4.6 Supporting Information

References

(1) Vasudevan, D. and Stone, A. T. Adsorption of 4-nitrocatechol, 4-nitro-2-aminophenol, and 4- nitro-1,2-phenylenediamine at the metal (hydr)oxide/water interface: Effect of metal (hydr)oxide properties. *J. Colloid Interf. Sci.* **1998**, 202, 1-19.

(2) Morgan, J. J. Manganese in natural waters and earth's crust: Its availability to organisms. In *Metal Ions in Biological Systems*, H. Sigel, Editor. 2000, Dekker: New York. 1-34.

(3) Murray, J. W. Surface chemistry of hydrous manganese-dioxide. *J. Colloid Interf. Sci.* **1974**, 46, 357-371.

(4) Tonkin, J. W., Balistrieri, L. S., and Murray, J. W. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Appl. Geochem.* **2004**, 19, 29-53.

(5) Toullec, J. Keto-enol equilibrium constant. In *The Chemistry of Enols*, Z. Rappoport, Editor. 1990, John Willey: Chichester, England. 323-398.

(6) Wong, F. M., Keeffe, J. R., and Wu, W. M. The strength of a low-barrier hydrogen bond in water. *Tetrahedron Lett.* **2002**, 43, 3561-3564.

(7) *pK_a Value Calculated Using Advanced Chemistry Development (ACD) Software Solaris v4.67 (1994-2004) being cited by the electronic database SciFinder Scholar*.

(8) Iglesias, E. Tautomerization of 2-acetylcyclohexanone. 1. Characterization of keto-enol/enolate equilibria and reaction rates in water. *J. Org. Chem.* **2003**, 68, 2680-2688.

(9) Iglesias, E. Keto-enol/enolate equilibria in the 2-acetylcyclopentanone system. An unusual reaction mechanism in enol nitrosation. *New J. Chem.* **2002**, 26, 1352-1359.

Table S4.1. Properties of Metal Oxides Included in This Study

Name	Metal Charge	Ionic Radius (nm)	Electronic Structure	BET Surface Area (m^2/g)	pH_{zpc}	Mineral Structure	Cation Exchanger?
TiO_2(s, Rutile)[a]	4.0	0.069	$[Ar]3d^0$	3.5	6.1	chain	no
MnO_2(s, Birnessite)	3.78	Mn^{IV}: 0.052[b] Mn^{III}: 0.070[b]	Mn^{IV}: $[Ar]3d^3$ Mn^{III}: $[Ar]3d^4$ (high spin)	174.3	2.3[c]	layer	yes

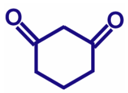
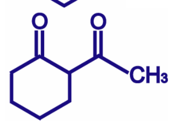
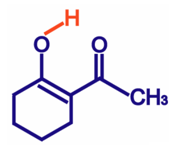
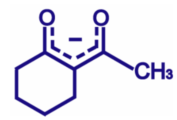
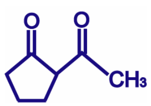
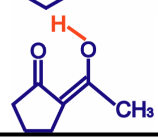
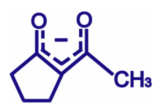
[a] properties obtained from Vasudevan and Stone *(1)* [b] from Morgan *(2)* [c] from Murray and coworkers *(3, 4)*

Table S4.2. Indirect Photometric Methods Developed for Analyzing Ionic Components from (a) Oxidation of Organic Substrates by MnO_2 or MnOOH, (b) Adsorption of Organic Substrate onto TiO_2, Using Capillary Electrophoresis

Analytes	Electrolyte	Wavelength (nm)
Oxidation Experiments		
malonic acid[1] formic acid[2] oxalic acid[2]	pH 7.8 5 mM phthalate, 12.5 mM Tris, 0.25 mM TTAB	229[1] 200[2]
tartronic acid[1] oxalic acid[2] glyoxylic acid[2] formic acid[2]	pH 7.8 5 mM phthalate, 12.5 mM Tris, 0.25 mM TTAB	200
Adsorption Experiments		
acetylacetone	pH 10.8 10 mM benzoate, 25 mM triethylamine, 0.25 mM TTAB	229
acetoacetatic acid	pH 7.8 5 mM phthalate, 12.5 mM Tris, 0.25 mM TTAB	209
dimethylmalonic acid	pH 7.8 5 mM phthalate, 12.5 mM Tris, 0.25 mM TTAB	229

[1] refers to the parent compound, [2] refers to the oxidation product.

Table S4.3. Properties and MnO_2 Reactivity Comparisons Among b-Diketones with Ring Structures

Structure Ketone (KH)	Predominant Enol (EH)	Enolate ion (E^-)	K_E	Ref.	pK_a^{eq}	Ref.	R_0 at pH 5.0 (μM/h)
	dimmer via intermolecular H-bonding		$> 10^{1.28}$ (i.e., enol content > 95%)	*(5, 6)*	5.26	*(7)*	19
			$10^{-0.14}$	*(8)*	9.85	*(8)*	17
			$10^{-0.40}$	*(9)*	8.25	*(9)*	231