Supporting Information

Structural Model Studies for the Peroxo Intermediate P and the Reaction Pathway from P → Q of Methane Monooxygenase Using Broken-Symmetry Density Functional Calculations

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Table S1. Property Comparisons for MMOH-Q Active Site Models (see Ref. 42) Obtained from OPBE Calculations in Gas-Phase and in COSMO Solvation Model with Different Dielectric Constants ε = 4.0, 10.0, and 80.0.[a]

	Model I	**Model II**	**Model III**	**Model IV**
COSMO (ε = 80.0)				
r(Fe1-Fe2)	2.667	2.720	2.799	2.736
Netspin(Fe1, Fe2)	3.06, –3.10	3.11, –3.15	3.17, –3.15	3.22, –3.23
E_{BS}	–746.2979	–746.4150	–746.2685	–746.5772
E_0	–746.4163	–746.5406	–746.3484	–746.6853
Heisenberg *J* value	–239	–253	–161	–218
δ_{Fe1}, δ_{Fe2}	0.23, 0.20	0.18, 0.22	0.21, 0.28	0.16, 0.19
ΔE_Q(Fe1), ΔE_Q(Fe2)	–0.46, –0.42	0.33, –0.33	–0.38, –0.28	0.70, 0.37
COSMO (ε = 10.0)				
r(Fe1-Fe2)	2.666	2.723	2.792	2.742
Netspin(Fe1, Fe2)	3.06, –3.10	3.12, –3.15	3.17, –3.15	3.22, –3.24
E_{BS}	–745.7254	–745.8416	–745.5028	–745.9527
E_0	–745.8453	–745.9689	–745.5851	–746.0640
Heisenberg *J* value	–242	–257	–166	–225
δ_{Fe1}, δ_{Fe2}	0.23, 0.20	0.18, 0.22	0.20, 0.29	0.16, 0.20
ΔE_Q(Fe1), ΔE_Q(Fe2)	–0.46, –0.45	0.34, –0.33	–0.42, –0.29	0.66, 0.40
COSMO (ε = 4.0)				
r(Fe1-Fe2)	2.663	2.724	2.779	2.737
Netspin(Fe1, Fe2)	3.06, –3.10	3.12, –3.16	3.16, –3.14	3.22, –3.24
E_{BS}	–744.8789	–744.9589	–744.2816	–744.9164
E_0	–745.0014	–745.0873	–744.3674	–745.0248
Heisenberg *J* value	–247	–259	–173	–219
δ_{Fe1}, δ_{Fe2}	0.23, 0.20	0.19, 0.22	0.20, 0.29	0.17, 0.20
ΔE_Q(Fe1), ΔE_Q(Fe2)	–0.48, –0.50	0.38, –0.37	–0.43, –0.27	0.63, 0.41
Gas-phase				
r(Fe1-Fe2)	2.669	2.721	2.726	2.727
Netspin(Fe1, Fe2)	3.07, –3.11	3.11, –3.15	3.17, –3.14	3.20, –3.27
E_{BS}	–741.3992	–741.6105	–740.0267	–741.4622
E_0	–741.5204	–741.7427	–740.1253	–741.5704
Heisenberg *J* value	–244	–267	–199	–218
δ_{Fe1}, δ_{Fe2}	0.25, 0.23	0.20, 0.24	0.17, 0.28	0.19, 0.20
ΔE_Q(Fe1), ΔE_Q(Fe2)	–0.61, –0.56	0.50, –0.43	–0.58, –0.28	0.52, 0.53

[a.] All calculated results with ε = 80.0 have been presented in Ref. 42.

Table S2. Property Comparisons for MMOH-Q Active Site Models (see Ref. 42) Obtained from PW91 Calculations in Gas-Phase and in COSMO Solvation Model with Dielectric Constants ε = 4.0 and 80.0.[a]

	Model I	**Model II**	**Model III**	**Model IV**
COSMO (ε = 80)				
r(Fe1-Fe2)	2.632	2.689	2.716	2.661
Netspin(Fe1, Fe2)	2.60, –2.52	1.96, –1.96	1.92, –1.95	2.75, –2.79
E_{BS}	–744.9582	–745.2274	–745.3409	–744.9822
E_0	–745.1707	–745.5668	–745.7125	–745.1587
Heisenberg *J* value	–429	–684	–749	–356
δ_{Fe1}, δ_{Fe2}	0.31, 0.18	0.17, 0.21	0.09, 0.28	0.11, 0.22
ΔE_Q(Fe1), ΔE_Q(Fe2)	–1.38, –1.12	2.31, 2.43	1.73, 2.68	0.23, 0.53
COSMO (ε = 4)				
r(Fe1-Fe2)	2.621	2.690	2.707	2.665
Netspin(Fe1, Fe2)	2.61, –2.58	2.01, –2.01	1.94, –1.98	2.80, –2.83
E_{BS}	–743.3339	–743.6850	–743.1846	–743.2807
E_0	–743.5407	–744.01480	–743.5472	–743.4516
Heisenberg *J* value	–417	–665	–731	–345
δ_{Fe1}, δ_{Fe2}	0.28, 0.20	0.17, 0.22	0.08, 0.29	0.12, 0.22
ΔE_Q(Fe1), ΔE_Q(Fe2)	1.11, 1.26	2.15, 2.40	1.57, 2.60	0.25, 0.42
Gas-phase				
r(Fe1-Fe2)	2.636	2.674	2.691	2.649
Netspin(Fe1, Fe2)	2.83, –2.77	2.15, –2.15	2.00, –2.10	2.89, –2.91
E_{BS}	–740.2750	–740.6291	–738.7113	–740.3355
E_0	–740.4461	–740.9241	–739.0610	–740.4987
Heisenberg *J* value	–345	–595	–705	–329
δ_{Fe1}, δ_{Fe2}	0.28, 0.20	0.18, 0.23	0.06, 0.32	0.19, 0.21
ΔE_Q(Fe1), ΔE_Q(Fe2)	0.94, –0.57	1.74, 2.08	1.24, 2.30	–0.50, –0.31

[a.] All calculated results with ε = 80.0 have been presented in Ref. 42.

Table S3. Geometries (Å and degree), Net-Spin Populations (NSP), Broken-Symmetry State Energies (E_{BS}), Spin-Projected Energies (E_0) (eV), Heisenberg J Values (cm^{-1}), Mössbauer Isomer Shifts (δ) ($mm\ s^{-1}$), Quadrupole Splittings (ΔE_Q) ($mm\ s^{-1}$), and η Values Calculated from OPBE and PW91 Functionals with $\varepsilon = 80.0$ for the μ-η^2,η^2 MMOH-Peroxo Active Site Models with and without a Terminal (t) H_2O (Figures 4-6), and Compared with Available Experimental Values.

	With $(H_2O)_t$ (Figs.4,5)		Without $(H_2O)_t$ (Fig.6)		Exp.
	OPBE	PW91	OPBE	PW91	
Geometry					
Fe1-Fe2	3.622	3.571	3.754	3.648	
Fe1-O1	2.057	2.030	2.118	2.051	
Fe2-O1	2.013	2.019	1.933	1.970	
Fe1-O2	1.989	2.010	1.938	1.964	
Fe2-O2	2.001	1.964	2.135	2.024	
O1-O2	1.442	1.482	1.439	1.500	
Fe1-O3	2.302	2.271	5.438	4.894	
Fe1-O4	1.954	1.950	1.914	1.897	
Fe1-N1	2.140	2.069	2.142	2.072	
Fe1-O5	1.984	1.998	1.909	1.921	
Fe2-O6	2.417	2.262	3.567	3.172	
Fe2-N2	2.127	2.082	2.084	2.054	
Fe2-O7	1.923	1.913	1.932	1.902	
Fe2-O8	1.954	1.977	1.917	1.924	
∠Fe1-O1-Fe2	125.7	123.8	135.8	130.3	
∠Fe1-O2-Fe2	130.4	128.0	134.3	132.4	
∠Fe1-O2-O1-Fe2	148.7	146.9	161.3	158.5	
O3···O9	3.361	3.070	3.052	2.721	
O3···O10	2.723	2.699	3.141	2.780	
NSP_{Fe1}	4.06	3.99	4.05	3.96	
NSP_{Fe2}	–4.01	–3.93	–4.04	–3.94	
E_{BS}	–745.7339	–743.4061	–745.9070	–743.2998	
E_0	–745.7928	–743.4849	–745.9760	–743.3976	
J	–95	–127	–111	–158	
Mössbauer parameters					
δ_{Fe1}	0.58	0.63	0.56	0.60	0.66
δ_{Fe2}	0.59	0.61	0.55	0.57	
ΔE_Q(Fe1)	0.52	–0.73	0.39	0.59	1.51
ΔE_Q(Fe2)	–0.76	–0.79	1.08	–1.00	
η(Fe1)	0.91	0.73	0.59	0.92	
η(Fe2)	0.87	0.91	0.95	0.85	

Table S4. Geometries (Å and degree), Net-Spin Populations (NSP), Broken-Symmetry State Energies (E_{BS}), Spin-Projected Energies (E_0) (eV), Heisenberg J Values (cm^{-1}), Mössbauer Isomer Shifts (δ) ($mm\ s^{-1}$), Quadrupole Splittings (ΔE_Q) ($mm\ s^{-1}$), and η Values Calculated from OPBE and PW91 Functionals with ε = 80.0 for the *trans*-μ-1,2a (Figure 7) and *trans*-μ-1,2b (Figure 8) MMOH-Peroxo Active Site Models.

	trans-μ-1,2a (Fig. 7)		*trans*-μ-1,2b (Fig. 8)		Exp.
	OPBE	PW91	OPBE	PW91	
Geometry					
Fe1-Fe2	4.542	4.445	4.667	4.394	
Fe1-O1	1.875	1.866	1.911	1.855	
Fe2-O2	1.880	1.870	1.906	1.881	
O1-O2	1.357	1.396	1.355	1.376	
Fe1-O3	4.516	4.064	5.183	4.700	
Fe1-O4	1.920	1.918	1.918	1.932	
Fe1-N1	2.065	2.035	2.145	2.049	
Fe1-O5	1.943	1.935	1.973	1.917	
Fe2-O6	4.266	4.111	4.202	3.397	
Fe2-N2	2.075	2.026	2.154	2.042	
Fe2-O7	1.912	1.892	1.915	1.890	
Fe2-O8	1.929	1.922	1.928	1.922	
∠Fe1-O1-O2	119.1	112.5	119.6	125.3	
∠Fe2-O2-O1	121.1	117.8	129.0	118.1	
∠Fe1-O1-O2-Fe2	157.1	154.6	–158.9	–128.8	
O3···O9	3.210	2.986	3.267	2.787	
O3···O10	3.211	2.913	3.275	2.815	
NSP_{Fe1}	4.07	4.00	4.12	3.97	
NSP_{Fe2}	–4.05	–3.97	–4.05	–3.95	
E_{BS}	–746.6790	–743.5229	–746.3852	–743.2875	
E_0	–746.7207	–743.5695	–746.4239	–743.3390	
J	–67	–75	–62	–83	
Mössbauer parameters					
δ_{Fe1}	0.49	0.51	0.56	0.53	0.66
δ_{Fe2}	0.52	0.52	0.56	0.52	
ΔE_Q(Fe1)	1.13	1.10	–1.03	0.82	1.51
ΔE_Q(Fe2)	0.99	1.01	–0.63	0.87	
η(Fe1)	0.29	0.28	0.89	0.12	
η(Fe2)	0.05	0.29	0.23	0.86	

Table S5. Geometries (Å and degree), Net-Spin Populations (NSP), Broken-Symmetry State Energies (E_{BS}), Spin-Projected Energies (E_0) (eV), Heisenberg J Values (cm^{-1}), Mössbauer Isomer Shifts (δ) ($mm\ s^{-1}$), Quadrupole Splittings (ΔE_Q) ($mm\ s^{-1}$), and η Values Calculated from OPBE and PW91 Functionals with ε = 80.0 for the *cis*-μ-1,2a (Figure 9) and *cis*-μ-1,2b (Figure 10) MMOH-Peroxo Active Site Models.

	cis-μ-1,2a (Fig. 9)		*cis*-μ-1,2b (Fig. 10)		Exp.
	OPBE	PW91	OPBE	PW91	
Geometry					
Fe1-Fe2	3.759	3.618	4.250	3.927	
Fe1-O1	1.888	1.899	1.893	1.892	
Fe2-O2	1.935	1.899	1.939	1.893	
Fe1-O9	2.599	2.260			
Fe2-O9	2.218	2.259			
O1-O2	1.335	1.368	1.337	1.366	
Fe1-O3	2.167	2.164	2.214	2.146	
Fe1-O4	2.006	2.020	1.944	1.939	
Fe1-N1	2.213	2.175	2.235	2.116	
Fe1-O5	2.074	2.095	2.036	2.020	
Fe2-O6	2.094	2.079	2.215	2.156	
Fe2-N2	2.207	2.136	2.236	2.107	
Fe2-O7	1.940	1.922	1.920	1.923	
Fe2-O8	2.171	2.206	1.971	1.970	
∠Fe1-O1-O2	135.4	128.9	140.6	127.6	
∠Fe2-O2-O1	123.3	123.7	133.6	127.1	
∠Fe1-O1-O2-Fe2	6.8	5.6	43.2	56.4	
O3···O9			3.423	2.688	
O3···O10	2.579	2.603	2.648	2.757	
O3···O11	3.070	2.764			
NSP_{Fe1}	3.99	3.93	4.02	3.92	
NSP_{Fe2}	–4.00	–3.87	–4.05	–3.93	
E_{BS}	–745.7757	–743.5911	–745.3993	–743.1727	
E_0	–745.8203	–743.6544	–745.4447	–743.2260	
J	–72	–102	–73	–86	
Mössbauer parameters					
δ_{Fe1}	0.65	0.71	0.67	0.62	0.66
δ_{Fe2}	0.59	0.62	0.65	0.60	
ΔE_Q(Fe1)	–1.75	–1.65	1.56	1.81	1.51
ΔE_Q(Fe2)	–0.84	–1.12	–1.01	–1.26	
η(Fe1)	0.68	0.29	0.76	0.96	
η(Fe2)	0.16	0.16	0.99	0.72	