Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Bromoperoxidase activity of amavadin dissected: a DFT investigation

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S1. Computational methods and models.

Density functional theory (DFT) have been used as implemented in the TURBOMOLE suite of programs.[A] A high quality level of theory (B-P86/TZVP[B,C]) has been adopted to treat explicitly (*no* effective-core potential is associated with the inner electron shells) the full electronic structure of all atoms composing the system under investigation. Such DFT scheme has been reported to be suitable for investigating reactivity and stereoelectronic features of bio-related vanadium compounds.[D-L]

All stationary points on the PES have been determined by means of energy gradient techniques and a full vibrational analysis has been carried out to further characterize the nature of each point.

Transition state (TS) structures have been searched by means of a procedure based on a *quasi*-Newton-Raphson algorithm or *updated*-Hessian method.[M]

As a preliminary step, the geometry optimization of a guess transition state structure is performed by constraining those molecular degrees of freedom which correspond to the reaction coordinate. These are actually those structural parameters changing most during reaction (therefore whose difference is maximized between reactants and products of each elementary reaction step). After performing the vibrational analysis of the guess TS structure, the negative eigenmode of vibration associated to the reaction is followed to locate the true transition state structure, which corresponds to the maximum energy point along the trajectory which joins two adjacent minima (i.e., reactants, products and reaction intermediates).

Solvent polarization effects have been considered for cationic species (**AH_2**) in explicit way by neutralizing the positive charge with a bromide ion placed in a spectator position, i.e. irrelevant related to the reaction center. The choice of Br^- is motivated by at least two reasons: it is actually present in solution as a reaction substrate and, as a counterion, it is intrinsically less polarizing (therefore introducing less bias into the system) than, for example, the smaller sized chloride ion. Further, one or two water molecules have been explicitly added to the system in the case of intramolecular proton transfers, since it is clear that water can easily shuttle protons among heteroatomic sites of the amavadin molecule.

The effects of ZPE, thermal and entropic contributions on the purely electronic ΔE_{SCF} values have been investigated (see **S2**) by means of evaluation of the approximated roto-translational partition function of each molecular species, at T=293 K and P=1 bar. The main approximations consist in the assumption of the ideal gas model (which allows one to substitute the PV term by RT –trivially calculated- into thermodynamics equations and also it allows one to neglect intermolecular interactions, thus simplifying the total *ensemble* partition function into a sum of *molecular* partition functions). Moreover, each single molecular partition function is further approximated by assuming the separability into different energy terms (electronic, vibrational, rotational and translational) of the molecular energy.

The Resolution of the Identity procedure[O] have been used for approximating high-computational demanding four-center integrals (describing the classical (Coulomb) electron-electron repulsive contribution to the total energy) through a combination of two three-center integrals. The mathematical procedure used to accomplish such task entails expanding the electron density ρ in

terms of an atom-centered and extremely large basis, which is called *auxiliary* basis set.

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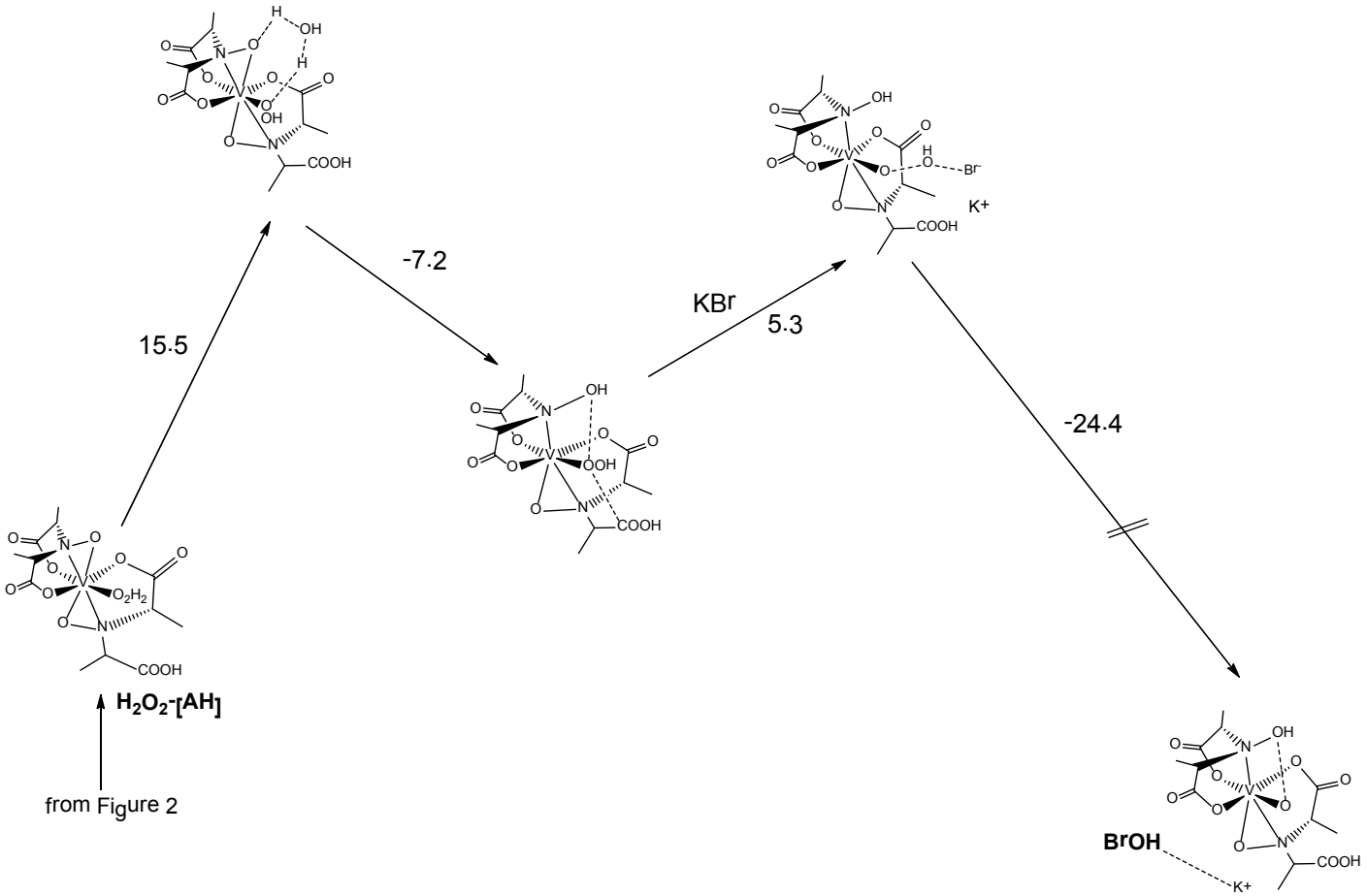
S2

Comparison of kinetic parameters ($\Delta E^{\ddagger}$ vs $\Delta G^{\ddagger}$, kcal/mol) associated to Figure2 of the main text

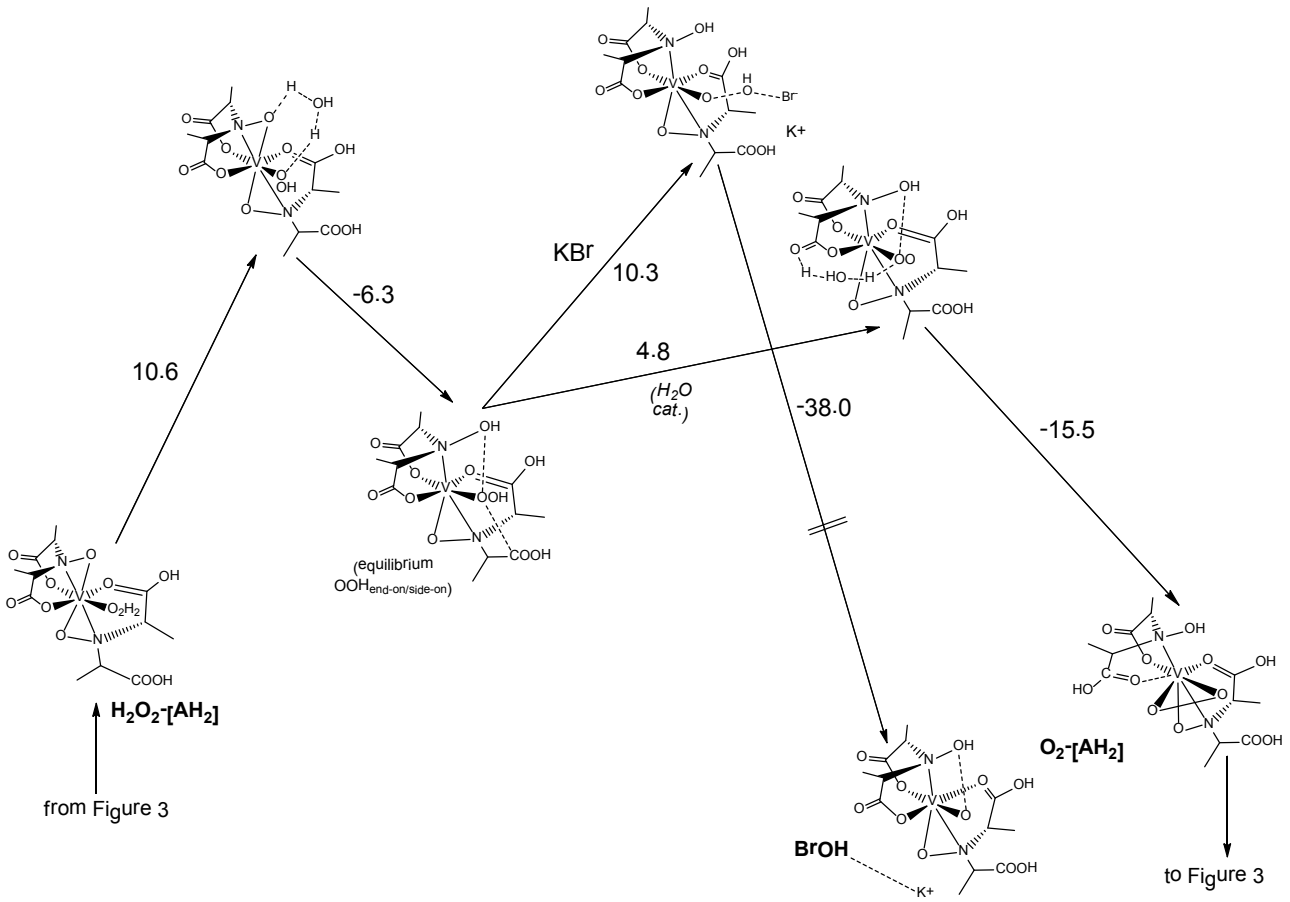
Reaction	$\Delta E^{\ddagger}$	$\Delta G^{\ddagger}$
H_2O_2 binding to V^V	8.6	8.3
H^+ transfer from bound H_2O_2 to ligated COO^-	8.1	7.6
H^+ transfer from bound HO_2^- to ligated COO^-	4.0	7.2
KBr oxidation on HO_2-amavadin	4.4	2.7
KBr oxidation on O_2-amavadin	12.8	12.9

S3

Alternative (less favored) pathway for KBr oxidation by mono-protonated amavadin (**AH**). The shown route, which is alternative to the energy profile reported in Figure 2 (main text), consists in the first proton transfer (from bound hydrogen peroxide) occurring toward the NO ligand in place of the more basic carboxylate.


15.5
-7.2
KBr
5.3
-24.4
H_2O_2-[AH]
from Figure 2
BrOH
K+

S4. Alternative (less favored) pathway for KBr oxidation by bis-protonated amavadin (**AH_2**). The shown route, which is alternative to the energy profile reported in Figure 3 (main text), consists in the first proton transfer (from bound hydrogen peroxide) occurring toward the NO ligand in place of the more basic carboxylate.



S5. Reaction pathways and energies obtained considering bulk solvation effects and corrections for dispersion effects.

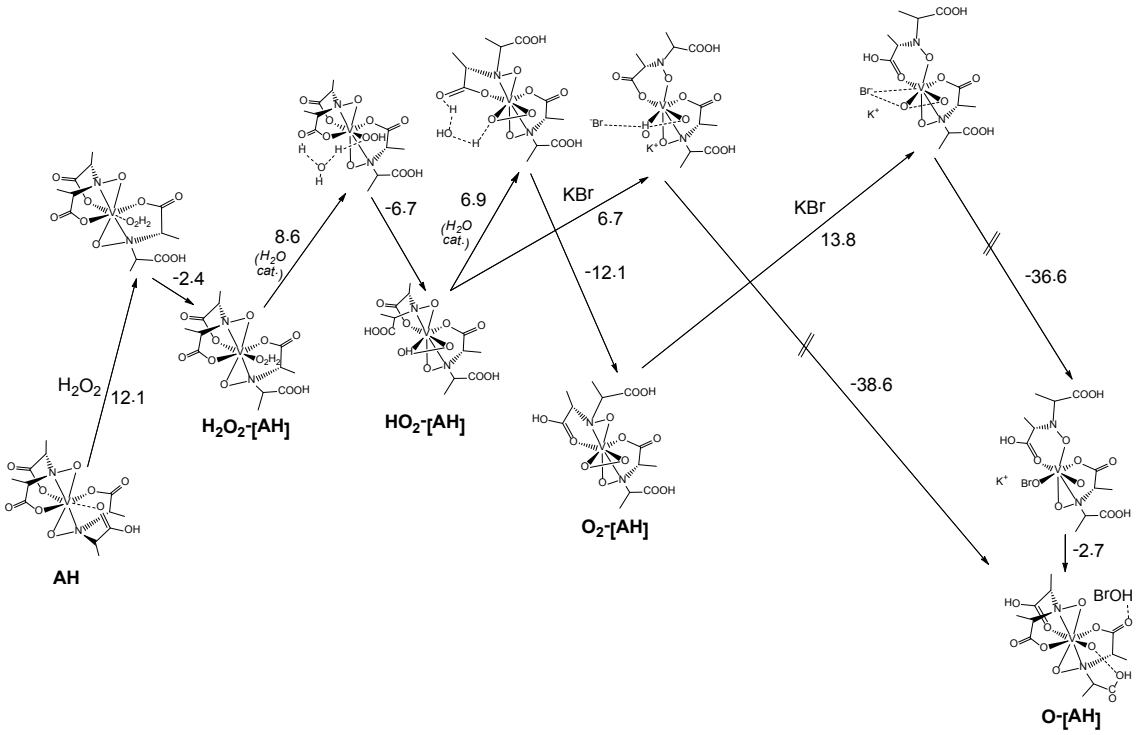


Figure 2a. Solvent corrected (COSMO, ε=80) pathway of bromoperoxidation catalyzed by monoprotonated amavadin (**AH**). Energies are in kcal/mol.

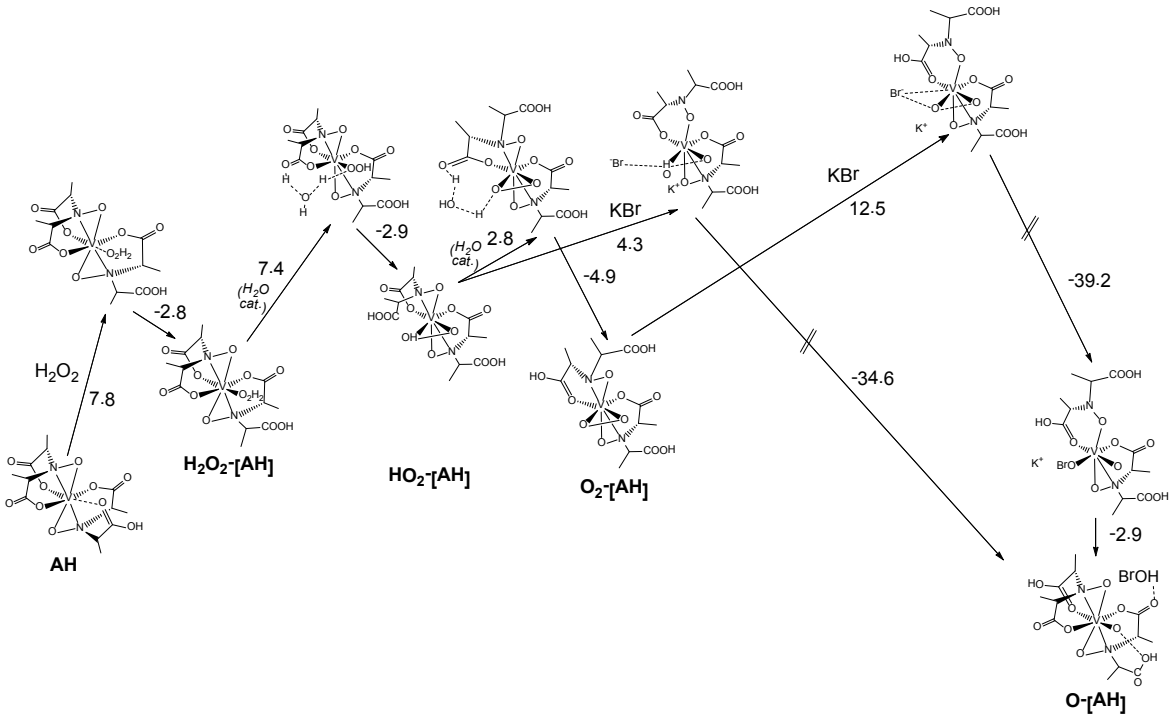


Figure 2b. Dispersion corrected pathway of bromoperoxidation catalyzed by monoprotonated amavadin (**AH**). Energies are in kcal/mol.

S6. Transition state structures (XYZ) presented in Figure 2 and Figure 3 of the main text.
S6 (i). *TS state structures of Figure 2 in the main text (KBr oxidation pathway on mono-protonated amavadin)*

Binding hydrogen peroxide to V

46

C	2.766240	2.811480	-1.395676
C	1.433503	2.062441	-1.402072
C	1.569692	0.608809	-1.881558
O	2.175518	0.293090	-2.887647
N	0.764157	2.028119	-0.083843
O	1.531058	1.475013	0.917104
V	0.185384	0.140344	0.598948
O	-1.730965	0.843214	-1.168418
O	-3.082616	0.939974	-0.599774
C	-0.005985	3.197067	0.413330
C	-0.721267	4.002774	-0.670850
C	-1.018361	2.651433	1.439866
O	-1.103898	1.319052	1.481147
O	-1.711741	3.386312	2.114626
O	0.922951	-0.278717	-1.118196
N	-0.431043	-1.915591	0.466206
C	0.368948	-2.798505	1.370170

C	1.416931	-3.633214	0.626321
O	-1.210645	-1.036904	1.194846
O	1.295283	-0.636716	1.931994
C	1.097115	-1.886909	2.368006
O	1.537126	-2.301391	3.420085
C	-1.195555	-2.657649	-0.618278
C	-2.704929	-2.573524	-0.423591
C	-0.775460	-2.198390	-2.023344
O	-1.351394	-1.342293	-2.679535
O	0.267311	-2.904797	-2.489802
H	0.557664	-2.485079	-3.329374
H	0.721624	2.538672	-2.092143
H	0.705319	3.833604	0.962735
H	-0.330855	-3.440218	1.930131
H	-0.867784	-3.700966	-0.531677
H	3.437665	2.392824	-0.635682
H	3.234189	2.697879	-2.381818
H	2.619174	3.881143	-1.194654
H	-0.012244	4.531054	-1.322372
H	-1.379432	3.364906	-1.274877
H	-1.340141	4.754710	-0.164320
H	2.016233	-4.165291	1.376556

H	0.969458	-4.382962	-0.038703
H	2.080775	-2.991849	0.032779
H	-3.078566	-1.549607	-0.537061
H	-3.192144	-3.209743	-1.175400
H	-2.979979	-2.937416	0.573934
H	-2.834929	0.946321	0.358205
H	-1.828304	0.076554	-1.800046

Proton transfer from bound H_2O_2 to carboxylate

49

C	-2.477506	-1.963778	-2.790798
C	-1.864543	-1.712181	-1.413185
C	-0.394484	-2.170482	-1.340282
O	-0.048194	-3.285102	-1.693390
N	-1.894475	-0.286562	-1.010098
O	-1.236067	0.529693	-1.896013
V	-0.079529	0.501029	-0.351144
O	-0.528477	-0.286135	1.478266
O	-1.216968	-1.570378	1.579455
C	-3.154377	0.343099	-0.480943
C	-4.149147	-0.634743	0.131902
C	-2.645953	1.380019	0.531581

O	-1.496374	1.879607	0.366809
O	-3.346057	1.623985	1.577729
O	0.457358	-1.275872	-0.843484
O	0.850011	1.611587	-1.648637
C	2.057500	2.109964	-1.418198
C	2.869673	1.301829	-0.394982
C	3.800033	0.351618	-1.152372
N	1.877555	0.610089	0.490933
O	0.957192	1.523586	0.961268
O	2.534054	3.063600	-2.007637
C	2.502908	-0.297277	1.544593
C	2.200806	0.133700	2.971479
C	2.162921	-1.781159	1.300385
O	1.355459	-2.443483	1.930991
O	2.954359	-2.307168	0.343650
O	-1.520150	1.411201	3.159931
H	-1.073686	0.672262	2.559316
H	2.606807	-3.202187	0.137068
H	-2.389952	-2.272161	-0.629631
H	-3.605582	0.879602	-1.332280
H	3.443146	2.003225	0.232626
H	3.583693	-0.213095	1.364949

H	-1.996910	-1.330089	-3.546620
H	-2.312858	-3.015831	-3.055704
H	-3.558345	-1.765558	-2.792648
H	-4.551437	-1.321770	-0.623255
H	-3.693817	-1.207337	0.949674
H	-4.983915	-0.058023	0.549002
H	4.403936	0.961195	-1.837324
H	4.484590	-0.194403	-0.491185
H	3.225627	-0.377784	-1.736058
H	1.155403	-0.058561	3.225794
H	2.840426	-0.441990	3.654919
H	2.421534	1.200156	3.103953
H	-0.442639	-2.121530	1.862038
H	-2.514035	1.697734	2.443589
H	-0.896409	2.160261	3.109895

Proton transfer from the V bound hydroperoxide to a second coordinated carboxylate

49

C	1.386863	2.609304	-2.385629
C	0.122224	1.850954	-1.978792
C	0.142968	0.401160	-2.486012
O	0.561757	0.098777	-3.594547

N	-0.179538	1.855904	-0.515293
O	0.767695	1.098800	0.197496
V	-0.771059	-0.050879	0.349049
O	-1.001226	-1.928691	0.587780
N	0.387025	-1.825754	0.813723
C	0.701398	-1.918084	2.279176
C	2.208199	-1.860316	2.557401
C	-0.423527	3.223897	0.062870
C	-1.261357	3.205369	1.345355
C	0.872499	4.034293	0.337894
O	1.886806	3.367062	0.924906
O	0.927091	5.223221	0.108965
O	-0.380656	-0.487399	-1.649253
O	-0.496383	0.179174	2.285586
C	0.029168	-0.755304	3.042859
O	0.063467	-0.730231	4.263236
O	-2.464832	0.358124	0.929209
O	-2.566498	0.106434	-0.453508
C	1.169749	-2.835607	0.002265
C	0.937788	-4.272431	0.488857
C	0.842094	-2.781354	-1.492944
O	-0.141724	-3.303979	-1.997387

O	1.822975	-2.182866	-2.189047
O	-2.419319	-1.862356	-1.942040
H	1.495490	-2.002144	-3.102138
H	-0.762752	2.309764	-2.452785
H	-0.962112	3.769370	-0.722663
H	0.268317	-2.852978	2.663922
H	2.217761	-2.537167	0.116647
H	2.258829	2.236833	-1.832706
H	1.558983	2.434179	-3.454957
H	1.288935	3.689205	-2.221152
H	-2.263192	2.807766	1.148658
H	-0.793598	2.593767	2.126970
H	-1.353070	4.236721	1.711217
H	2.336551	-1.764458	3.642611
H	2.739851	-2.763477	2.230776
H	2.665017	-0.981879	2.080070
H	-0.127937	-4.525360	0.435948
H	1.484714	-4.968314	-0.161976
H	1.297394	-4.419304	1.513917
H	-2.746272	-1.263748	-1.135976
H	1.651444	2.399691	0.952846
H	-2.071849	-2.721667	-1.596205

H -1.499381 -1.339909 -2.090658

KBr oxidation on the V-hydroperoxide species

48

C -2.594210 -3.372133 -2.177441

C -2.321134 -2.176856 -1.258510

N -1.556505 -1.077342 -1.906373

C -2.367392 -0.205241 -2.836494

C -1.565739 0.690993 -3.838154

O -2.044811 1.729372 -4.236859

C -1.579766 -2.592017 0.015051

O -0.465951 -1.946485 0.276915

V 0.289438 -0.544335 -0.899940

O -0.076084 1.106639 -1.430077

O -2.033112 -3.459211 0.766896

O -0.357956 -1.549128 -2.432222

O 1.393050 -0.087362 0.510145

N 2.628511 -0.570269 0.957662

C 2.980213 0.255417 2.163772

C 1.706425 0.223219 3.022103

O 1.052531 1.391399 3.035662

O	1.880945	-1.167195	-1.739477
C	3.161710	-1.283537	-1.384913
O	3.947614	-1.895351	-2.086610
O	-0.931644	0.946197	0.081105
Br	-2.001197	0.703066	2.365147
C	3.646226	-0.544408	-0.117582
C	4.959519	-1.140753	0.388475
C	-3.380343	0.626664	-2.052784
O	-0.432711	0.191160	-4.361189
C	3.489734	1.669578	1.872116
O	1.319792	-0.786124	3.599018
K	-0.728067	-2.384561	2.996215
H	0.100517	1.227805	3.301841
H	-3.266048	-1.729659	-0.920387
H	-2.899111	-0.909284	-3.504962
H	3.807336	0.500435	-0.454844
H	3.736565	-0.330945	2.704119
H	-1.653750	-3.778096	-2.570106
H	-3.103324	-4.150952	-1.596412
H	-3.241634	-3.090379	-3.018848
H	-4.153592	0.003542	-1.585153
H	-2.880030	1.219533	-1.279970

H	-3.869035	1.311077	-2.755131
H	5.646327	-1.251633	-0.457655
H	5.435391	-0.502276	1.144610
H	4.787554	-2.136950	0.818161
H	2.782535	2.226056	1.244908
H	3.614697	2.223825	2.811773
H	4.466501	1.642238	1.371116
H	-0.273702	1.432658	0.633987
H	-0.165466	-0.610510	-3.832582

KBr oxidation on the V-peroxo species

48

C	-1.449905	2.871520	-2.218976
C	-1.162404	1.387797	-2.557975
N	-1.786169	0.384741	-1.667651
C	-3.255518	0.455629	-1.656147
C	-3.899679	-0.643734	-0.778494
O	-5.019544	-0.461097	-0.335256
C	0.344395	1.211196	-2.570042
O	1.051721	0.911393	-1.609144
V	0.298454	-0.360476	0.118314
O	-0.581988	-1.948268	0.117959

O	0.502233	-1.529048	-1.235372
O	0.889508	1.501411	-3.760100
O	-1.336576	0.623083	-0.327946
O	1.520260	-0.977393	1.437154
N	2.387276	-0.333661	0.555400
C	3.466665	-1.248666	0.016734
C	3.771745	-1.006378	-1.485216
O	2.827320	-1.354793	-2.373083
O	0.533419	1.414025	1.106470
C	1.675993	1.746561	1.665367
O	1.800815	2.664226	2.471026
C	2.890649	0.928788	1.188194
C	3.756776	1.777188	0.254163
C	-3.841998	0.306089	-3.071242
O	-3.267041	-1.812040	-0.635473
C	3.162998	-2.723384	0.288698
O	4.855614	-0.588626	-1.848824
H	1.954307	-1.590610	-1.914809
H	-1.512638	1.167231	-3.574114
H	-3.606152	1.409635	-1.216714
H	3.471004	0.632007	2.078209
H	4.394216	-0.966685	0.537215

H	-1.085600	3.105737	-1.211082
H	-0.950791	3.534412	-2.938065
H	-2.528562	3.070790	-2.271553
H	-3.647131	1.188743	-3.695715
H	-3.431303	-0.583477	-3.568933
H	-4.930104	0.192589	-2.990105
H	4.051088	2.682426	0.800932
H	4.664758	1.250389	-0.064701
H	3.193234	2.074919	-0.639387
H	2.199530	-3.029890	-0.135665
H	3.960448	-3.329104	-0.164360
H	3.141375	-2.918556	1.366506
H	-2.282406	-1.738435	-0.759788
H	1.858725	1.350629	-3.686844
K	-1.898353	1.824752	2.085859
Br	-1.397957	-1.393888	2.249641

S6 (II). *TS state structures of Figure 3 in the main text (KBr oxidation pathway on double-protonated amavadin)*

Binding of hydrogen peroxide to V

48

C	-0.876809	2.433532	3.016389
C	-1.391388	2.168592	1.601788
N	-1.641528	0.728727	1.290639
C	-2.919997	0.110784	1.757946
C	-2.912379	-0.058235	3.285507
O	-2.038933	-0.599181	3.925232
C	-0.441171	2.759663	0.529038
O	-0.171570	1.978379	-0.528767
V	-0.776060	0.178589	-0.474637
O	-2.471647	0.835499	-1.201899
C	-2.649539	0.896973	-2.523627
O	-3.714364	1.171298	-3.042655
O	-0.001319	3.885981	0.628498
O	-0.511634	-0.063922	1.372656
O	-0.929496	-1.140250	-1.810963
N	-0.395725	-0.022217	-2.458264
C	1.019301	-0.230844	-2.848954
C	1.647005	1.031376	-3.445439
O	1.150969	-0.353846	-0.443797
C	1.751298	-0.642520	-1.556846
O	2.856477	-1.198876	-1.640026
C	-1.377552	0.623592	-3.362183

C	-1.661432	-0.176624	-4.629271
C	-3.172611	-1.257192	1.116087
O	-4.064382	0.432693	3.823017
O	-0.185782	-2.808775	1.247537
O	0.481716	-4.101604	1.456694
H	-2.362222	2.663577	1.438889
H	-3.701884	0.821753	1.462599
H	1.069468	-1.072545	-3.556159
H	-0.952561	1.610995	-3.602900
H	-0.004283	1.805470	3.234982
H	-0.575928	3.487390	3.070172
H	-1.648750	2.252976	3.773607
H	-3.290088	-1.149755	0.029819
H	-2.367295	-1.969057	1.344388
H	-4.115138	-1.663368	1.507591
H	2.716990	0.838456	-3.594983
H	1.210266	1.280780	-4.421802
H	1.536558	1.885476	-2.764720
H	-1.975523	-1.198495	-4.378921
H	-2.482067	0.312478	-5.168874
H	-0.783036	-0.220360	-5.287136
H	-4.043061	0.220967	4.781477

H	0.048198	-2.329714	2.069596
H	1.374601	-3.906870	1.072152
H	3.296171	-2.077011	-0.408886
Br	3.667569	-3.091745	0.656991

Proton transfer from the V-bound H_2O_2 to carboxylate

51

C	-3.031617	0.481134	-2.733036
C	-2.259275	1.378196	-1.761096
C	-2.745874	1.177844	-0.319971
O	-3.929095	1.273381	-0.030601
N	-0.781487	1.180554	-1.797382
O	-0.426576	-0.128421	-1.536296
V	0.111248	0.662996	0.135852
O	1.363102	0.642698	1.675554
N	0.097550	0.625770	2.213183
C	-0.237896	1.911907	2.890099
C	0.337865	2.042427	4.294960
C	-0.156496	1.756129	-3.056056
C	0.511523	3.112131	-2.858483
C	0.752057	0.687410	-3.681979
O	0.082196	-0.008714	-4.626817

O	1.923420	0.476590	-3.417645
O	-1.804804	0.913043	0.566084
O	1.658530	1.514200	-0.688324
O	2.392751	0.271879	-0.724701
O	0.003948	-1.278176	0.517355
C	-0.055963	-1.727129	1.738640
C	-0.251799	-0.668632	2.841000
C	-1.681901	-0.712059	3.384138
O	0.097580	2.790356	0.675525
C	0.342096	2.915075	1.895561
O	1.168594	3.806233	2.359552
O	-0.011466	-2.921629	2.048550
O	2.859830	3.710994	0.535806
H	-2.419760	2.441293	-2.003512
H	-0.995911	1.871620	-3.756394
H	0.482655	-0.867121	3.637729
H	-1.334982	2.000013	2.869117
H	-2.819429	-0.575275	-2.527026
H	-4.103458	0.661069	-2.582278
H	-2.783779	0.694872	-3.781727
H	-0.140898	3.764199	-2.262429
H	1.471268	3.014531	-2.346382

H	0.664442	3.587003	-3.837644
H	-1.879156	-1.733877	3.731921
H	-1.812771	-0.034238	4.238422
H	-2.406310	-0.452672	2.603043
H	1.423812	1.885686	4.284276
H	0.146486	3.055124	4.673257
H	-0.126422	1.326423	4.983446
H	0.686054	-0.713594	-4.947744
H	2.468875	2.918200	0.066890
H	2.325196	0.078036	-1.700000
H	0.203961	-4.103524	0.851602
H	1.864153	3.980240	1.574924
H	3.682844	3.372201	0.929358
Br	0.396820	-5.228226	-0.104278

Proton transfer from the V-bound hydroperoxide to coordinated NO

54

C	-0.359273	-2.941136	2.764831
C	0.740180	-2.383015	1.858411
N	0.873521	-0.894680	1.939186
C	1.682671	-0.457147	3.145470
C	1.113296	0.810756	3.801645

O	0.002021	0.881427	4.272783
C	0.526921	-2.785252	0.389862
O	0.430187	-1.772545	-0.461343
V	0.531013	0.102791	0.112456
O	1.450963	1.700329	1.077347
O	0.589678	1.940173	-0.058184
O	0.474657	-3.957022	0.054807
O	-0.351441	-0.274044	1.729554
O	-1.342887	0.297012	-0.432614
C	-1.814534	0.206668	-1.644557
C	-0.817096	-0.135754	-2.756311
C	-1.048364	-1.583625	-3.207039
O	2.556748	-0.152678	-0.545437
C	2.773280	-0.510548	-1.717746
O	3.999215	-0.820873	-2.119661
N	0.564006	0.240511	-2.266643
O	0.808722	1.520315	-2.669439
O	-3.012691	0.327896	-1.921184
C	3.172320	-0.434730	2.816598
O	2.040794	1.805077	3.900936
C	1.672518	-0.682137	-2.726399
C	2.104678	-0.477268	-4.177480

O	3.592883	2.579196	0.200334
O	3.124034	2.390814	-2.271103
H	1.720697	-2.788858	2.151870
H	1.491560	-1.230120	3.909273
H	-1.008320	0.551587	-3.591336
H	1.308163	-1.708656	-2.560589
H	-1.330974	-2.506369	2.502655
H	-0.402586	-4.028099	2.621520
H	-0.156477	-2.734369	3.825087
H	3.490449	-1.405045	2.410197
H	3.418513	0.345319	2.089552
H	3.747045	-0.250331	3.733106
H	-2.106161	-1.665742	-3.491668
H	-0.449170	-1.840059	-4.091190
H	-0.851219	-2.303549	-2.404539
H	2.526296	0.522721	-4.322388
H	2.856282	-1.229527	-4.449069
H	1.242766	-0.592057	-4.845483
H	1.588824	2.542221	4.363733
H	-4.211997	0.481034	-0.731776
H	4.613078	-0.658714	-1.370633
H	2.116203	2.038604	-2.414988

H	3.262474	3.122324	-2.894073
H	3.445960	2.595765	-0.842232
H	3.688701	3.500209	0.496682
H	2.436234	2.039892	0.703021
Br	-5.377582	0.557046	0.190398

KBr oxidation on the V-bound hydroperoxide species

50

C	-2.451299	-3.363309	1.128547
C	-1.336445	-2.329447	1.244686
C	0.057796	-2.929628	0.934444
O	0.308847	-4.100007	1.197949
N	-1.516705	-1.147131	0.329445
O	-1.149097	-1.448583	-0.945311
V	0.292960	-0.195161	-0.165272
O	1.172410	-0.665957	-2.106952
C	2.367582	-0.325272	-2.171961
O	2.941810	0.109758	-3.270425
C	-2.837520	-0.421729	0.528713
C	-2.891415	0.240157	1.902951
C	-3.204634	0.511074	-0.634168
O	-3.449012	1.776046	-0.229760

O	-3.453808	0.128997	-1.771839
O	0.914756	-2.071207	0.442588
O	0.329989	0.209602	1.778711
C	1.472132	0.285396	2.390829
C	2.746382	0.046139	1.553389
C	3.869324	1.030176	1.876374
O	1.680128	1.217680	-0.253028
N	2.333400	0.066585	0.132146
C	3.259539	-0.382462	-0.935893
C	3.842278	-1.781619	-0.712482
O	-0.080338	1.703920	-2.543572
O	-0.732702	1.045673	-0.878548
O	1.589192	0.486168	3.610507
Br	0.709328	1.928932	-4.683432
K	-1.423517	-0.425182	-3.418927
H	-1.274703	-1.924503	2.266682
H	-3.603992	-1.213078	0.458781
H	4.053705	0.372514	-1.047779
H	3.045380	-0.991649	1.767968
H	-2.647264	-3.608672	0.075043
H	-2.102902	-4.277018	1.626117
H	-3.383998	-3.039828	1.610868

H	-2.743044	-0.488009	2.708309
H	-2.123075	1.013950	2.001109
H	-3.876787	0.701591	2.042419
H	4.399080	-2.092164	-1.607179
H	4.549476	-1.769649	0.127489
H	3.039658	-2.498563	-0.500755
H	3.593037	2.044923	1.560736
H	4.029210	1.033727	2.961593
H	4.810785	0.743536	1.386872
H	-3.737626	2.267620	-1.027043
H	0.013937	2.631665	-2.239334
H	2.233414	0.444303	-3.913916
H	0.306662	0.128429	4.480822
Br	-0.841568	-0.375793	5.331769

KBr oxidation on the V-bound *peroxo species*

50

C	1.460581	2.083718	3.518248
C	1.617389	1.128757	2.335351
C	1.288788	-0.325562	2.740315
O	1.748300	-0.804098	3.767706
N	0.809826	1.515133	1.135451

O	-0.565797	1.480277	1.336843
V	-0.245357	-0.069353	0.263663
O	-0.164119	0.659201	-1.307137
O	-1.828945	0.146648	-1.047363
C	1.319659	2.772555	0.449269
C	2.057483	2.536555	-0.860954
C	0.143599	3.750553	0.324066
O	0.047714	4.532046	1.423109
O	-0.602145	3.871172	-0.634784
O	0.503304	-0.959662	1.903303
O	1.631611	-0.654530	-0.372153
C	1.874186	-1.858025	-0.725221
C	0.825213	-2.920810	-0.386955
C	0.853776	-4.150466	-1.287612
N	-0.517088	-2.255971	-0.276591
C	-1.479609	-2.970976	0.655473
C	-0.872331	-3.814567	1.791119
O	-2.018140	-0.717069	1.353514
C	-2.354064	-1.898347	1.266260
O	-3.510470	-2.343066	1.755307
O	2.965378	-2.224351	-1.233921
O	-1.121738	-2.262872	-1.575690

K	-2.411493	2.443635	-2.058650
Br	-4.175876	-0.149330	-1.068160
Br	5.043223	-0.082877	-1.306718
H	2.657576	1.115370	1.970498
H	2.010569	3.225386	1.173614
H	-2.103305	-3.602813	0.008075
H	1.091817	-3.196797	0.643781
H	0.406943	2.157151	3.816503
H	2.031008	1.666207	4.357293
H	1.840957	3.091083	3.301550
H	2.847512	1.781914	-0.735597
H	1.379250	2.194806	-1.647856
H	2.532464	3.478642	-1.171860
H	-1.696108	-4.202736	2.405623
H	-0.328490	-4.678231	1.389642
H	-0.211830	-3.211397	2.425399
H	0.562703	-3.892373	-2.311185
H	1.877967	-4.542951	-1.300053
H	0.179031	-4.935094	-0.917915
H	-0.728489	5.119225	1.300044
H	-4.037185	-1.560134	2.029169
H	-1.565046	-1.339107	-1.594631

H	3.906989	-1.222740	-1.284573