

On the factors affecting product distribution in laccase-catalyzed oxidation of a lignin model compound vanillyl alcohol: experimental and computational evaluation

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Table S1 Computed total energy values at DFT((U)B3LYP)/6-311++G(2df,2p) level of theory for all products and intermediates ($10^3 \text{ kcal mol}^{-1}$).

	dG _s PCM E _{tot}	E _{tot} (gas phase)	dG (298.15 K)	Hf (298.15 K)	dG (318.15 K)
1	-336.6165558	-336.6095805	-336.5255135	-336.4953605	-336.5275705
1R	-336.2188473	-336.2073760	-336.1319150	-336.1014650	-336.1339850
1P ⁻	-336.3126613	-336.2505168	-336.1757318	-336.1457078	-336.1777728
2	-672.4769651	-672.4640643	-672.2941403	-672.2482273	-672.2972763
2QQ (RR.SS)	-672.4399431	-672.4219224	-672.2550344	-672.2072474	-672.2582964
2QQ (meso)	-672.4402958	-672.4211332	-672.2538332	-672.2066872	-672.2570512
2QHQ (RR.SS)	-672.7023151	-672.6531198	-672.4789558	-672.4308408	-672.4822398
2QHQ (meso)	-672.7041667	-672.6586234	-672.4823984	-672.4360794	-672.4855614
2PQ	-672.4595791	-672.4434703	-672.2765383	-672.2282743	-672.2798323
2PQH	-672.7231089	-672.6769043	-672.5013543	-672.4537523	-672.5046043
2PQ ⁻	-672.1526762	-672.1016277	-671.9426957	-671.8956067	-671.9459107
2PP ⁻	-672.1828309	-672.1345262	-671.9747792	-671.9289162	-671.9779112
(2PQ ⁻ →2PP ⁻)TS	-672.1470819	-672.096,9530	-671.939,5220	-671.893,2180	-671.9426370
3	-672.4629861	-672.4512165	-672.2829335	-672.2358575	-672.2861465
3Q	-672.4414818	-672.4268693	-672.2592223	-672.2119193	-672.2624503
3QH	-672.7028314	-672.6549693	-672.4792403	-672.4323003	-672.4824443
3P ⁻	-672.1607348	-672.1110126	-671.9526836	-671.9050206	-671.9559366
4	-335.8660531	-335.8586744	-335.7886464	-335.7595954	-335.7906214
4R	-335.4638252	-335.4539758	-335.3924078	-335.3630728	-335.3944008
4CAT	-336.0922604	-336.0415716	-335.9651816	-335.9351366	-335.9672256
4Q	-335.8499063	-335.8371210	-335.7672160	-335.7380610	-335.7691980
4QH	-336.125511	-336.0767082	-335.9981482	-335.9690472	-336.0001272
4P ⁻	-335.5685687	-335.5176521	-335.4560611	-335.4274111	-335.4580081
(1+1)Q	-672.4447167	-672.4305468	-672.2626708	-672.2158108	-672.2658688
(1+4)Q	-671.6934143	-671.6791892	-671.5245982	-671.4793872	-671.5276842
6	-264.7619459	-264.7545276	-264.6889516	-264.6626206	-264.6907396
6R	-264.3605745	-264.3516357	-264.2948537	-264.2679647	-264.2966787
6BzR	-264.3615687	-264.3544098	-264.2979878	-264.2712648	-264.2998038
(6+6R)TS	-529.1043466	-529.0921315	-528.9603125	-528.9186965	-529.0921315
phenol	-192.9009767	-192.8963854	-192.8491274	-192.8268384	-192.8506384
phenolate	-192.5987890	-192.5410947	-192.5025167	-192.4804887	-192.5040097
O ₂	-94.28962326	-94.28896257	-94.29852057	-94.28455857	-94.29946157
H ₂ O	-47.96387896	-47.95835046	-47.95661446	-47.94274946	-47.95755046
OH ⁻	-47.64777409	-47.56137833	-47.56636433	-47.55408033	-47.56719333

Table S2 Calculated free energy changes in water and gas phase for reaction steps depicted in **Figs 2 and 3** of the article (at 298.15 K, kcal mol⁻¹).

Reaction	ΔG_s	ΔG_g
$1 + \frac{1}{4} O_2 \rightarrow 1R + \frac{1}{2} H_2O$	-11.8	-10.1
$4 + \frac{1}{4} O_2 \rightarrow 4R + \frac{1}{2} H_2O$	-7.3	-7.4
$2\ 1R \rightarrow 2QQ\ (RR.\ SS)$	-2.2	8.8
$2\ 1R \rightarrow 2QQ\ (meso)$	-2.6	10.0
$2QQ + (PhO^-)H^+ \rightarrow 2QHQ + (PhO^-)\ (RR.SS)$	26.2	-221.8
$2QQ + (PhO^-)H^+ \rightarrow 2QHQ + (PhO^-)\ (meso)$	24.7	-226.5
$2QHQ + (PhO^-) \rightarrow 2PQ + (PhO^-)H^+\ (RR.SS)$	-45.8	200.3
$2QHQ + (PhO^-) \rightarrow 2PQ + (PhO^-)H^+\ (meso)$	-44.0	203.7
$2PQ + (PhO^-)H^+ \rightarrow 2PQH + (PhO^-)$	25.0	-222.7
$2PQH + (PhO^-) \rightarrow 2 + (PhO^-)H^+$	-42.4	205.1
$2QQ + (PhO^-) \rightarrow 2PQ^- + (PhO^-)H^+\ (RR.SS)$	-1.3	310.2
$2QQ + (PhO^-) \rightarrow 2PQ^- + (PhO^-)H^+\ (meso)$	-0.9	309.0
$2PQ^- + (PhO^-)H^+ \rightarrow 2PQ + (PhO^-)$	-18.3	331.7
$2PQ + (PhO^-) \rightarrow 2PP^- + (PhO^-)H^+$	-11.8	299.6
$2PP^- + (PhO^-)H^+ \rightarrow 2 + (PhO^-)$	-5.6	-317.3
$2PQ^- \rightarrow (2PQ^- \rightarrow 2PP^-)TS$	-3.2	5.6
$2\ 1R \rightarrow 3Q$	-3.8	4.6
$3Q + (PhO^-)H^+ \rightarrow 3QH + (PhO^-)$	27.2	-217.9
$3QH + (PhO^-) \rightarrow 3 + (PhO^-)H^+$	-48.7	194.2
$3Q + (PhO^-) \rightarrow 3P^- + (PhO^-)H^+$	-7.8	304.4
$3P^- + (PhO^-)H^+ \rightarrow 3 + (PhO^-)$	-13.7	-328.1
$2\ 1R \rightarrow 4Q + 1$	-28.8	-28.9
$1R + 4R \rightarrow 4Q + 4$	-33.3	-31.5
$4Q + (PhO^-)H^+ \rightarrow 4QH + (PhO^-)$	13.0	-228.8
$4QH + (PhO^-) \rightarrow 4 + (PhO^-)H^+$	-29.1	207.4
$4Q + (PhO^-) \rightarrow 4P^- + (PhO^-)H^+$	-7.2	309.0
$4P^- + (PhO^-)H^+ \rightarrow 4 + (PhO^-)$	-8.9	-330.5
$1R + 1R \rightarrow 4CAT + 1P^-$	32.8	122.9
$1R + 4R \rightarrow 4CAT + 4P^-$	21.8	103.1
$4CAT + (PhO^-) \rightarrow 4Q + (PhO^-)H^+$	-46.2	-148.6
$1P^- + (PhO^-)H^+ \rightarrow 1 + (PhO^-)$	-15.3	-3.2
$2\ 1R \rightarrow (1+1)Q$	-7.0	1.2
$1R + 4R \rightarrow (1+4)Q$	-10.7	-0.3
$(1+1)Q \rightarrow 4Q + 1$	-21.7	-30.1
$(1+4)Q \rightarrow 4Q + 4$	-22.5	-31.3
$6 + 6R \rightarrow 6BzR + 6$	-1.0	-3.1
$6 + 6R \rightarrow (6 + 6R)TS$	18.2	23.5



