

Supporting information for

Entropy and Enthalpy Contributions to the Kinetics of Proton Coupled Electron Transfer to the $\text{Mn}_4\text{O}_4(\text{O}_2\text{PPh}_2)_6$ Cubane

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Experimental

Materials. $\text{Mn}_4\text{O}_4(\text{O}_2\text{PPh}_2)_6$ (**1**) was prepared as described elsewhere¹. All other materials were of analytical purity from commercial sources and were used as received. Monodeuterated phenols were prepared by exchange using CD_3OD in approximately 500-fold excess in CH_2Cl_2 solution².

Kinetic Measurements. The reactions of phenols with **1** were monitored by UV-Vis spectrophotometry on an HP-8452A spectrophotometer in CH_2Cl_2 solution. Constant temperature was maintained using a Neslab Endocal RTE-5DD circulating water bath. All measurements were made at $25.0 \pm 0.1^\circ\text{C}$ unless otherwise stated. The change in the absorbance at 342 nm was monitored. This wavelength reflects the change in concentration of **1** and is located in the center of a region of the spectrum that bleaches upon reaction of phenols with **1**.

Data analysis. All data points represent an average of five separate experimental trials. Initial rates were calculated directly from the initial slopes of the absorbance vs. time traces, yielding $(-dA/dt)$. The pseudo-first order rate constant k_{obs} was determined by fitting the slope from a plot of $\ln(A_t - A_\infty)$ vs. time:

$$\ln(A_t - A_\infty) = -k_{\text{obs}} * t + \text{constant}$$

The second order rate constant is obtained by fitting the corresponding equation:

$$K_{\text{obs}} = k_2 [\text{phenol}]$$

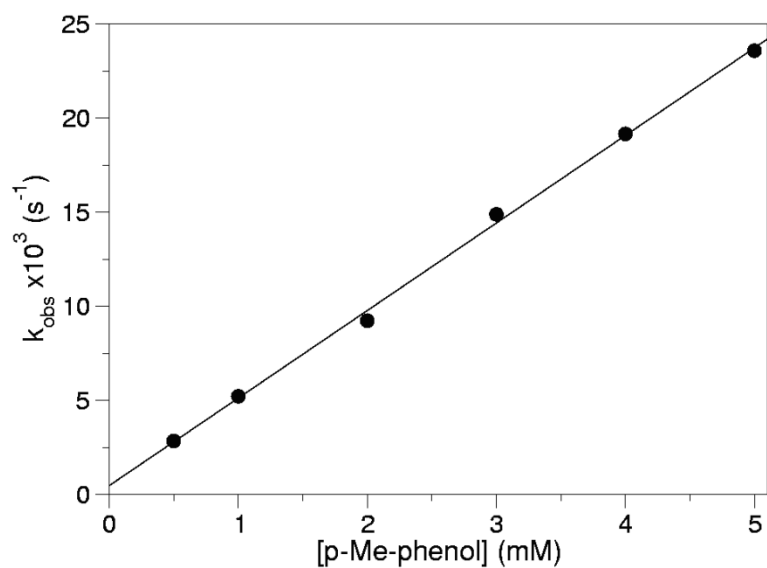


Figure S1: Pseudo-first order rate constant k_{obs} as a function of the concentration of *p*-Me-phenol for the reaction between **1** and *p*-Me-phenol at 25.0°C. Conditions: $[\mathbf{1}] = 0.10 \text{ mM}$ in CH_2Cl_2 ; $[\text{p-Me-phenol}] = 0.50\text{-}5.0 \text{ mM}$.

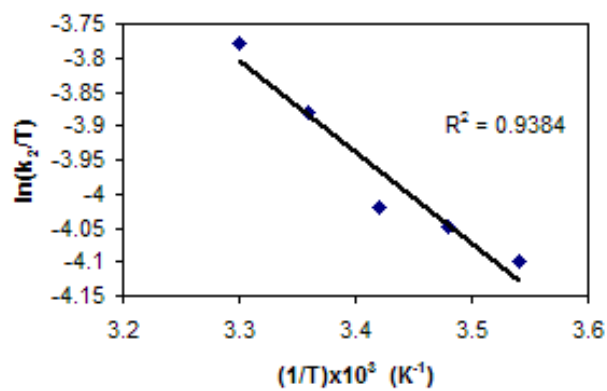


Figure S2: Temperature dependence of the reaction between **1** and *p*-Me-phenol. Conditions: $[\mathbf{1}] = 0.10 \text{ mM}$ in CH_2Cl_2 ; $[\text{p-Me-phenol}] = 3.0 \text{ mM}$.

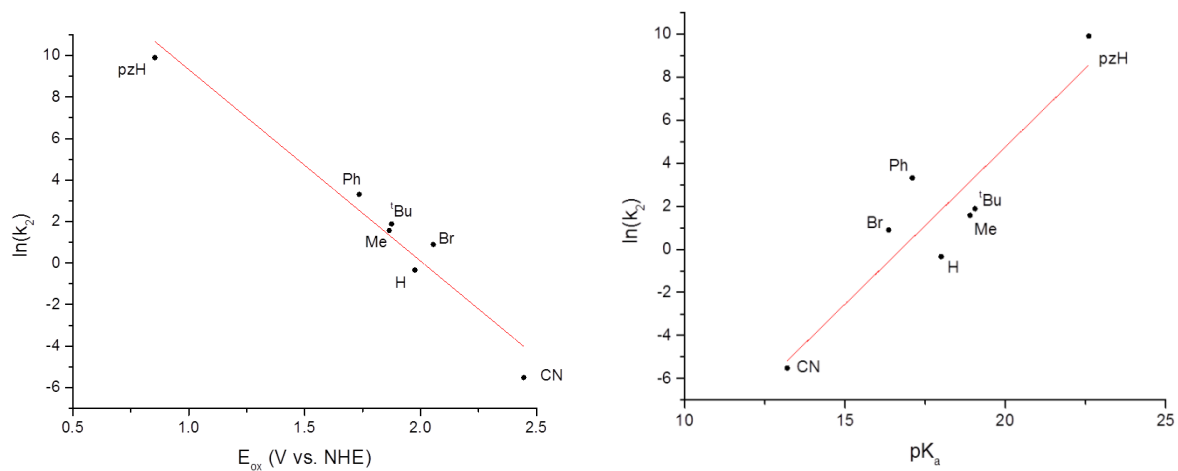


Figure S3: Dependence of the $\ln(k_2)$ on the oxidation potential of the phenol and pK_a of the phenolic proton. Conditions: $[1] = 0.10$ mM in CH_2Cl_2 ; $[p\text{-X-phenol}] = 3.0$ mM.

Table S1. Comparison of μ -O-H BDE's for Mn complexes

<i>Species</i>	<i>Mn ox. state</i>	<i>O-H BDE</i>	<i>Ref.</i>
1H	Mn ₄ (3III,IV)	84-99	This work
(Mn ₂ (L-X) ₂ (μ -O)(μ -OH)) ^{+a}	Mn ₂ (III,IV)	76-79	3
(Mn ₂ (μ -O)(μ -OH)(bpy) ₄) ^{3+b}	Mn ₂ (2III)	84	3,4
(Mn ₂ (μ -O)(μ -OH)(phen) ₄) ^{3+c}	Mn ₂ (2III)	79	5
(Mn ₂ (μ -O)(μ -OH)(bispicen) ₂) ^{3+d}	Mn ₂ (2III)	76	6

a. L-X = 2-hydroxy-1,3-bis(3,5-X₂-salicylideneamino)propane (X= Cl, H or tBu)

b. Bpy= 2,2' bipyridine

c. Phen= 1,10-phenanthroline

d. Bispicen= N,N'-bis[2-methyl(pyridyl)ethane-1,2-diamine]

References

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