Supporting Information

References Full Reference #20

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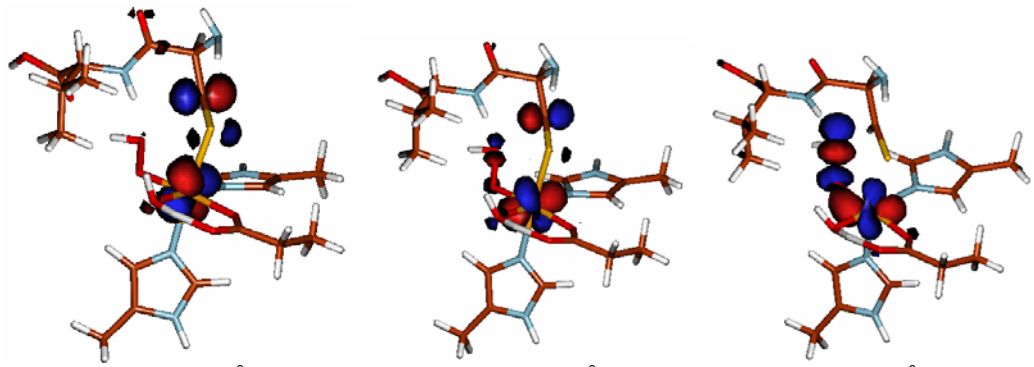
Figure S1 Alleviation of backbonding with O-O bond elongation
As the O-O bond is elongated mixing with the C-S π* orbital is reduced and the d_{xy} orbital rotates and interacts with the hydroperoxide σ* orbital.



O-O = 1.5Å O-O = 1.6Å O-O = 1.7Å

Table S1 Key Computational Results

	Bond Length (Å)			Spin Density				
OO	Fe-S	Fe-O	S-C	Fe	O(prox)	O(dist)	S	C
Model 1								
1.46	2.50	1.94	1.65	3.84	0.15	0.02	0.05	-0.26
1.60	2.54	1.90	1.65	3.79	0.14	0.01	0.05	-0.19
1.70	2.89	1.78	1.64	3.75	0.17	-0.16	0.03	0.00
1.90	2.83	1.72	1.64	3.79	0.26	-0.35	0.05	-0.01
2.20	2.76	1.66	1.65	3.53	0.42	-0.24	0.07	-0.01
2.50	2.64	1.63	1.65	3.01	0.62	0.10	0.10	-0.01
Model 2								
1.42	2.44	1.89	1.67	3.82	0.19	0.02	0.00	-0.25
1.60	2.54	1.92	1.64	3.70	0.11	0.03	0.03	-0.03
1.75	2.53	1.73	1.82	3.79	0.01	-0.15	0.16	0.00
1.90	2.37	1.66	1.86	3.04	0.62	0.10	0.11	-0.01
2.05	2.32	1.65	1.88	3.04	0.61	0.07	0.13	-0.01
Model 3								
1.42	2.44	1.89	1.67	3.82	0.19	0.02	0.00	-0.25
1.60	2.50	1.91	1.64	3.72	0.12	0.03	0.03	-0.08
1.75	2.68	1.76	1.63	3.73	0.21	-0.22	0.01	0.07
1.90	2.70	1.72	1.63	3.79	0.31	-0.39	0.02	0.06
2.05	2.71	1.69	1.64	3.78	0.37	-0.48	0.03	0.06
Free(2.20)	2.78	1.68	1.64	3.67	0.45	-0.48	0.01	0.09

Table S2 Spin Densities from Elongation of the O-O bond with the dipole present

	Spin Density		
O-O (Å)	Fe	O (prox)	O (dist)
1.75	3.76	0.16	0.00
1.90	3.77	0.24	-0.31
2.05	3.73	0.32	-0.39
2.20	3.59	0.40	0.00

Table S3 Cartesian Coordinates of Optimized IPNS-ACV-Fe^{II}-Peroxide (Model 1)

Atom	X	Y	Z
C	2.394007	-2.264633	1.330973
N	1.605436	-1.133044	1.445520
C	1.188543	-1.093504	2.704090
N	1.680047	-2.159461	3.395994
C	2.456378	-2.927673	2.535435
Fe	1.025291	0.177297	-0.158453
O	2.607274	-0.581714	-1.263451
C	3.035883	-0.297749	-2.444075
C	4.244234	-1.093783	-2.945894
C	4.701368	-2.216254	-2.017796
C	3.134931	-4.191713	2.950798
N	2.403460	1.762493	0.373586
C	3.724547	1.682557	0.391177
N	4.270423	2.909490	0.614839
C	3.238880	3.831809	0.742489
C	2.089043	3.088434	0.592655
C	3.479314	5.287521	0.960925
S	-0.320710	-1.603954	-1.265666
C	-1.368124	-2.155431	-0.110721
C	-2.714716	-2.740130	-0.402081
N	-2.730507	-3.597239	-1.583714
O	-0.444280	1.031647	0.770263
O	-1.258529	0.260804	1.710500
O	0.573119	1.494784	-1.845448
C	-3.837009	-1.633115	-0.500893
O	-4.888494	-1.908636	-1.085056
N	-3.588031	-0.434687	0.090782
C	-4.584107	0.622350	0.062677
C	-4.697617	1.274777	1.430095
O	-3.826692	1.335011	2.288145
C	-4.325131	1.728675	-1.018127
C	-4.184382	1.087981	-2.405230
C	-3.119723	2.620508	-0.686030
O	2.560975	0.577264	-3.213042
O	-5.901449	1.866712	1.596769
H	-5.862307	2.314570	2.469937
H	-5.543126	0.140491	-0.180256
H	-5.237389	2.352244	-1.014860
H	-4.139723	1.871845	-3.177813
H	-3.257186	0.496624	-2.470521
H	-5.024802	0.416249	-2.633663
H	-2.941078	3.331000	-1.508979
H	-3.285778	3.215405	0.226830
H	-2.195537	2.037359	-0.532763
H	-2.687210	-0.271183	0.568344
H	-3.708463	-3.627036	-1.898399
H	-2.209593	-3.117592	-2.327220
H	-1.113421	-2.007441	0.942820
H	-1.913845	0.930264	2.008939
H	3.686940	-4.610267	2.098226
H	3.857160	-4.030207	3.769163
H	2.414757	-4.956977	3.286584

H	1.489301	-2.369080	4.370307
H	0.501379	-0.355869	3.106095
H	2.855787	-2.515717	0.381607
H	5.580079	-2.737624	-2.431350
H	4.970736	-1.828325	-1.023975
H	3.901636	-2.958949	-1.877321
H	3.983390	-1.483929	-3.943438
H	5.058288	-0.368989	-3.123264
H	-0.243724	1.241439	-2.310163
H	1.339651	1.239752	-2.480808
H	2.517693	5.814783	1.027035
H	4.031834	5.486449	1.895253
H	4.048861	5.741977	0.132441
H	5.262135	3.119785	0.655528
H	4.299538	0.777960	0.224639
H	1.052796	3.409649	0.616438
H	-3.014081	-3.348712	0.473758

Table S4 Cartesian Coordinates of Optimized IPNS-ACOV-Fe^{II}-Peroxide (Models 2 & 3)

Atom	X	Y	Z
C	-2.150520	-2.714020	-0.476916
N	-1.358521	-1.651373	-0.861528
C	-1.237284	-1.727642	-2.177515
N	-1.922399	-2.804003	-2.652288
C	-2.516986	-3.453331	-1.577012
Fe	-0.453657	-0.180903	0.418424
O	-0.935272	-1.662339	1.965554
C	-3.341814	-4.685890	-1.714623
N	0.139727	1.145638	-1.191211
C	1.358532	1.262194	-1.836339
C	1.337199	2.333917	-2.701194
N	0.060381	2.867361	-2.562764
C	-0.627622	2.128329	-1.650081
C	2.367730	2.911816	-3.614638
O	1.342447	-1.121786	0.130370
C	1.931596	-2.012084	0.847296
O	1.427342	-2.629441	1.823496
S	0.529331	1.022150	2.296991
C	0.145728	2.637856	2.082932
C	-0.162744	3.550324	3.241273
O	-2.091320	0.747161	0.609554
O	-2.297944	2.137959	0.804492
C	3.373691	-2.364083	0.473571
C	4.037171	-1.403496	-0.510745
N	1.090692	4.237120	3.591698
H	0.915490	4.912753	4.342586
H	1.742642	3.542569	3.968440
H	0.467551	3.134979	1.158387
H	-1.524660	2.408468	1.398952
H	3.292412	2.322396	-3.548375
H	2.043135	2.905531	-4.669221
H	2.618882	3.952606	-3.348938
H	-0.294720	3.688501	-3.042080

H	-1.627194	2.352423	-1.284620
H	2.162868	0.568832	-1.613330
H	5.082037	-1.695685	-0.704563
H	3.502111	-1.395922	-1.472257
H	4.036887	-0.375710	-0.117348
H	3.941441	-2.427119	1.415743
H	3.361981	-3.391907	0.069416
H	-1.060949	-1.222754	2.825995
H	-0.021753	-2.146635	2.017249
H	-3.694080	-5.003132	-0.723686
H	-4.231829	-4.526467	-2.347177
H	-2.770240	-5.524720	-2.147307
H	-1.986181	-3.085221	-3.625079
H	-0.670822	-1.044522	-2.802089
H	-2.377421	-2.871467	0.572078
H	-0.888424	4.328232	2.940068
H	-0.623231	2.960185	4.058835

Table S5 Cartesian Coordinates from the Transition State of IPNS-ACV-Peroxide O-O Bond Cleavage (Model 1)

Atom	X	Y	Z
C	2.438642	-2.211706	1.413955
N	1.610804	-1.104783	1.470836
C	1.083642	-1.090551	2.688499
N	1.543948	-2.150558	3.409626
C	2.414947	-2.886615	2.613240
Fe	1.087480	0.218682	-0.131081
O	2.666048	-0.580781	-1.236210
C	2.990600	-0.473027	-2.476023
C	4.206605	-1.279723	-2.940368
C	4.730663	-2.283733	-1.916657
C	3.090840	-4.135883	3.075699
N	2.475092	1.790608	0.376898
C	3.792791	1.697964	0.286570
N	4.366317	2.916141	0.479636
C	3.357897	3.846669	0.701293
C	2.192067	3.116315	0.636286
C	3.634225	5.296323	0.914142
S	-0.337483	-1.575163	-1.237173
C	-1.393514	-2.089860	-0.083799
C	-2.718372	-2.717763	-0.367813
N	-2.718116	-3.587416	-1.536650
O	-0.314790	1.112244	0.794807
O	-1.357578	0.311973	1.707034
O	0.646137	1.434045	-1.887229
C	-3.855360	-1.618941	-0.482834
O	-4.893131	-1.917776	-1.078962
N	-3.629142	-0.413301	0.100503
C	-4.631729	0.636716	0.026595
C	-4.799267	1.304193	1.382414
O	-3.954967	1.396128	2.261649
C	-4.330828	1.731131	-1.054677
C	-4.161682	1.079489	-2.433692
C	-3.122657	2.609480	-0.696885
O	2.410854	0.244545	-3.333193

O	-6.022982	1.869972	1.503160
H	-6.020281	2.330227	2.370676
H	-5.579197	0.149454	-0.246816
H	-5.233861	2.367442	-1.080265
H	-4.088724	1.856693	-3.210822
H	-3.240014	0.477102	-2.472331
H	-5.003796	0.415806	-2.679149
H	-2.918667	3.318092	-1.515599
H	-3.299941	3.205495	0.212758
H	-2.207431	2.017251	-0.525693
H	-2.735146	-0.217623	0.589167
H	-3.694321	-3.637784	-1.853565
H	-2.201614	-3.112137	-2.285929
H	-1.172751	-1.871550	0.965753
H	-1.915103	1.066525	1.990028
H	3.718582	-4.535831	2.267747
H	3.742249	-3.961098	3.948967
H	2.366020	-4.920579	3.351179
H	1.276970	-2.375840	4.362332
H	0.340556	-0.374648	3.028943
H	2.986364	-2.439869	0.505423
H	5.614365	-2.817944	-2.302462
H	5.015509	-1.785457	-0.978140
H	3.962642	-3.033911	-1.673969
H	3.928679	-1.777294	-3.883501
H	4.991392	-0.552704	-3.215651
H	-0.248771	1.284579	-2.239445
H	1.297298	1.039778	-2.579635
H	2.688881	5.835320	1.065537
H	4.265073	5.477341	1.801293
H	4.139317	5.752971	0.045991
H	5.360266	3.116591	0.443191
H	4.339696	0.789692	0.058258
H	1.164597	3.446192	0.750911
H	-3.009704	-3.315913	0.517643

Table S6 Cartesian Coordinates of Optimized IPNS-ACV-β Lactam Fe^{IV}-oxo (Model 1)

Atom	X	Y	Z
C	2.158068	2.733272	0.831306
N	2.390237	1.435938	0.418168
C	3.702131	1.304893	0.296733
N	4.320096	2.472457	0.621195
C	3.349593	3.410532	0.961338
Fe	0.808783	0.152976	-0.221781
O	0.759280	1.680152	-1.788855
C	3.670091	4.825097	1.331263
N	1.144589	-1.356994	1.290177
C	1.916935	-2.502097	1.253112
C	1.633291	-3.302664	2.337453
N	0.660292	-2.599845	3.040153
C	0.391301	-1.440676	2.381073
C	2.151715	-4.638712	2.768253
O	2.202805	-0.841584	-1.267677
C	2.715415	-0.626563	-2.438308
O	2.475674	0.354432	-3.180186

S	-0.877654	-0.953793	-1.377404
C	-2.280024	-1.186963	-0.241430
C	-3.366016	-2.238635	-0.703421
C	-4.390283	-1.111184	-0.448760
N	-3.400421	-0.193251	-0.156297
C	-3.635901	1.050280	0.567581
C	-3.667165	2.326722	-0.312514
C	-2.379586	2.548771	-1.109752
O	-0.245755	0.921877	0.763342
C	3.691728	-1.680837	-2.972278
C	4.327440	-2.623610	-1.948600
N	-3.240991	-2.827618	-2.023116
O	-5.606611	-1.001567	-0.437865
C	-2.776983	1.103216	1.831385
O	-2.445560	2.363048	2.192417
O	-2.504206	0.131881	2.520616
C	-4.887585	2.292079	-1.246102
H	-1.902806	2.258624	3.002701
H	-4.667337	0.928894	0.960808
H	-3.795939	3.168387	0.389264
H	-4.948098	3.226233	-1.827138
H	-4.817294	1.455017	-1.958173
H	-5.829838	2.170933	-0.688851
H	-2.429807	3.503459	-1.658014
H	-1.493452	2.553115	-0.460420
H	-2.260355	1.735505	-1.846160
H	-4.120291	-3.299858	-2.252895
H	-3.110604	-2.087852	-2.719347
H	-1.886776	-1.402356	0.758892
H	2.906920	-4.989780	2.051915
H	2.626544	-4.600842	3.763316
H	1.352413	-5.397730	2.806395
H	0.196144	-2.911451	3.887307
H	-0.363292	-0.717460	2.681678
H	2.605828	-2.673050	0.433820
H	5.043839	-3.300696	-2.439967
H	4.872597	-2.070576	-1.166805
H	3.563867	-3.241594	-1.454902
H	3.127149	-2.266326	-3.719335
H	4.458711	-1.136346	-3.545186
H	-0.119420	1.573300	-2.201063
H	1.426163	1.278251	-2.451266
H	2.740068	5.366207	1.552012
H	4.314036	4.888171	2.224655
H	4.178318	5.358915	0.510939
H	5.321518	2.635681	0.598615
H	4.217058	0.406141	-0.024216
H	1.142625	3.082526	0.983935
H	-3.481011	-3.048375	0.035963

Table S7 Cartesian Coordinates of Optimized IPNS-Thiocarboxylate Fe^{II} (Model 2)

Atom	X	Y	Z
C	2.871525	1.194494	-0.940189
N	2.323899	-0.000448	-0.783955
C	3.370577	-0.905435	-0.787215

C	4.573502	-0.251983	-0.945968
N	4.226032	1.090789	-1.042910
Fe	0.224534	-0.399929	-0.346320
O	0.565833	-0.353316	1.636583
C	1.013474	-1.292335	2.397663
O	1.407235	-2.424244	2.012172
C	5.987596	-0.735806	-1.009894
N	-0.430895	1.646926	-0.307872
C	-1.101451	2.308653	-1.243065
N	-1.652639	3.441068	-0.721149
C	-1.324902	3.511900	0.626554
C	-0.561135	2.389069	0.854192
C	-1.787065	4.608984	1.529788
O	-0.162661	-0.417730	-2.440683
O	0.710407	-2.511787	-0.472268
C	1.078169	-0.970525	3.891006
C	-0.088777	-0.108463	4.384348
S	-2.293254	-1.229637	0.007107
C	-3.197160	-0.908293	-1.433414
C	-4.736874	-1.037429	-1.379233
N	-5.395400	-1.412551	-0.137750
O	-2.722205	-0.568836	-2.543514
H	-5.021917	-2.318388	0.163814
H	-5.087905	-0.765865	0.596203
H	-1.175488	-0.521320	-2.583798
H	-1.400870	4.437320	2.543784
H	-1.433260	5.601078	1.201053
H	-2.887173	4.651654	1.597565
H	-2.236718	4.099200	-1.226540
H	-1.229228	1.988825	-2.272162
H	-0.117981	2.033148	1.778527
H	-0.006761	0.080491	5.466776
H	-0.108051	0.859390	3.864840
H	-1.054001	-0.602987	4.196686
H	1.135146	-1.923720	4.436830
H	2.033836	-0.445558	4.073358
H	-0.147375	-2.980482	-0.471959
H	1.048764	-2.601201	0.497998
H	6.007114	-1.829330	-0.907561
H	6.471500	-0.481371	-1.968005
H	6.606040	-0.315720	-0.198883
H	4.873812	1.862982	-1.161682
H	2.330454	2.134899	-0.976503
H	3.184392	-1.968703	-0.672631
H	-5.132276	-0.064422	-1.720874
H	-5.010126	-1.758905	-2.168575
H	0.301263	-1.118306	-2.925607