Supplementary Data

Oxygen and Proton Reduction by Decamethylferrocene in Non-Aqueous Acidic Media

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Computational Details

Density functional theory computations were performed using double-ζ plus polarization basis sets with the NWCHem 5.3 program.[1] For carbon and oxygen, one set of pure spherical harmonic *d* functions with orbital exponents $\alpha_d(C) = 0.75$ and $\sigma_d(O) = 0.85$ were added to the Huzinaga-Dunning standard contracted DZ sets designated as 9s5p/4s2p. For H, a set of *p* polarization functions $\sigma_p(H) = 0.75$ is added to the Huzinaga-Dunning DZ sets. For Fe, the loosely contracted DZP basis set using the Wachters' primitive set was augmented by two sets of *p* functions and one set of *d* functions, contracted and designated (14s11p6d/10s8p3d).[2,3]
The structures were energy minimized using the BP86[5,6] functional, which has been shown to be a valuable tool for the assessment of structures and energies of transition metal complexes. Both restricted and unrestricted methods were used to explore the spin multiplicity of the ground state of the investigated adducts. Full geometry optimizations were performed in gas phase. The influence of the solvent was tested implicitly with the COSMO continuum solvation model using the dielectric constant of dicholorethane (i.e. ε=10.36).[4] The transition state structures were first located using constraints in the geometry optimization and further optimized using the eigenvector-following algorithm. All stationary points were characterized as minima or transition state structures by computing the harmonic vibrational frequencies by numerical differentiation. Zero-point corrected energies are given in scheme 1.
An alternative mechanistic routes occurring via the formation of a superoxoiron [DMFc–O_2], prior to protonation (i.e. protonation last), is given in Figure S2. The endothermic nature of the spin-forbidden process along with the approximated height of the crossing point (~25 kcal mol^{-1}, vide infra) contrast with the lower energy-barrier (<15 kcal mol^{-1}) of the pathway presented in Scheme 1. Similarly, the superoxide intermediate $[DMFc–O_2H]^+$ resulting from the insertion of triplet molecular oxygen O_2 to form the $[DMFc–O_2H]^+$ adduct is not energetically favorable (Figure S1). Note that height of crossing point in Figure 2S was approximated by mapping out each surface (singlet and triplet) for several values of the chosen reaction coordinate (i.e. $R_c=R_{Fe-O}$). While the crossing point between the one-dimensional curves is a rough approximation to the lowest energy crossing point between the two surfaces, the spin-forbidden reaction is clearly endothermic.

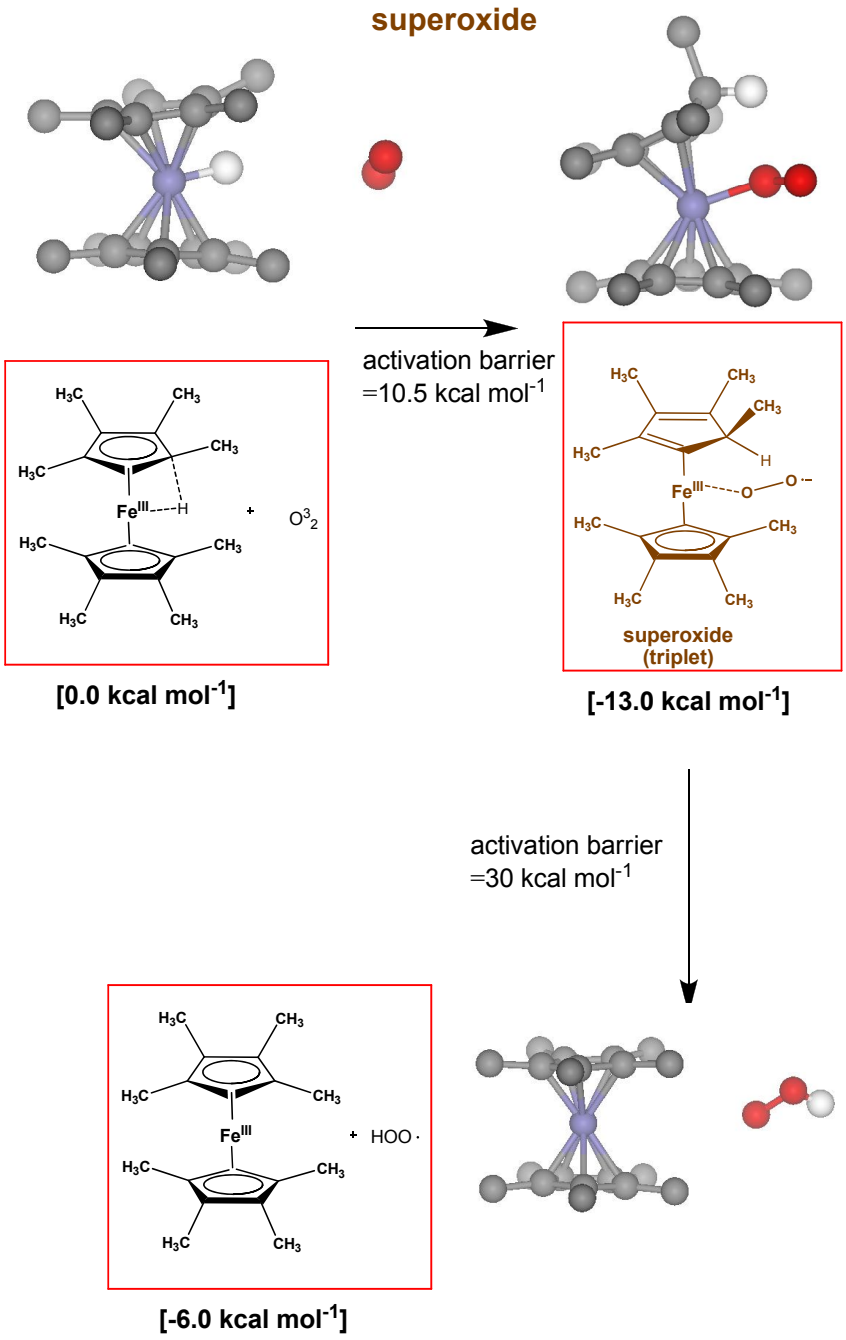

Figure S1: Gas phase zero-point corrected energies computed at the BP86/DZP level.

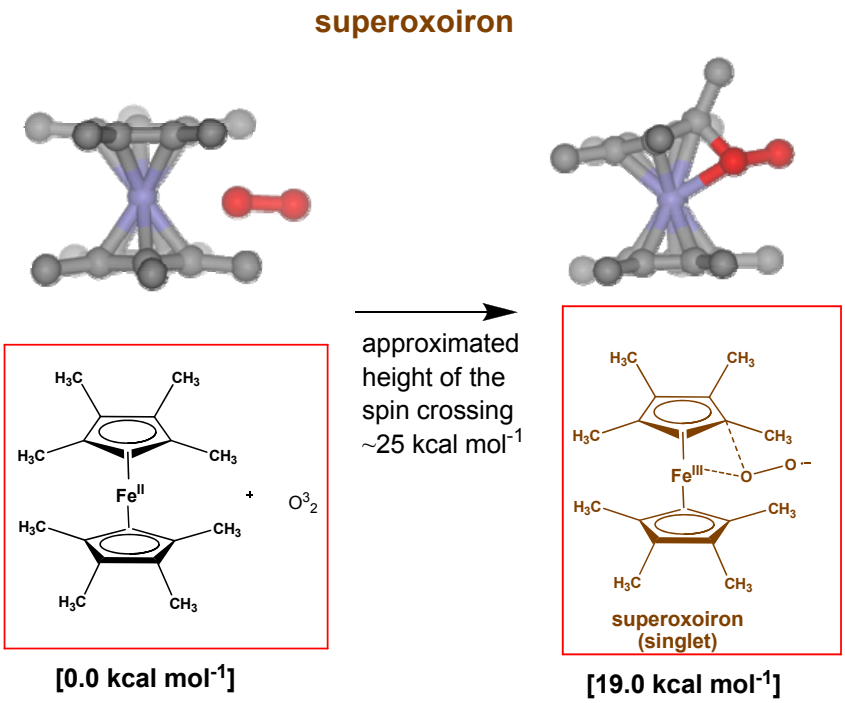

Figure S2: Gas phase zero-point corrected energies computed at the BP86/DZP level.

Structures and associated Spin quantum number

[DMFcH]S=O + O_2 s=1

C	-1.199144	-1.618093	-1.039127
C	-1.712443	-1.503955	0.306914
C	-0.609414	-1.626993	1.236603
C	0.591905	-1.807172	0.473579
C	0.221176	-1.806913	-0.947396
Fe	-0.280258	-0.006619	-0.046947
C	-0.550853	1.698047	-1.203720
C	0.740363	1.727972	-0.518004
C	0.480689	1.666913	0.925027
C	-0.940313	1.611601	1.107117
C	-1.573725	1.634470	-0.199198
C	-1.650094	1.685272	2.428731
C	1.525939	1.775409	1.998238
C	2.037305	2.178670	-1.150973
C	-3.048202	1.758782	-0.457783
C	-0.754953	1.849177	-2.684485
C	-3.165735	-1.456638	0.681886
C	-0.713230	-1.704781	2.733653
C	1.947803	-2.134940	1.031298
C	1.144326	-2.114178	-2.095127
C	-2.014073	-1.649009	-2.301618
H	1.096083	0.129585	-0.642545
H	-3.356405	1.253949	-1.388473
H	-3.656258	1.361013	0.369218
H	-3.308579	2.828866	-0.568405
H	-1.825253	2.745367	2.694161
H	-2.634202	1.190254	2.406331
H	-1.058735	1.237681	3.243433
H	2.477000	1.304568	1.696602
H	1.740124	2.838702	2.220511
H	1.199316	1.304007	2.939695
H	2.152303	1.804979	-2.181145
H	2.037511	3.283309	-1.191996
H	2.916269	1.864422	-0.568889
H	-1.704458	1.397725	-3.014796
H	-0.785762	2.921060	-2.961826
H	0.060490	1.385172	-3.264167
H	0.179750	-1.292302	3.232892
H	-1.598504	-1.176042	3.121762
H	-0.801825	-2.763334	3.045347
H	-3.535577	-2.489910	0.828373
H	-3.342333	-0.915268	1.626148
H	-3.787566	-0.997792	-0.102871
H	2.757502	-1.871205	0.333379
H	2.140196	-1.618274	1.986638
H	2.020948	-3.221996	1.225416
H	0.826977	-1.616666	-3.026431
H	2.184139	-1.815018	-1.886542
H	1.145212	-3.203858	-2.287814
H	-2.912655	-1.013391	-2.234037
H	-1.430640	-1.321211	-3.177785
H	-2.359566	-2.680743	-2.504315
O	4.653911	-0.329856	-0.609827
O	4.834494	0.121929	0.522211

[DMFc(III)]S=1/2 + HO_2 s=1/2

C	-0.706515	1.821813	1.066246
C	-1.568976	1.775232	-0.097127
C	-0.719581	1.622196	-1.268179
C	0.654859	1.576030	-0.813388
C	0.657448	1.701174	0.620654
Fe	-0.519883	0.008512	-0.007324
C	-0.873131	-1.582892	1.309205
C	0.420141	-1.792251	0.706858
C	0.248059	-1.853262	-0.719741
C	-1.157049	-1.685385	-1.015274
C	-1.860072	-1.519784	0.246791
C	-1.796364	-1.818119	-2.369750
C	1.333986	-2.121580	-1.723311
C	1.717375	-1.966494	1.444714
C	-3.351649	-1.484743	0.434832
C	-1.171488	-1.560918	2.782473
C	-3.050890	2.027720	-0.115426
C	-1.172101	1.692116	-2.700243
C	1.868788	1.503136	-1.695674
C	1.879471	1.737257	1.494243
C	-1.153292	2.054279	2.482573
H	6.365527	-0.248933	-0.060228
H	-3.642816	-0.903241	1.325350
H	-3.871449	-1.051698	-0.435447
H	-3.740697	-2.511746	0.571881
H	-2.020029	-2.881508	-2.579831
H	-2.748473	-1.265900	-2.432535
H	-1.140606	-1.455628	-3.178481
H	2.317574	-1.762816	-1.379193
H	1.422642	-3.212032	-1.893321
H	1.121696	-1.658651	-2.701428
H	1.678166	-1.525140	2.453883
H	1.934211	-3.045120	1.567613
H	2.573720	-1.518159	0.912709
H	-2.040503	-0.925758	3.020551
H	-1.406334	-2.583170	3.135812
H	-0.314743	-1.200038	3.375158
H	-0.482870	1.164326	-3.379823
H	-2.179663	1.267539	-2.841281
H	-1.212256	2.747492	-3.031517
H	-3.247981	3.112629	-0.210725
H	-3.542938	1.531097	-0.967761
H	-3.546358	1.685428	0.807991
H	2.727523	1.036571	-1.184970
H	1.670803	0.938651	-2.622064
H	2.174292	2.524404	-1.994892
H	1.666696	1.392234	2.519715
H	2.701291	1.126485	1.084984
H	2.250125	2.777640	1.572222
H	-2.189795	1.718533	2.650872
H	-0.506712	1.543090	3.214997
H	-1.118932	3.135981	2.714499
O	5.568712	0.276186	0.231392
O	4.515256	-0.392062	-0.264788

[DMFcH…O_2]S=1

C	1.804691	-0.361460	-1.091201
C	1.898736	-0.799629	0.296840
C	1.694863	0.356149	1.160529
C	1.577610	1.508346	0.320904
C	1.584081	1.059095	-1.071988
Fe	0.037168	0.032254	-0.054490
C	-1.301602	-1.238574	-1.066456
C	-1.992788	0.019788	-0.638380
C	-1.854491	0.045474	0.871898
C	-1.138671	-1.116313	1.277600
C	-0.843541	-1.927274	0.095745
C	-0.948493	-1.576918	2.695506
C	-2.553124	0.987324	1.789926
C	-3.290532	0.492070	-1.293990
C	-0.385264	-3.362177	0.110184
C	-1.337164	-1.754538	-2.474289
C	2.444981	-2.111905	0.771073
C	1.890631	0.403066	2.646707
C	1.676373	2.901598	0.819474
C	1.569685	1.939205	-2.281449
C	2.102018	-1.194549	-2.301582
H	-1.204822	0.826152	-1.019480
H	0.240355	-3.617887	-0.767988
H	0.172113	-3.619948	1.024674
H	-1.288087	-4.004703	0.074371
H	-1.826884	-2.179649	2.997791
H	-0.054597	-2.207456	2.803770
H	-0.859131	-0.731819	3.397348
H	-2.438898	2.017509	1.446084
H	-3.635407	0.745519	1.807717
H	-2.172124	0.903206	2.820548
H	-3.218449	0.438992	-2.390538
H	-4.120410	-0.150043	-0.950490
H	-3.472997	1.528507	-0.991777
H	-0.573463	-2.525123	-2.655367
H	-2.327860	-2.212593	-2.668660
H	-1.192771	-0.941620	-3.208944
H	1.205493	1.126236	3.120485
H	1.738103	-0.582542	3.114415
H	2.927897	0.724069	2.865983
H	3.534909	-1.984575	0.928271
H	2.008705	-2.434676	1.729757
H	2.295584	-2.904932	0.027251
H	1.461787	3.615441	0.040625
H	0.986621	3.087046	1.662541
H	2.709838	3.079332	1.179606
H	1.188221	1.411151	-3.172449
H	0.948976	2.809978	-2.097437
H	2.603108	2.273606	-2.503800
H	1.839115	-2.250717	-2.136340
H	1.557907	-0.836934	-3.194171
H	3.186137	-1.140776	-2.521745
O	-0.643596	2.277520	-0.363872
O	-1.703071	3.133477	-0.032080

[DMFcO$_2$]S=0

C	-1.259274	1.266991	-1.228883
C	-1.942004	0.009648	-1.083186
C	-2.204985	-0.191323	0.325740
C	-1.698094	0.950707	1.047484
C	-1.141899	1.866541	0.093538
Fe	-0.134673	0.016150	-0.034095
C	0.512108	-1.946662	-0.184502
C	1.301791	-1.090662	-1.013972
C	2.177193	-0.205273	-0.144707
C	1.499719	-0.356289	1.206429
C	0.631547	-1.488256	1.185085
C	1.543484	-1.224331	-2.491175
C	3.694116	-0.219767	-0.249484
C	1.921575	0.443707	2.403112
C	0.038775	-2.164598	2.391559
C	-0.193241	-3.195473	-0.635665
C	-2.426061	-0.864724	-2.207654
C	-3.050313	-1.289710	0.911416
C	-1.845804	1.208760	2.522505
C	-0.527091	3.196881	0.388642
C	-0.838219	1.926328	-2.512888
H	-2.962629	-2.234171	0.347627
H	-2.793560	-1.497771	1.963581
H	4.014424	-0.171500	-1.305050
H	4.097366	0.660018	0.278056
H	-4.119762	-0.999877	0.889866
H	4.099083	-1.142205	0.202934
H	-2.788030	1.752431	2.733995
H	-3.411179	-0.513143	-2.573260
H	2.911211	0.111550	2.778291
H	2.438158	-1.845547	-2.702631
H	-1.873499	0.272072	3.104990
H	-2.550955	-1.914774	-1.894450
H	2.030043	1.501135	2.098981
H	1.718817	-0.232775	-2.944090
H	-1.015562	1.821125	2.911397
H	-1.734734	-0.848080	-3.067744
H	1.200275	0.357913	3.234603
H	0.688823	-1.692756	-3.009034
H	0.591155	3.116295	0.366586
H	0.126014	2.447015	-2.392378
H	-0.859328	-2.753563	2.143864
H	-1.089231	-3.418453	-0.032392
H	-0.818520	3.936932	-0.378657
H	-1.590154	2.672990	-2.837182
H	0.777932	-2.861226	2.834257
H	0.487422	-4.064925	-0.542802
H	-0.843956	3.581024	1.373023
H	-0.728017	1.193676	-3.330709
H	-0.233716	-1.440560	3.177919
H	-0.498959	-3.134562	-1.693000
O	1.652351	1.157200	-0.658103
O	2.231728	2.233654	0.009294

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