004
H	5.256493	2.432639	-1.928324
H	2.592697	2.558508	-1.119412
H	3.083076	-0.679427	2.801755

H	0.266328	2.380912	2.359160
H	1.326182	2.650658	4.674919
H	3.102166	0.861996	5.117985
C	0.909994	-2.294206	1.346214
C	0.797041	-3.669749	1.957910
H	1.720231	-3.932792	2.479274
H	-0.055544	-3.720327	2.636556
H	0.646709	-4.398802	1.154380
H	1.416806	0.287350	-3.755871
C	1.426009	-0.793605	-3.676100
C	0.423810	-1.619242	-4.402107
H	2.337700	-1.250638	-3.312583
H	0.253131	-2.571945	-3.889545
H	0.750149	-1.861455	-5.428819
H	-0.539465	-1.105632	-4.494695

6. Prod-Cl (-2560.111537)

C	-1.092782	2.172158	-0.288628
N	-0.963661	1.093956	-1.044303
C	-1.643112	1.354522	-2.219926
C	-2.191180	2.606701	-2.165257
N	-1.831451	3.113108	-0.931525
Fe	0.196208	-0.648424	-0.677944
Cl	0.418577	3.079991	3.085329
N	-1.118408	-1.774853	0.619754
C	-0.697610	-1.992312	1.855541
N	-1.597446	-2.746923	2.535527
C	-2.648121	-3.031589	1.683619
C	-2.332943	-2.419421	0.500561
O	1.867379	-1.016888	-2.312644
C	0.915573	-1.520661	-2.951967
C	1.124267	-2.111441	-4.332248
O	-0.277880	-1.555837	-2.462032
O	1.405421	-0.238789	0.722124
H	0.814630	-3.160976	-4.333698
H	0.490435	-1.589045	-5.055604
H	2.169365	-2.032789	-4.633027
H	-1.507256	-3.049395	3.492956
H	-3.493565	-3.626711	1.989714
H	0.233887	-1.604352	2.243451
H	-2.888149	-2.405693	-0.424780
H	-0.676280	2.311298	0.698641
H	-2.060387	4.025083	-0.567500
H	-2.782829	3.169624	-2.869116
H	-1.676586	0.615769	-3.005878
H	2.323864	-0.307339	0.433423
C	1.978483	2.167160	2.723161
H	2.628008	2.904069	2.248085
H	1.709882	1.377982	2.009803
C	2.583833	1.613076	3.997963
H	1.906804	0.901583	4.478273
H	2.825777	2.402217	4.715432
H	3.508819	1.081866	3.744225

7. Prod-OH (-2560.139266)

C	-1.75392200	-1.55480900	2.07444100
N	-1.42373900	-1.31437600	0.81690800

C	-2.21135400	-2.14285600	0.03956600
C	-3.02584300	-2.89063100	0.84483100
N	-2.72235000	-2.50331200	2.13681500
Fe	0.11971400	0.05035100	0.12828900
O	1.55769600	-1.58325400	-0.43097000
C	0.93253600	-1.72159100	-1.52740300
O	-0.05436900	-0.97260200	-1.81419900
N	-0.96371100	1.70750100	-0.68245600
C	-1.46915000	1.83021500	-1.96202600
C	-2.09230700	3.04136400	-2.09303000
N	-1.96272600	3.65853700	-0.86253000
C	-1.27572500	2.82192600	-0.04341400
O	2.07986600	1.01018100	-0.57378800
Cl	0.34286500	0.98398400	2.33176300
C	1.37698200	-2.77126200	-2.52580400
C	2.86006200	2.09993000	-0.06150400
C	3.76253700	1.68759200	1.09169200
H	0.51763500	-3.36731200	-2.84564900
H	1.77305900	-2.27551200	-3.41814600
H	2.14451600	-3.41795700	-2.09934900
H	-3.13590400	-2.86414500	2.98245800
H	-3.77028500	-3.63984200	0.62767300
H	-1.31741800	-1.05649700	2.92751700
H	-2.11413800	-2.13855100	-1.03452200
H	-1.02612700	3.02817500	0.98725300
H	-2.31456300	4.56902300	-0.61082700
H	-2.60128600	3.50907400	-2.92053200
H	-1.33207800	1.03883900	-2.68245300
H	2.59214200	0.18506500	-0.56458200
H	3.44800500	2.53428300	-0.88272100
H	4.33768900	2.54960200	1.44724300
H	3.16474600	1.29657200	1.91811300
H	4.47993500	0.92081400	0.77405900
H	2.13526500	2.84833900	0.26842700

Protonated Structures (Model M1)

8. Int3 (-2560.502875)

C	3.631061	1.915667	-1.703863
N	4.252347	0.688200	-1.569341
C	2.512876	1.852027	-0.923145
C	3.522151	-0.075525	-0.734140
N	2.455538	0.604186	-0.321225
C	3.159735	0.981422	4.524433
N	2.055915	1.808293	4.607040
C	2.998900	0.265667	3.373387
C	1.270578	1.586332	3.535993
N	1.815030	0.651008	2.761787
Fe	0.996650	-0.131922	0.978491
Cl	-0.566741	1.468822	0.816072
O	0.205098	-1.771076	1.894723
O	2.298715	-1.829897	1.293579
O	0.145593	-1.177182	-0.711118
H	-0.251922	-0.658007	-1.456154
H	3.767477	-1.084770	-0.442270
H	5.110535	0.403857	-2.020835
H	4.030620	2.700228	-2.325964
H	1.750066	2.594967	-0.751242

H	3.626434	-0.498439	2.945002
H	0.340474	2.096654	3.339389
H	1.860420	2.469540	5.345702
H	3.936336	0.978146	5.272148
H	-0.560116	-1.751760	-0.376137
C	1.315792	-2.416928	1.845244
C	1.429847	-3.784137	2.443207
H	1.576876	-3.682456	3.524242
H	0.504985	-4.342909	2.288649
H	2.281968	-4.318208	2.022103
H	-1.469338	1.107217	-2.254315
C	-1.198846	0.301535	-2.932742
C	-2.250368	-0.619324	-3.446423
H	-0.280407	0.434158	-3.501210
H	-1.831724	-1.543928	-3.856718
H	-2.806174	-0.139438	-4.269968
H	-2.992503	-0.870061	-2.681933

9. TSprot-Cl (-2560.500259)

C	4.221436	1.910950	-1.573673
N	4.878257	0.727749	-1.293981
C	2.979646	1.783066	-1.020285
C	4.046736	-0.071539	-0.597092
N	2.881552	0.541426	-0.412556
C	2.396087	1.093100	4.489168
N	1.253991	1.837146	4.264115
C	2.565680	0.330938	3.369252
C	0.769406	1.520608	3.047023
N	1.543800	0.605115	2.472710
Fe	1.250094	-0.301805	0.589876
Cl	-0.418791	1.095017	-0.034060
O	0.419873	-2.028362	1.328882
O	2.597092	-1.872508	1.261967
O	0.822495	-1.456163	-1.273555
H	0.243898	-0.927507	-1.846037
H	4.292404	-1.058903	-0.238344
H	5.822436	0.493222	-1.566430
H	4.685039	2.712544	-2.125580
H	2.155650	2.479001	-1.016059
H	3.326924	-0.397382	3.141913
H	-0.117946	1.952246	2.610491
H	0.842635	2.504536	4.901290
H	2.966193	1.172294	5.400679
H	0.275971	-2.192665	-0.956291
C	1.569645	-2.545478	1.583012
C	1.670489	-3.876386	2.265029
H	1.586078	-3.721499	3.346496
H	0.848124	-4.525622	1.959744
H	2.633390	-4.343554	2.056031
H	-1.808841	1.853681	-2.473363
C	-1.914514	0.777041	-2.526516
C	-3.142634	0.113287	-2.035335
H	-1.232842	0.260113	-3.198104
H	-3.003508	-0.957846	-1.860914
H	-3.945765	0.206201	-2.787768
H	-3.516059	0.578882	-1.119202

10. Prodprot-Cl (-2560.55587)

N	1.632115	-0.820248	2.533212
C	1.692698	0.489334	2.982069
C	1.165440	0.563325	4.240881
N	0.776244	-0.723070	4.555024
C	1.071013	-1.525569	3.510493
Fe	2.125388	-1.771589	0.742572
O	1.190480	-0.445855	-0.590303
N	4.199609	-1.847637	0.640595
C	5.186570	-1.233403	1.393242
C	6.412365	-1.627608	0.937065
N	6.157803	-2.494051	-0.107557
C	4.822399	-2.604994	-0.258229
Cl	-1.126381	1.598708	0.413263
O	1.850609	-3.159794	-0.935764
C	1.217718	-3.900594	-0.118507
C	0.608853	-5.205205	-0.554317
O	1.067117	-3.503513	1.091643
C	-1.855908	2.721495	-0.854326
C	-1.976759	2.046181	-2.204429
H	4.948055	-0.562690	2.203972
H	7.413233	-1.379691	1.251476
H	6.851273	-2.970245	-0.666916
H	4.328914	-3.216611	-0.998932
H	0.856612	-2.583356	3.468826
H	0.336254	-1.017787	5.415254
H	1.031374	1.389538	4.920265
H	2.102585	1.282400	2.375585
H	0.772181	-5.970031	0.208206
H	1.017253	-5.524691	-1.513049
H	-0.473931	-5.074916	-0.655733
H	0.481876	0.197137	-0.396814
H	-1.200258	3.591768	-0.872606
H	-2.822950	3.002322	-0.437878
H	-0.997869	1.766722	-2.603923
H	-2.436379	2.750310	-2.906649
H	-2.609457	1.156833	-2.152518
H	0.978188	-0.896676	-1.420235