

Theoretical Study on the Peroxyl Radicals Scavenging Activity of Esculetin and its Regeneration in Aqueous Solution

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Electronic Supplementary Information (ESI)

Transition states geometries calculated in water.

H₂ES

TS-6a(R=OOH)

H=-798.367591

G=-798.422860

if=-2354.8602

S2=0.766127

S2A=0.750203

0 2

O	-0.0399592704	-0.0673530582	-0.0597558058
C	-0.0699026091	-0.0820397918	1.3188360388
O	1.0022034908	-0.0834676748	1.8816343824
C	-1.3669998356	-0.0951688024	1.9572047315
H	-1.3680603478	-0.1110235415	3.0360663151
C	-2.494628575	-0.0854920263	1.2252785336
H	-3.4654631921	-0.094302825	1.7024478721
C	-2.4384981312	-0.0644169401	-0.2102218192
C	-3.5656542174	-0.0506832976	-1.0193434389
H	-4.555771513	-0.0554655877	-0.5841010288
C	-3.4331205881	-0.0327140226	-2.4075273205
O	-4.4773271884	0.0165009959	-3.2309400635
H	-4.82149104	-1.0120710375	-3.4184569548
C	-2.1294412847	-0.0354915247	-2.9877531408
O	-2.0129957701	-0.0300267163	-4.3232143961
H	-2.9016926656	0.0144396214	-4.7096540096
C	-0.9981495401	-0.0458244722	-2.194331969
H	-0.0094697344	-0.0436400514	-2.6288049809
C	-1.1711661697	-0.059352397	-0.8210414325
O	-4.8627764354	-2.3094708608	-3.4914986254
O	-3.7929962655	-2.6594306669	-2.740210088
H	-3.0673171243	-2.8089518903	-3.3700633021

TS-6a(R=OOCH₃)

H=-837.644004

G=-837.702200

if=-2586.4469

S2=0.765938

S2A=0.750201

0 2

O	-0.0115629423	-0.0272719588	0.0441607274
C	-0.026088929	0.0062027727	1.4224162768
O	1.0513079819	-0.0197854683	1.9741401039
C	-1.3149604193	0.0713466658	2.074659804
H	-1.302883916	0.1020228755	3.1531448325
C	-2.4504918996	0.0868940045	1.3551898827
H	-3.4151321876	0.1326298707	1.8428259425
C	-2.4115627804	0.0427654157	-0.0807267083
C	-3.5476426303	0.0451051049	-0.8757203823
H	-4.531977601	0.0749219508	-0.4282441366
C	-3.433126687	-0.0046359882	-2.2665583241
O	-4.4817234832	-0.011094349	-3.0792609718
H	-4.9048982931	-1.0509802979	-3.0591859166
C	-2.1342318245	-0.0395578729	-2.8592903306
O	-2.0348481697	-0.0708226941	-4.1937859419
H	-2.9310184253	-0.0585689322	-4.5665894676

C	-0.9934519673	-0.0461166388	-2.0791465798
H	-0.0104961367	-0.0805825912	-2.5251922235
C	-1.150539323	-0.0105052024	-0.7049781892
O	-5.0256025352	-2.3107758784	-2.9236484279
O	-3.8305921869	-2.6366107196	-2.3796860827
C	-2.9794882758	-3.222959314	-3.3778324753
H	-2.9045034672	-2.5465912782	-4.227436261
H	-3.4062118425	-4.1775563832	-3.6796558966
H	-2.0161481018	-3.3593006338	-2.8944031288

TS-6a(R=OOCHCH₂)

H=-875.728674

G=-875.788322

if=-2792.8869

S2=0.764946

S2A=0.750177

0 2

O	0.0329700119	0.0745328278	-0.0316054082
C	0.0483450338	0.0823179049	1.3479413103
O	1.1357970867	0.1640597383	1.8741199349
C	-1.222989036	-0.008816215	2.0294603352
H	-1.1878612654	-0.0034100145	3.1078420739
C	-2.3716563965	-0.091260126	1.3350154403
H	-3.3237877614	-0.1571364515	1.8445363196
C	-2.363066474	-0.0965153162	-0.1014838297
C	-3.5124434841	-0.190460395	-0.8728677506
H	-4.4845000056	-0.2654868769	-0.404264759
C	-3.4246603388	-0.2073367399	-2.2660855281
O	-4.4865137444	-0.3129586736	-3.0581777131
H	-4.7406125145	-1.4042516272	-3.1235784899
C	-2.1428043409	-0.1210342385	-2.8856461256
O	-2.0694814018	-0.185961714	-4.2220728766
H	-2.9720035184	-0.2545672307	-4.5729151512
C	-0.9901817585	-0.0203660881	-2.1338822905
H	-0.0178901081	0.0334059261	-2.601158374
C	-1.1178986905	-0.0133624077	-0.7539873654
O	-4.68432253	-2.6827888241	-3.0929577306
O	-3.4765434665	-2.8838085064	-2.5018313289
C	-2.5140880124	-3.280993109	-3.3999482383
H	-2.8631171935	-3.3511816285	-4.4198416022
C	-1.291228826	-3.5330322142	-2.9481385902
H	-0.5290709846	-3.8506316282	-3.643193052
H	-1.0493152353	-3.428677212	-1.8991426623

TS-7a(R=OOH)

H=-798.365356

G=-798.420046

if=-2773.1318

S2=0.772976

S2A=0.75039

0 2

O	0.0263380852	0.0748689332	0.0367863316
C	-0.020751288	0.0603717054	1.4030758677
O	1.0374002869	0.1071065953	1.9923561732
C	-1.3272326244	-0.0117630883	2.030360955
H	-1.3359991191	-0.0246175433	3.1094423981
C	-2.4495043914	-0.0538520585	1.2925175462

H	-3.4224766134	-0.104444777	1.7624162491
C	-2.3805673875	-0.0318285823	-0.1433127928
C	-3.5163692232	-0.0651043107	-0.9499049842
H	-4.500366665	-0.1080397403	-0.5043425138
C	-3.3776769388	-0.0349788474	-2.3237168212
O	-4.4665779872	-0.0623530228	-3.1167351912
H	-4.1870764589	0.0247481027	-4.0401357306
C	-2.0804623832	0.012834593	-2.9141169302
O	-1.9987423585	0.0595448931	-4.2374091725
H	-2.1345843259	-0.9611430749	-4.6333326192
C	-0.9410988616	0.0423181796	-2.1020549793
H	0.0415891245	0.0819034293	-2.5491761024
C	-1.1067642107	0.0295960251	-0.7397438221
O	-2.3658412422	-2.2368982359	-4.7331064461
O	-2.4819963595	-2.6016134145	-3.4357406026
H	-3.4375352695	-2.6561603336	-3.2620904994

TS-7a(R=OOCH₃)

H= -837.641530

G= -837.698682

if= -2828.7862

S2=0.775072

S2A=0.750467

0 2

O	0.0029684652	-0.2956002768	-0.0481389725
C	0.0521031164	-0.2863853797	1.3172530804
O	1.1404839584	-0.4277394933	1.8326033174
C	-1.1963845226	-0.1103993818	2.0348697561
H	-1.1283391888	-0.1096776889	3.1119374851
C	-2.3587563597	0.0439717882	1.3775757088
H	-3.2881130581	0.1775451272	1.9148408074
C	-2.3915424653	0.0334386755	-0.0592546726
C	-3.5718426217	0.1912672806	-0.7846690413
H	-4.5125315483	0.333257891	-0.2709862245
C	-3.5315893616	0.1624144962	-2.1642281371
O	-4.6580444361	0.3158875665	-2.883199742
H	-4.4290366431	0.2718492048	-3.8248277828
C	-2.2942956663	-0.0363357736	-2.845808779
O	-2.3177722852	-0.0687043006	-4.1680306593
H	-2.2426212263	-1.1497649907	-4.4687059283
C	-1.1071890469	-0.179439133	-2.1134408337
H	-0.1686111954	-0.3290141975	-2.6277623023
C	-1.1734342988	-0.1443357618	-0.744222434
O	-2.3091792216	-2.4223512059	-4.4391789941
O	-2.6723385177	-2.6350285475	-3.1549355338
C	-4.0717032234	-2.9508755615	-3.083470819
H	-4.640092555	-2.1637713998	-3.5755036771
H	-4.2368005076	-3.9108191065	-3.5690479768
H	-4.3026348996	-3.0028131647	-2.0232840254

TS-7a(R=OOCHCH₂)

H= -875.726422

G= -875.786136

if= -3586.5911

S2=0.775012

S2A=0.750517

0 2

O	-0.0610355681	-0.1692939437	-0.0548682452
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C	-0.0441915316	-0.1690047429	1.3121243648
O	1.0384344737	-0.2553705343	1.8511169637
C	-1.3164169325	-0.0639859755	2.0008175636
H	-1.2741980857	-0.0617692478	3.079173233
C	-2.4704128965	0.021737618	1.3158992444
H	-3.4180907273	0.0982971476	1.8319473694
C	-2.4691442379	0.013135416	-0.1202542385
C	-3.6399519735	0.0962156649	-0.8745064473
H	-4.6005682471	0.1628828943	-0.3828208702
C	-3.563830072	0.0798850907	-2.2511785677
O	-4.6853830449	0.1189246787	-2.9949015644
H	-4.4338670963	0.1012068682	-3.9316808601
C	-2.3018488768	-0.0225286475	-2.9053148314
O	-2.2925158386	-0.050803822	-4.229990809
H	-2.2458620969	-1.1370681721	-4.5303980473
C	-1.1270533374	-0.1018930611	-2.1463144775
H	-0.1685709469	-0.1848369547	-2.6384451324
C	-1.2271424847	-0.0837735831	-0.7775782265
O	-2.3304659878	-2.4071040305	-4.5500072247
O	-2.7784009937	-2.6651875622	-3.2919743822
C	-4.109970093	-2.9859464599	-3.2693157151
H	-4.5915858936	-2.9582770694	-4.235754497
C	-4.6710774138	-3.2911293676	-2.1024705385
H	-5.7188455735	-3.549184113	-2.0765638555
H	-4.0974628307	-3.2862914971	-1.185672289

HES⁻

TS-6a(R=OOH)

H= -797.912594

G= -797.967068

if= -2089.9146

S2=0.763645

S2A=0.750144

-1 2

O	2.3531465167	-1.025568575	-0.3109122358
C	3.4864474221	-0.4553253316	0.2143314969
O	4.4798116195	-1.1497469226	0.256126946
C	3.3886179295	0.91187999	0.6642406417
H	4.2856883861	1.3492838949	1.0725585925
C	2.2190529663	1.5885336273	0.5675652806
H	2.1544070472	2.6145219944	0.9078025857
C	1.0553543749	0.9779627063	0.0247573815
C	-0.1860556442	1.6162212283	-0.0856269191
H	-0.3036479964	2.6362054843	0.2573917019
C	-1.2703163036	0.9638724427	-0.633839855
O	-2.4484615026	1.5954908664	-0.7700350954
H	-3.1553601463	1.0079696254	-0.3571039204
C	-1.1717247577	-0.4122646053	-1.1245714703
O	-2.1626887817	-0.969603542	-1.6487696049
C	0.1000501096	-1.0477004298	-0.9568644966
H	0.2262510346	-2.0677618112	-1.291230322
C	1.1542777506	-0.3627961887	-0.4166480904
O	-3.709505318	0.2068107462	0.9069127513
O	-2.5340303487	-0.2300736678	1.4130113733
H	-2.2151978379	0.4793825877	1.9911452387

TS-6a(R=OOCH₃)

H= -837.193260
G= -837.250474
if= -2870.6893
S2=0.764179
S2A=0.750163

-1 2

O	2.3692218887	-1.0296377742	-0.3210740681
C	3.5040788068	-0.4649027711	0.2029414525
O	4.4968216478	-1.1603725466	0.2406512219
C	3.4104917705	0.9019456098	0.6592445161
H	4.3096704413	1.3348172478	1.0678636255
C	2.2436896102	1.5822279915	0.5691506467
H	2.1824696822	2.6063274583	0.9153486383
C	1.076260792	0.9766158981	0.0247368317
C	-0.1638021117	1.6171687963	-0.0782536833
H	-0.2776876592	2.6328268788	0.2781113248
C	-1.2554406652	0.9765408424	-0.6290444271
O	-2.4319715819	1.610268652	-0.7460944634
H	-3.1296184716	1.0719134901	-0.2157822895
C	-1.1505805984	-0.3892297758	-1.1404661608
O	-2.1371449743	-0.9512009043	-1.6775073043
C	0.1157305216	-1.0346935503	-0.9709705347
H	0.2350387519	-2.0526073244	-1.3144490588
C	1.1733389234	-0.3606219161	-0.4241508722
O	-3.7665027069	0.23260575	0.8414852873
O	-2.6597892155	-0.2642964781	1.4292930373
C	-2.6664899558	-1.6921142183	1.3432387718
H	-2.7160988396	-1.9745648645	0.2921388664
H	-3.526523544	-2.0704175422	1.8930706328
H	-1.7370945123	-2.0203289494	1.8006120091

TS-6a(R=OOCHCH₂)

H= -875.278094
G= -875.339146
if= -2374.0481
S2=0.767449
S2A=0.750233

-1 2

O	-2.357732438	-0.7117537915	-0.8247045115
C	-3.4285480536	-0.0108902697	-0.3278983628
O	-4.4632930779	-0.0718812938	-0.9576267441
C	-3.222523728	0.7293138804	0.8932589045
H	-4.071975332	1.2731856648	1.2745254607
C	-2.0151080585	0.7262065011	1.5084949147
H	-1.8696816037	1.284858268	2.4245713945
C	-0.9167538282	-0.0006031832	0.9742755863
C	0.3622710286	-0.0259005216	1.5481061806
H	0.5643415668	0.5542825398	2.4392598689
C	1.3834649148	-0.7318121626	0.9634048998
O	2.6250893099	-0.7029156865	1.4959157766
H	3.2464089391	-0.4307585764	0.7658985973
C	1.1720598149	-1.5338979755	-0.2427981444
O	2.1032277807	-2.2123239909	-0.731248145
C	-0.1389781831	-1.4669072623	-0.818108033
H	-0.3424220173	-2.0181323357	-1.7252695079
C	-1.1233176194	-0.729530107	-0.2214703156
O	3.655124972	0.6759714275	-0.4326681876
O	2.4235898782	0.8831651662	-0.9466068246

C	1.8810766048	2.080843225	-0.5733282207
H	2.525455311	2.6723628234	0.0614964892
C	0.663667447	2.4063591477	-0.9934264256
H	0.2390824759	3.3553552046	-0.7062817093
H	0.0925108959	1.734083308	-1.6179699411

Transition states geometries calculated in
pentylethanoate.

TS-6a(R=OOH)

H= -798.361227
G= -798.415894
if= -1883.9716
S2=0.766598
S2A=0.750213

0 2

O	-0.0299598583	-0.0254625246	-0.067427341
C	-0.0613478891	-0.0747819726	1.3153877953
O	0.9919298227	-0.0761565809	1.8891405556
C	-1.3750482052	-0.120450272	1.9362413448
H	-1.3862598804	-0.1565328968	3.0147585857
C	-2.4942917499	-0.117584647	1.1947802069
H	-3.4693639764	-0.1526486506	1.6630539703
C	-2.42342785	-0.0695467978	-0.2419365536
C	-3.5407507624	-0.0713931742	-1.0653817869
H	-4.5363407971	-0.1118109615	-0.6441830017
C	-3.3920577681	-0.0308946729	-2.4514791577
O	-4.4103360382	-0.0062297855	-3.2993767559
H	-4.8286733131	-1.0214786587	-3.3927387694
C	-2.0819763158	0.021401336	-3.0138478012
O	-1.9609577531	0.0648131149	-4.3441812722
H	-2.8534450323	0.118728063	-4.7193218079
C	-0.9610253453	0.0238115627	-2.2073136717
H	0.0330232891	0.0647844916	-2.6282095686
C	-1.1467804889	-0.0249372605	-0.8332235931
O	-4.9272793359	-2.3096071871	-3.4439388109
O	-3.9522673116	-2.6941881815	-2.5860839814
H	-3.2340414477	-3.025280912	-3.1501690878

TS-6a(R=OOCH₃)

H= -837.641568
G= -837.699448
if= -2252.6889
S2=0.767348
S2A=0.750236

0 2

O	-0.0079367551	-0.0192630779	0.0454863494
C	-0.0169827712	-0.0209263734	1.42924624
O	1.0456942561	-0.0263006346	1.9857589964
C	-1.3209631367	-0.0170170226	2.0719194378
H	-1.3157162098	-0.0184170108	3.1511174858
C	-2.4520927466	-0.0122479649	1.3484733887
H	-3.4193200983	-0.0100011585	1.8339040943
C	-2.4051382854	-0.0092734032	-0.0900725984
C	-3.5361836817	-0.0048307833	-0.8941047802

H -4.5249226197 -0.0103849602 -0.45507213
C -3.411375614 -0.0077637436 -2.285138998
O -4.436447573 0.0046381581 -3.1159235785
H -4.8966387545 -1.0371631394 -3.1129081658
C -2.1066692438 -0.0005849649 -2.8666471981
O -2.0119246475 0.0044604234 -4.1996448814
H -2.9140381668 0.0648834105 -4.5523848556
C -0.972375756 -0.0060997975 -2.0801390718
H 0.0152823561 -0.0008132935 -2.51746063
C -1.1370424327 -0.0126193177 -0.7024364413
O -5.0437587574 -2.2724168022 -3.0435546183
O -3.9319551168 -2.6437988596 -2.3696647667
C -3.0147186155 -3.2890119953 -3.2629266623
H -2.7935602082 -2.6322729283 -4.1032654188
H -3.4594832079 -4.2181731372 -3.6156624506
H -2.1220391332 -3.4858712597 -2.674487607

TS-6a(R=OOCHCH₂)

H= -875.728514

G= -875.787339

if= -2086.2453

S2=0.765879

S2A=0.750201

0 2

O 0.0701570315 -0.2109024469 -0.3779182041
C 0.1143602952 -0.4065728914 0.9929938948
O 1.1985019954 -0.4844412446 1.5005382846
C -1.1636944541 -0.4986496285 1.6786422966
H -1.1186027259 -0.6478816894 2.7465529776
C -2.321652442 -0.401035539 1.0046017426
H -3.2702718769 -0.4691213514 1.5215395325
C -2.3285695304 -0.2065960321 -0.4209167877
C -3.4890127302 -0.1274211802 -1.1804406176
H -4.4602157123 -0.219873502 -0.7133371761
C -3.411854468 0.0140862908 -2.5654560021
O -4.4624456576 -0.0351715412 -3.3659864371
H -4.7717825191 -1.126551655 -3.4428638206
C -2.131795154 0.1531848028 -3.1859592605
O -2.0878499204 0.2983376594 -4.514396704
H -3.0034087243 0.3135674714 -4.834056399
C -0.9731452885 0.089990725 -2.4461187689
H -0.0019325771 0.1679288727 -2.9127958553
C -1.0854320032 -0.1174504027 -1.0743586116
O -4.7858051994 -2.3893132922 -3.4276549299
O -4.0724318407 -2.6627860097 -2.304067302
C -2.7982459766 -3.0778767204 -2.5683263469
H -2.5565900389 -3.1320855367 -3.621053044
C -1.9883224894 -3.35969516 -1.5518699192
H -0.9817779236 -3.6908874648 -1.7584638001
H -2.3234060675 -3.2891943456 -0.5264245752

TS-7a(R=OOH)

H= -798.358348

G= -798.413048

if= -2063.7847

S2=0.775961

S2A=0.75049

0 2

O -0.0139464163 -0.0315127101 -0.020931883
C -0.0124613951 -0.0426607651 1.3500924534
O 1.04807968 -0.0636112406 1.9132606968
C -1.3142007752 -0.0265750142 2.0087781503
H -1.2955762674 -0.0347711849 3.0880392701
C -2.4558975537 -0.0021615675 1.3025509114
H -3.4161525933 0.0106571127 1.8011078093
C -2.4237818316 0.007621312 -0.1358853427
C -3.5826341252 0.0360162478 -0.9144866636
H -4.5554507867 0.0555288362 -0.4434932904
C -3.4770480965 0.0430395925 -2.2898592171
O -4.5708252995 0.0700277826 -3.067514055
H -4.2763471421 0.1613719436 -3.9860602694
C -2.1946515075 0.0153177898 -2.9114222797
O -2.1704673023 0.0386500684 -4.2323717751
H -2.0110400945 -0.9909564937 -4.6034662437
C -1.0342003738 -0.0035738325 -2.128916309
H -0.0623165982 -0.022662308 -2.600904435
C -1.1615507154 -0.0081853909 -0.7604551135
O -2.0681755348 -2.2759442087 -4.7018612092
O -2.2060834792 -2.6446386826 -3.4063263162
H -3.1279260841 -2.9402903622 -3.3246415573

TS-7a(R=OOCH₃)

H= -837.638638

G= -837.696406

if= -2378.7215

S2=0.776753

S2A=0.750525

0 2

O -0.0019636031 -0.3074357467 -0.0373814944
C 0.0623485396 -0.2867762147 1.33174463
O 1.1368344566 -0.437139315 1.8480588739
C -1.1928583179 -0.0832339647 2.0461405469
H -1.1249141377 -0.0693338829 3.1234027332
C -2.3533389558 0.0773382664 1.3892085606
H -3.2797929174 0.2293811999 1.9275580343
C -2.3884103694 0.0511843269 -0.0483114889
C -3.5681487195 0.2197133817 -0.77627005
H -4.5066353558 0.3805494301 -0.2637894086
C -3.524989083 0.1847712172 -2.1542027408
O -4.636723596 0.3456709307 -2.8883685352
H -4.3670740447 0.3580088707 -3.8199982912
C -2.2887606575 -0.0317188976 -2.8341817424
O -2.3271651004 -0.0567134913 -4.1491460903
H -2.2498032882 -1.1512613152 -4.4671177205
C -1.1055792206 -0.1876170866 -2.0994630713
H -0.1678636175 -0.3493328115 -2.6117702807
C -1.1694516962 -0.146518015 -0.7278786955
O -2.3746840851 -2.3893963555 -4.4870602158
O -2.6976118911 -2.6525580491 -3.2023526612
C -4.0777207875 -3.0282893939 -3.1140049457
H -4.7023138581 -2.2353117879 -3.5234233629
H -4.2271554237 -3.9544942485 -3.6662944966
H -4.2735215791 -3.1729103809 -2.0547144672

TS-7a(R=OOCHCH₂)

H= -875.724127

G= -875.784485

if= -2403.9546

S2=0.776757

S2A=0.750576

0 2

O	-0.0810543846	-0.3002287214	-0.0678141862
C	-0.0471827122	-0.2932601578	1.3026950239
O	1.0175073499	-0.4347349932	1.8413437266
C	-1.3203671023	-0.1137200098	1.990814132
H	-1.2759729715	-0.1045045574	3.0693169789
C	-2.4695285496	0.0303395154	1.3097343749
H	-3.4093230536	0.1637183018	1.8296317981
C	-2.4735386059	0.0106742864	-0.1276006899
C	-3.6413152212	0.1556446816	-0.8813255205
H	-4.5952390512	0.2839109832	-0.3886454409
C	-3.5685471745	0.1253781452	-2.256627819
O	-4.6722435365	0.2321574552	-3.0111714896
H	-4.3889243942	0.2318148421	-3.9384205958
C	-2.3139554367	-0.0540890266	-2.910209729
O	-2.3251021739	-0.0842249607	-4.2285423094
H	-2.2411303347	-1.166196315	-4.5405751694
C	-1.143354151	-0.1876904603	-2.1528504525
H	-0.1917193947	-0.3254071903	-2.6464460478
C	-1.2363900984	-0.1571144353	-0.7819007051
O	-2.3631461786	-2.4253786228	-4.5857717652
O	-2.7467633582	-2.7048485396	-3.3143222778
C	-4.0694242786	-3.0410734832	-3.2372478914
H	-4.5974253529	-2.9869674449	-4.1787583606
C	-4.5778750904	-3.3968218986	-2.0628316738
H	-5.6222004477	-3.662713072	-2.0013987496
H	-3.9677104568	-3.42703218	-1.170236439