

Supplementary Information

Binuclear O₂ activation and hydrogen transfer mechanism for aerobic oxidation of alcohols

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1. Evaluation of density functionals

In order to evaluate the density functional dependency of this copper catalytic system, we calculated single point electronic energies of **7**, **TS_{7,8}**, **13**, **TS_{13,14}**, **26**, and **TS_{24,25}**, which are the key steps in the aerobic oxidation of 1-phenylethanol into acetophenone catalyzed by phenCu complexes, using other nine widely-used functionals, including ω B97X,¹ ω B97X -D,² B3LYP,³ B3PW91,⁴ HSE06,⁵ PBEh1PBE,⁶ TPSSh,⁷ M06-L,⁸ and TPSS,^{7a} on M06 optimized structures. Table S1 shows the absolute and relative electronic energies of **7** and **TS_{7,8}** with different functionals. **TS_{7,8}** is the binuclear triplet-spin transition state for proton transfer between 1-phenylethanol and O₂ without spin-crossover. In this process, the M06-L functional has the lowest relative energy of 14.3 kcal/mol, while the B3LYP functional has the highest relative energy of 20.7 kcal/mol. In general, the functionals contain dispersion corrections have lower relative electronic energies between **7** and **TS_{7,8}**. Such results indicate the importance of dispersion correction in density functionals for the calculations of binuclear reactions. Table S2 shows the absolute and relative electronic energies of **13** and **TS_{13,14}**, which is the mononuclear triplet-spin transition state for hydrogen transfer between DBADH₂ and O₂ with spin-crossover. In this process, the TPSS and M06-L functionals have the lowest and highest relative energies of 14.5 and 21.2 kcal/mol, respectively. Table S3 shows the absolute and relative electronic energies of **24** and **TS_{24,25}** with different functionals. In this process, M06 has the lowest relative energy of 17.0 kcal/mol, while the ω B97X functional has the highest relative energy of 23.1. With the above results, we can conclude that this copper catalyzed aerobic alcohol oxidation reaction system has a moderate dependence of density functionals.

Table S1. Absolute and relative electronic energies of **7** and **TS_{7,8}** calculated by using different functionals.

Functionals	<i>E</i> (Hartree)		<i>ΔE</i> (kcal/mol)
	7	TS_{7,8}	7 → TS_{7,8}
ω B97X	-4959.843235	-4959.813053	18.9
TPSS	-4960.587240	-4960.557930	18.4
B3LYP	-4960.271486	-4960.238508	20.7
B3PW91	-4959.547947	-4959.515906	20.1
ω B97X-D	-4959.736434	-4959.712142	15.2
PBEh1PBE	-4957.973169	-4957.943771	18.4
HSE06	-4957.937633	-4957.908423	18.3
TPSSh	-4960.342228	-4960.311033	19.6
M06-L	-4959.932899	-4959.910140	14.3
M06	-4958.917400	-4958.893387	15.1

Table S2. Absolute and relative electronic energies of **13** and **TS_{13,14}** calculated by using different functionals.

Functionals	<i>E</i> (Hartree)		<i>ΔE</i> (kcal/mol)
	13	TS_{13,14}	13 → TS_{13,14}
ω B97X	-3165.464421	-3165.435330	18.3
TPSS	-3166.073189	-3166.050095	14.5
B3LYP	-3165.818969	-3165.792896	16.4
B3PW91	-3165.201682	-3165.177759	15.0
ω B97X-D	-3165.364635	-3165.333948	19.3
PBEh1PBE	-3163.990173	-3163.965865	15.3
HSE06	-3163.960459	-3163.936118	15.3
TPSSh	-3165.878231	-3165.854660	14.8
M06-L	-3165.598930	-3165.565175	21.2
M06	-3164.768600	-3164.735113	21.0

Table S3. Absolute and relative electronic energies of **24** and **TS_{24,25}** calculated by using different functionals.

Functionals	<i>E</i> (Hartree)		ΔE (kcal/mol)
	24	TS_{24,25}	24 \rightarrow TS_{24,25}
ω B97X	-4884.706811	-4884.670051	23.1
TPSS	-4885.405601	-4885.376413	18.3
B3LYP	-4885.1108260	-4885.077959	20.6
B3PW91	-4884.416468	-4884.384950	19.8
ω B97X-D	-4884.608884	-4884.572919	22.6
PBEh1PBE	-4882.884924	-4882.850159	21.8
HSE06	-4882.849906	-4882.815263	21.7
TPSSh	-4885.175242	-4885.141769	21.0
M06-L	-4884.781502	-4884.749901	19.8
M06	-4883.794000	-4883.766859	17.0

2. Evaluation of spin states

In order to ensure a reliable evaluation of the proposed reaction mechanism and find out the change of spin states in the reaction, we examined the relative free energies of most key structures at different spin-states using the same computational methods described in the text. The calculation results are listed in Table S4. All structures were optimized individually at different spin-states. The structures reported in the text are the spin-states with lower relative free energies. We can see many spin-crossovers between singlet and triplet states along the reaction pathways, but all doublet states are much more stable than the corresponding quartet states.

Table S4. Absolute and relative free energies of key structures with different spin states.

Complexes	<i>G</i> (Hartree)		ΔG (kcal/mol)
	Singlet	Triplet	Singlet \rightarrow Triplet
2	-3012.854620	-3012.845526	5.7
TS_{3,4}	-3398.518793	-3398.493244	16.0
4	-3398.610841	-3398.549299	38.6
7	-4958.440201	-4958.466737	-16.7
8	-4958.422997	-4958.440336	-10.9
12	-3014.088329	-3014.020209	42.7
13	-3164.308344	-3164.347692	-24.7
14	-3164.315802	-3164.315256	0.3
20	-2362.726301	-2362.638227	55.3

23	-4574.019260	-4574.056560	-23.4
24	-4883.330438	-4883.344713	-9.0
TS_{24,25}	-4883.320878	-4883.326512	-3.5
28	-5609.785542	-5609.799732	-8.9
TS_{28,29}	-5609.773569	-5609.774642	-0.7
Complexes	G (Hartree)		ΔG (kcal/mol)
	Doublet	Quartet	Doublet \rightarrow Quartet
9	-2362.113123	-2362.017906	59.7
10	-2596.332200	-2596.221630	69.4
15	-3013.473895	-3013.389313	53.1
22	-2287.013769	-2286.917373	60.5

References

1. J.D. Chai, M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106.
2. J.D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.
3. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785-789.
4. (a) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B.*, 1993, **48**, 4978-4978. (b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B.*, 1992, **46**, 6671-6687.
5. (a) T. M. Henderson, A. F. Izmaylov, G. Scalmani and G. E. Scuseria, *J. Chem. Phys.*, 2009, **131**, 044108. (b) A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.
6. M. Ernzerhof and J. P. Perdew, *J. Chem. Phys.*, 1998, **109**, 3313-3320.
7. (a) J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401-146601. (b) V. N. Staroverov, G. E. Scuseria, J. M. Tao and J. P. Perdew, *J. Chem. Phys.*, 2003, **119**, 12129-12137.
8. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.