Electronic Supplementary Information

Effect of Brønsted acid on the reactivity and selectivity of the oxoiron(V) intermediates in C-H and C=C oxidation reactions

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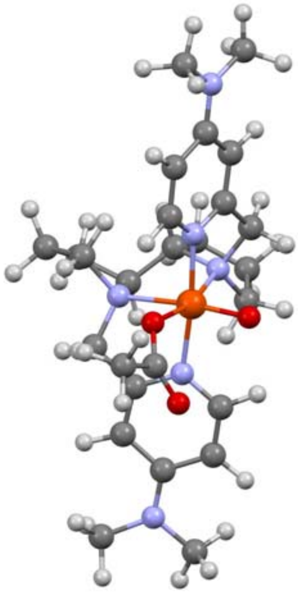
DFT calculations: Computational details.

Geometry optimization and frequency analysis of the $[(L)Fe(O)(OAc)]^{2+}$, $[^{H}LFe^{V}{=}O(OAc)]^{3+}$, $[LFe^{IV}{-}OH(OAc)]^{3+}$ intermediates with different multiplicities, as well as HOAc, OAc^{-}, $HClO_4$, $HClO^{-}$, were carried with the B3PLYP density functional theory scheme (DFT) with D3 corrections[S1] using GAUSSIAN 16 program suite,[S2] with the def2-TZVPP[S3] basis set for the Fe atom and 6-311G(d)[S4] basis set for other atoms. Solvation effects (with CH_3CN) were incorporated using polarized continuum model (PCM) method[S5,S6] as implemented in GAUSSIAN 16. The stationary points were ascertained by vibrational frequency analysis with no imaginary frequencies. Bond orders, spin densities and partial charges were computed using DDEC6 atomic population analysis.[S7,S8] The Gibbs energies reported in this paper were sum of electronic and thermal free energies.

DFT optimized Cartesian coordinates and potential energies (Ha) for the calculated structures are presented below.

^{2}[(^{NMe2}PDP)Fe^V=O(OAc)]$^{2+}$ in acetonitrile



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6	-4.847100	0.496531	-0.263593
6	-4.087821	-0.532073	-0.887209
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6	-6.940484	1.538112	0.431947
7	-6.196072	0.464845	-0.225476
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6	2.673612	0.253141	-1.628473
6	4.042030	0.165441	-1.600280
6	4.701591	0.109800	-0.342303
6	3.895487	0.118307	0.826816
6	2.523604	0.187564	0.700230
6	1.592840	0.234039	1.878037
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6	-0.487718	-3.803074	0.022953
6	-0.691094	-2.311644	0.398324
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6	-0.749040	-0.032175	2.540320
6	-0.493394	-1.076411	3.632492
6	0.016763	-2.319092	2.859136
6	0.325995	-1.815769	1.423969
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1	4.325329	0.034833	1.813920
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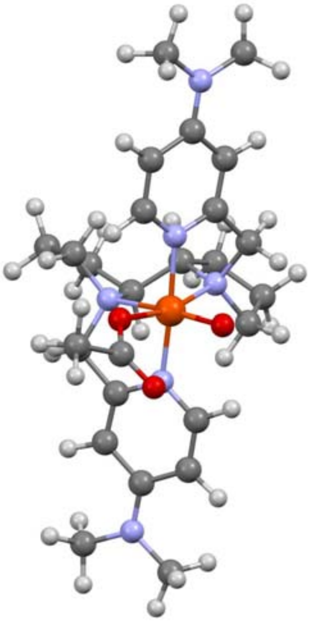
1	6.829102	-0.737073	1.526532
1	6.263579	0.953867	1.637637

$^{4}[(^{NMe2}PDP)Fe^{V}{=}O(OAc)]^{2+}$ in acetonitrile



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6	4.030001	0.397302	-1.540195
6	4.714514	0.184173	-0.305805
6	3.893815	0.071735	0.855628
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6	0.183874	-3.661999	-1.676452
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6	-0.622206	-2.344316	0.255325
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6	-0.734949	-0.230191	2.564000
6	-0.450324	-1.344642	3.575429
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6	0.379951	-1.909152	1.319628
7	6.050548	0.094783	-0.238848
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8	0.065686	2.109693	0.435846
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6	0.376881	4.401729	0.853608
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6	-6.868302	-0.668677	-0.954785
6	6.721133	-0.111335	1.048685
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1	-2.211884	-2.339166	-1.847473
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1	1.444768	1.148037	2.276515
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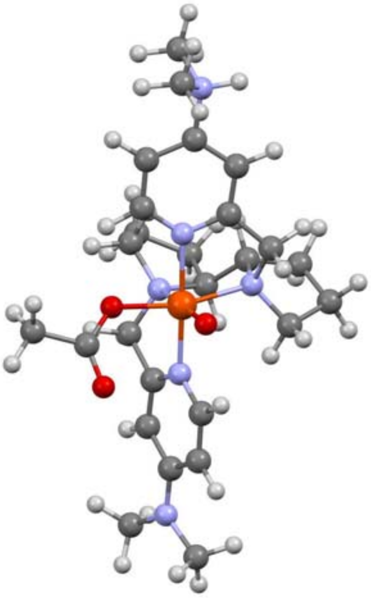
$^{2}[(^{HNMe2}PDP)Fe^{V}{=}O(OAc)]^{3+}$ in acetonitrile



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6	4.000461	0.276043	-1.629356
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6	3.883158	0.188449	0.797856
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6	1.589035	0.208555	1.874728
6	6.863489	0.020952	-1.499466
7	-0.460701	-1.660246	-0.869392
6	0.565075	-2.428884	-1.646032
6	0.234714	-3.901402	-1.390999
6	-0.331793	-3.921847	0.051852
6	-0.594623	-2.439099	0.421295
7	0.285539	-0.396159	1.491816
6	-0.734842	-0.147811	2.558044
6	-0.427839	-1.174538	3.652852
6	0.116978	-2.403246	2.881462
6	0.402817	-1.896888	1.442763
7	6.032264	0.210571	-0.309575
8	-0.170574	0.708647	-2.077501
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8	1.698422	2.980030	-0.792972
6	-6.894949	1.376902	-1.171391
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1	-4.733061	2.114937	0.705607
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1	-2.211477	-2.650642	-1.636257

1	-1.573491	-1.321082	-2.616120
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1	-6.444610	-0.918185	1.348087
1	2.063637	0.377193	-2.560870
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1	1.403674	1.243465	2.163473
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1	6.398683	-0.674164	-2.192640
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1	0.545818	-2.118451	-2.688246
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1	6.240564	1.128185	1.581034
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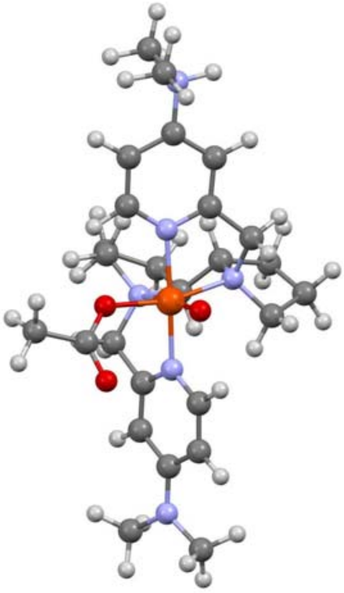
^{4}[(^{HNMe2}PDP)Fe^V=O(OAc)]$^{3+}$ in acetonitrile



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6	3.981116	0.275587	-1.636876
6	4.667076	0.218629	-0.391130
6	3.877422	0.182056	0.791107
6	2.505686	0.204886	0.690696
6	1.593572	0.212496	1.882203
6	6.843165	0.030346	-1.529126
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6	0.577879	-2.426884	-1.633711
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6	6.737395	0.358376	0.938239
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1	-1.558083	-1.317075	-2.610263
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1	1.554607	-2.180774	-1.223157
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1	6.249486	1.096404	1.569536
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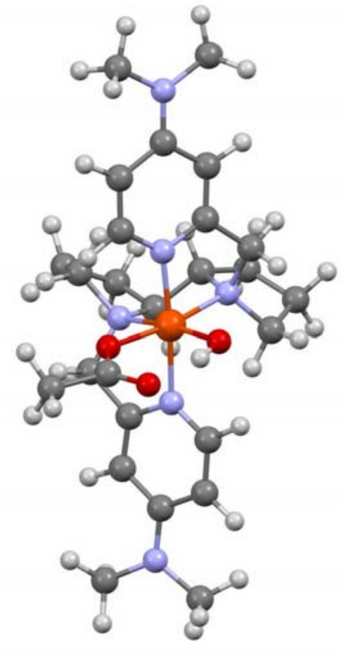
^{2}[(^{NMe2}PDP)Fe^{IV}–OH(OAc)]$^{3+}$ in acetonitrile



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7	1.943579	0.227177	-0.440143
6	2.699637	0.349547	-1.542732
6	4.078217	0.359197	-1.483322
6	4.704146	0.258246	-0.218892
6	3.889765	0.140106	0.930657
6	2.516466	0.131092	0.776136
6	1.556572	0.054445	1.922750
6	6.936258	0.084353	-1.274585
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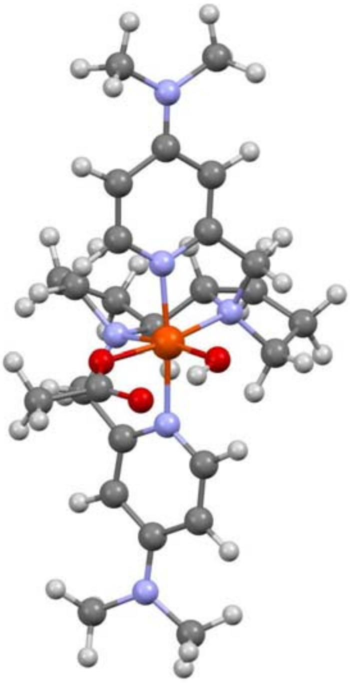
7	0.257715	-0.502725	1.441683
6	-0.790878	-0.349398	2.510370
6	-0.497386	-1.472342	3.509197
6	0.083133	-2.622369	2.646318
6	0.363272	-2.003667	1.254994
7	6.072855	0.277262	-0.111259
8	-0.072305	0.896138	-2.074303
8	0.165737	2.054238	0.390265
6	0.449793	3.194779	-0.197190
6	0.702552	4.318144	0.773129
8	0.503996	3.344283	-1.417281
6	-6.902583	-0.584833	-0.844654
6	6.743127	0.494408	1.167967
1	-2.073936	2.173888	0.955567
1	-4.510347	2.263509	1.051487

1	-4.556375	-1.297939	-1.454408
1	-2.303967	-2.366629	-1.854209
1	-1.636232	-0.952504	-2.685660
1	-7.947082	1.324330	0.476511
1	-6.655591	2.492422	0.190218
1	-6.634781	1.472816	1.648628
1	2.166528	0.444409	-2.477745
1	4.637226	0.484647	-2.398161
1	4.306721	0.018735	1.919284
1	1.960937	-0.538771	2.742952
1	1.372307	1.064471	2.288508
1	7.901883	-0.275966	-0.930017
1	6.501011	-0.629421	-1.967920
1	7.078007	1.050401	-1.771003
1	1.468670	-2.066168	-1.464821
1	0.449867	-1.815879	-2.882934
1	-0.675143	-3.969684	-2.495211
1	0.959850	-4.350878	-1.978317
1	0.315290	-4.381126	0.309038
1	-1.334900	-4.455854	-0.279138
1	-1.660357	-2.302269	0.598156
1	-1.762464	-0.491433	2.046358
1	-0.753084	0.657821	2.918161
1	0.220629	-1.146583	4.262738
1	-1.406599	-1.765077	4.033048
1	-0.621176	-3.449718	2.553318
1	0.995542	-3.028375	3.080759
1	1.368342	-2.232099	0.900639
1	0.883461	5.246141	0.234964
1	-0.155260	4.432097	1.438681
1	1.567987	4.072234	1.392399
1	-6.716926	-0.555522	-1.921124
1	-7.963850	-0.429171	-0.677593
1	-6.638025	-1.573978	-0.463357
1	7.713434	0.945254	0.975044
1	6.898086	-0.476597	1.651502
1	6.157517	1.143934	1.811112
1	0.093229	1.889239	-2.082781

^{4}[(^{NMe2}PDP)Fe^{IV}–OH(OAc)]$^{3+}$ in acetonitrile



Energy = -2832.8260538 Ha, G = -2832.234116 Ha

26	-0.082482	0.363064	-0.426691
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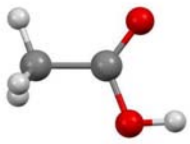
6	-2.671719	1.440718	0.440726
6	-4.037988	1.472970	0.487895
6	-4.805690	0.477153	-0.186953
6	-4.062990	-0.508092	-0.903064
6	-2.695363	-0.461089	-0.915601
6	-1.833602	-1.393057	-1.709522
6	-6.877689	1.500196	0.587261
7	-6.146440	0.465155	-0.149235
7	1.941274	0.222541	-0.440188
6	2.698747	0.344598	-1.542882
6	4.076655	0.355621	-1.483050
6	4.703393	0.259244	-0.218074
6	3.887800	0.142537	0.931464
6	2.515053	0.130321	0.776688
6	1.555190	0.053851	1.923254
6	6.935208	0.091012	-1.273600
7	-0.516288	-1.531600	-1.009569
6	0.479053	-2.238574	-1.882336
6	0.098530	-3.716274	-1.773015
6	-0.416780	-3.873216	-0.320051
6	-0.654065	-2.433877	0.201670
7	0.256964	-0.503844	1.441474
6	-0.792561	-0.350806	2.509301
6	-0.499259	-1.473658	3.508287
6	0.081911	-2.623597	2.645726
6	0.362896	-2.004824	1.254640
7	6.070631	0.279938	-0.110059
8	-0.069031	0.894609	-2.074318
8	0.165425	2.054269	0.388771
6	0.448765	3.194321	-0.199721
6	0.700564	4.318911	0.769294
8	0.503625	3.342256	-1.420097
6	-6.900332	-0.582804	-0.842829
6	6.740897	0.494447	1.170009
1	-2.070315	2.173876	0.956651

1	-4.506436	2.264183	1.053421
1	-4.554511	-1.296282	-1.453754
1	-2.303482	-2.365299	-1.855559
1	-1.634715	-0.951263	-2.686182
1	-7.943762	1.325683	0.480233
1	-6.652455	2.493830	0.193232
1	-6.630564	1.473831	1.651358
1	2.166360	0.437236	-2.478408
1	4.635356	0.477814	-2.398505
1	4.304287	0.024048	1.920621
1	1.959497	-0.539064	2.743705
1	1.370258	1.063870	2.288698
1	7.901126	-0.268561	-0.929116
1	6.501916	-0.622735	-1.968231
1	7.075598	1.057914	-1.768452
1	1.469135	-2.069492	-1.466336
1	0.450253	-1.818082	-2.884331
1	-0.677729	-3.970316	-2.495608
1	0.957362	-4.353521	-1.980478
1	0.316013	-4.381782	0.307810
1	-1.334816	-4.457123	-0.278594
1	-1.660338	-2.302787	0.596476
1	-1.763743	-0.493298	2.044635
1	-0.755389	0.656401	2.917166
1	0.218309	-1.147723	4.262168
1	-1.408695	-1.766536	4.031664
1	-0.622277	-3.450984	2.552218
1	0.994089	-3.029540	3.080695
1	1.368201	-2.233090	0.900882
1	0.882161	5.246147	0.230055
1	-0.158127	4.433773	1.433544
1	1.565171	4.073729	1.389986
1	-6.714959	-0.553060	-1.919333
1	-7.961496	-0.426833	-0.675408
1	-6.636022	-1.572211	-0.462042
1	7.710502	0.947157	0.978019
1	6.897015	-0.477302	1.651398
1	6.155056	1.142247	1.814664
1	0.094555	1.888681	-2.082741

[1]HOAc in acetonitrile



Energy = -229.1559894 Ha, G = -229.121624 Ha

6	-6.969421	-0.009771	0.229723
8	-7.981246	0.878205	0.110316
8	-6.478887	-0.569071	-0.722341
6	-6.565187	-0.190016	1.666658
1	-5.737136	-0.891852	1.732493
1	-8.205046	0.957769	-0.830191
1	-7.412688	-0.562141	2.246569
1	-6.273789	0.770778	2.096173

[1]AcO^- in acetonitrile

Energy = -228.6759018 Ha, G = -228.654900 Ha

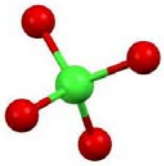
6	-7.038196	0.052422	0.196705
8	-8.032268	0.811199	0.060633
8	-6.378240	-0.511771	-0.711571
6	-6.577058	-0.188938	1.659099
1	-5.791941	-0.945606	1.726741
1	-7.426225	-0.491840	2.279901
1	-6.197673	0.747633	2.083091

[1]$HClO_4$ in acetonitrile

Energy = -761.4109732 Ha, G = -761.413650 Ha

17	-7.017913	-0.350057	0.275369
8	-8.206141	0.848629	0.040854
8	-7.731850	-1.251983	1.162838
8	-6.734968	-0.892571	-1.050752
8	-5.879695	0.332155	0.885253
1	-7.832833	1.519627	-0.563062

[1]ClO_4^- in acetonitrile



Energy = -761.0016187 Ha, G = -761.014883 Ha

17	-7.108149	-0.299015	0.187473
8	-8.118184	0.721218	-0.234761
8	-7.709626	-1.198194	1.220470
8	-6.691777	-1.109695	-0.998740
8	-5.912964	0.391387	0.763759

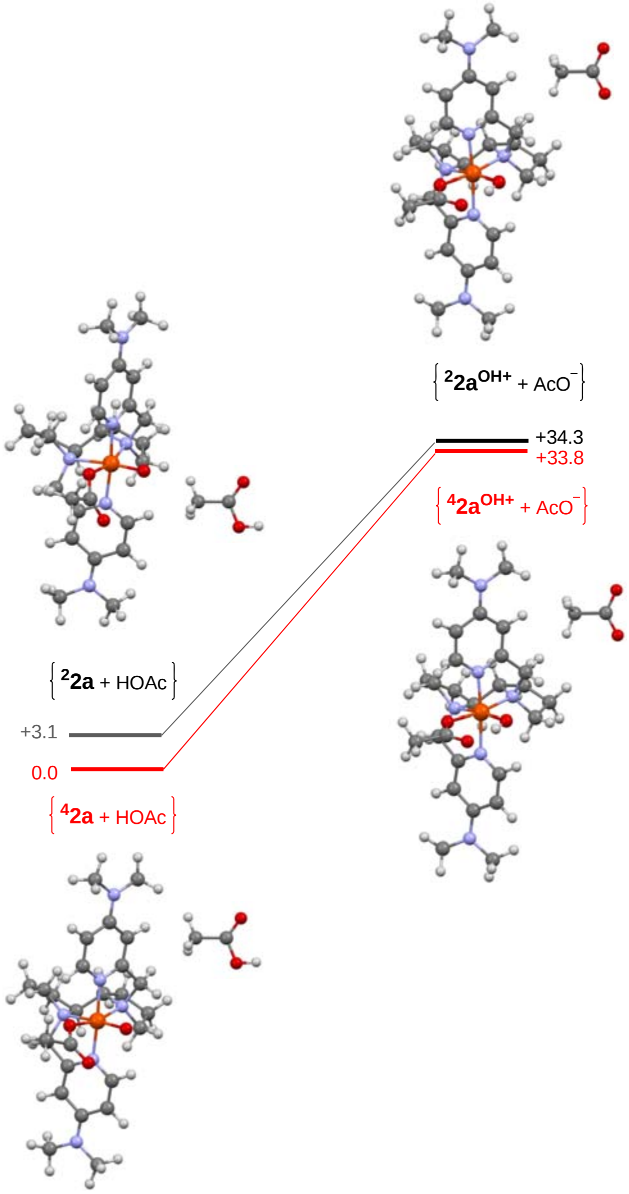
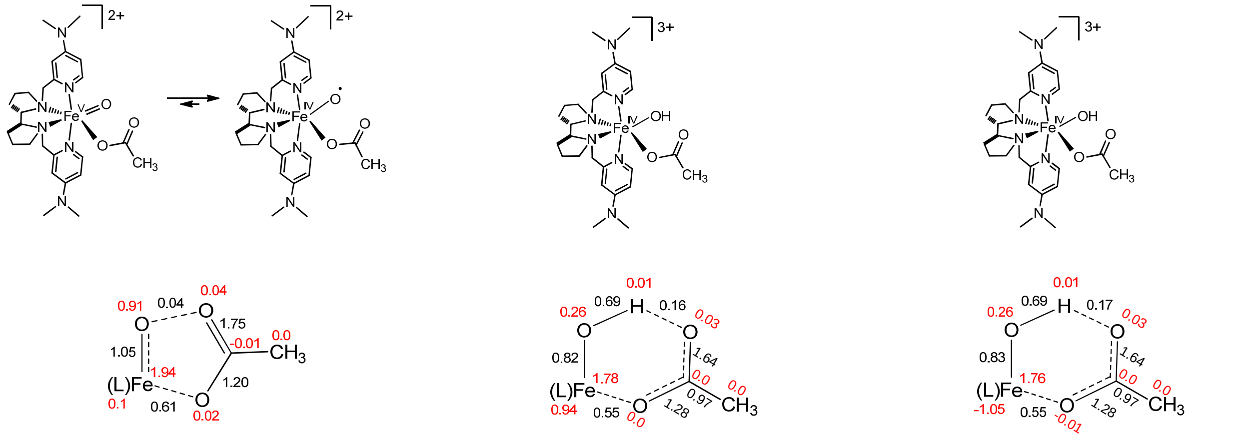


Figure S1. Optimized geometries and relative free energies (kcal/mol) of the non-protonated intermediates of the type {**2a**+HOAc} as well as protonated at terminal oxygen {$\mathbf{2a}^{\mathbf{NH+}}$+AcO^{-}}-on the S = 3/2 (red) and the S = 1/2 (black) energy surfaces. C grey, H light grey, N violet, O red, Cl green, Fe orange.



^{4}[(^{Me2N}PDP)Fe^{IV}-O$^{\bullet}$(OAc)]$^{2+}$ (^{4}**2a**)
(from ref. 50)

^{4}[(^{Me2N}PDP)Fe^{IV}-OH(OAc)]$^{3+}$ (^{4}**2a^{OH+}**)
(this work)

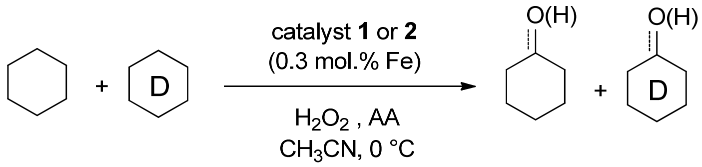
^{2}[(^{Me2N}PDP)Fe^{IV}-OH(OAc)]$^{3+}$ (^{2}**2a^{OH+}**)
(this work)

Figure S2. Selected computed partial bond orders and spin densities, and formal structural representations for the densities (in numbers of spins) for the intermediates ^{4}[(^{NMe2}PDP)Fe^{IV}–OH(OAc)]$^{3+}$ (^{4}**2a^{OH+}**) and ^{2}[(^{NMe2}PDP)Fe^{IV}–OH(OAc)]$^{3+}$ (^{2}**2a^{OH+}**), compared with those for the parent intermediate [(^{NMe2}PDP)Fe^{V}=O(OAc)]$^{2+}$ (**2a**).[50] Bond orders and spin densities and are in black and red, respectively.

KIE measurements

Cyclohexane (100 μmol), cyclohexane-d_{12} (100 μmol), acetic acid (110 μmol) and, if necessary, $HClO_4$ (5 μmol) were added to the solution of the iron complex in CH_3CN (400 μL), and the mixture was thermostated at 0 °C. Then, 100 μL of the oxidant solution in CH_3CN was injected by a syringe pump over 30 min upon stirring. The resulting mixture was stirred for 2.5 h at 0 °C and the solution was submitted to GC-MS analysis. Kinetic isotope effect was calculated as *KIE* = k_H/k_D = ln(1−(C_6H_{12} conversion)/100) / ln(1−(C_6D_{12} conversion)/100).

Table S1. Kinetic isotope effects for the oxidations of cyclohexane/d_{12}-cyclohexane on catalysts **1** and **2** in the absence and in presence of $HClO_4$ [a]



entry	catalyst	carboxylic acid	strong acid	k_H/k_D	ref.
1	**1**	AA	–	4.0	[48]
2	**1**	AA	$HClO_4$	4.2	this work
3	**2**	AA	–	1.6	this work
4	**2**	AA	$HClO_4$	1.5	this work

[a] At 0 °C, [catalyst]:[cyclohexane]:[d_{12}-cyclohexane]:[H_2O_2]:[acetic acid](:[$HClO_4$]) = 1 μmol : 100 μmol : 100 μmol : 200 μmol : 110 μmol (: 5 μmol), oxidant was added by a syringe pump over 30 min, and the mixture was stirred for an additional 2.5 h, followed by GC-MS analysis.

Supplementary references

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[S8] T. A. Manz. Introducing DDEC6 atomic population analysis: part 3. Comprehensive method to compute bond orders. *RSC Adv.* **2017**, *7*, 45552-45581.