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Supporting Information

**Hydrogen atom transfer reactions of ferrate(VI) with phenols and hydroquinone.
Correlation of rate constants with bond strengths and application of the Marcus
cross relation.**

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Experimental Section

Materials. Potassium ferrate (K_2FeO_4) (>98%) was prepared according to a literature method.¹ All phenols and hydroquinone were of reagent grade and were purchased from Aldrich. Phenol and 4-methoxyphenol were recrystallized from petroleum ether.² D_2O (99.8 atom % D, Acrôs) was used as received. Water for kinetic experiments was distilled twice from alkaline permanganate. Ionic strength was maintained with sodium perchlorate. The pD values for all D_2O solutions were determined by using a pH meter with the relationship $pD = pH_{meas} + 0.4$.

Kinetics. Kinetic experiments were performed using either an Agilent 8453 diode array spectrophotometer or a Hi-Tech SF-61 stopped-flow spectrophotometer. The concentrations of phenols were at least in 10-fold excess of that of ferrate(VI). Stock solutions of ferrate(VI) were prepared in sodium hydroxide solution at $pH = 10$, at this pH ferrate(VI) is stable for >20 h at 23 °C. Stock solutions of phenol were prepared in NaH_2PO_4/Na_2HPO_4 buffer. The reaction was started by mixing the ferrate solution. The reaction progress was monitored by observing absorbance changes at 510 nm and 400 nm. Pseudo-first-order rate constants, k_{obs} , were obtained by nonlinear least-squares fits of A_t vs t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively.

Second-order rate constants were obtained from plots of k_{obs} vs concentration of organic substrates. The y-intercept of the plots should be related to the rate constants for the self-decay of ferrate, and they are more or less constant for the various phenol derivatives. For H2Q since the rate is much faster, self-decay of ferrate is negligible. There is a slightly negative intercept in Figure 3, which we think is due to instrumental error of the stopped-flow, since the reaction is very fast and is close to the limit of our instrument.

The pH of the reaction mixture was determined by mixing an equal volume of organic substrate with ferrate and the pH was then measured using a pH meter. The pH of the reaction mixture usually increased by less than 0.1 pH unit after mixing and remained constant throughout the reaction.

Product analysis.

Product of phenol oxidation. In a typical experiment, 1.0 ml ferrate (1.2 μmol) solution (pH = 10) was added to 1.5 ml phenol (19.7 μmol) solution (pH = 7). The mixture was stirred for 10 minutes and then analyzed by GC and GC-MS using cyclohexanone as internal standard. The results indicate that 0.78 μmol phenol was consumed and 0.39 μmol *p*-benzoquinone was produced.

Product of hydroquinone oxidation. In a typical experiment, 0.9 ml ferrate (5.66 μmol) solution (pH = 10) was added to 1.0 ml hydroquinone (106.9 μmol) solution (pH = 6.2) under argon. The mixture was analyzed by GC and GC-MS using cyclohexanone as internal standard. The results indicate that 6.76 μmol *p*-benzoquinone was generated.

Calculations

BDFEs of the phenols in H₂O. According to equations (4)-(6) in the main text, BDFE_g is obtained by equation (4) using BDE_g and $S^\circ(\text{H}^\cdot) = 27.42 \text{ cal K}^{-1} \text{ mol}^{-1}$. Then BDFE_g is converted to BDFE_{H₂O} according to equation (5) based on $\Delta G^\circ_{\text{H}_2\text{O}}(\text{H}^\cdot)$ in H₂O⁵ and the difference in the free energies of solvation of X-PhO[·] and X-PhOH. The free energies of solvation of X-PhO[·] and X-PhOH are estimated by equation (6). α_2^{H} is H-bonding acidity parameter of solvent and solute and is obtained from ref 3. β_2^{H} is H-bonding basicity parameter of solvent and solute and is obtained from ref 4 and 5.

H-atom self-exchange rates of phenol and hydroquinone in H₂O. The H-atom self-exchange rates in water, $k_{22}(\text{PhOH})$ and $k_{22}(\text{H}_2\text{Q})$, were obtained according to the relationship shown in equation (16).⁵

$$\log(k_{\text{solv1}}) - \log(k_{\text{solv2}}) = -8.3\alpha_2^{\text{H}}(\text{PhOH}/\text{H}_2\text{Q})[\beta_2^{\text{H}}(\text{solv1}) - \beta_2^{\text{H}}(\text{solv2})] \quad (16)$$

Using $\alpha_2^{\text{H}}(\text{PhOH}) = 0.596$,³ $\beta_2^{\text{H}}(\text{water}) = 0.38$, $\beta_2^{\text{H}}(\text{DTBP}) = 0.35$, $\beta_2^{\text{H}}(\text{CCl}_4) = 0^4$ and $\alpha_2^{\text{H}}(\text{H}_2\text{Q}) = 0.34$ ⁶, the H-atom self-exchange rate of phenol and hydroquinone in H₂O, are $2.27 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $2.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

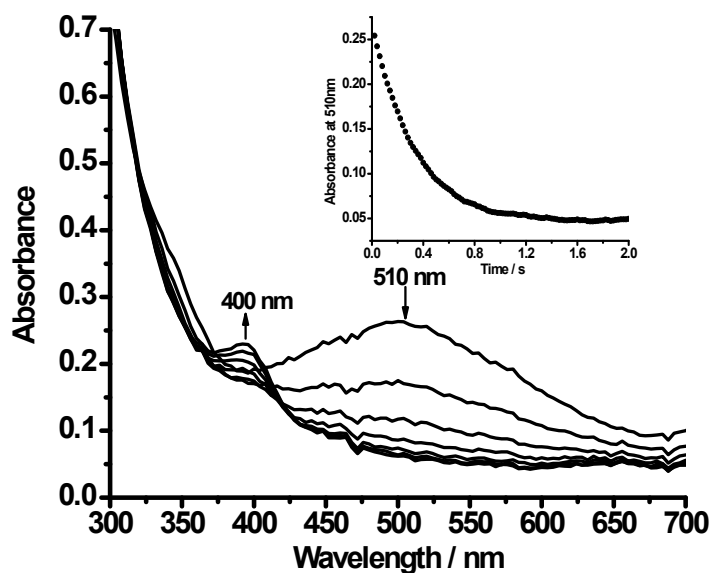


Figure S1 Spectral changes at 0.075s intervals during the first step of the oxidation of phenol (1.80×10^{-2} M) by ferrate(VI) (3.00×10^{-4} M) at 298.0K ($I = 0.3$ M; pH = 7.2). Inset shows the absorbance-time trace at 510 nm.

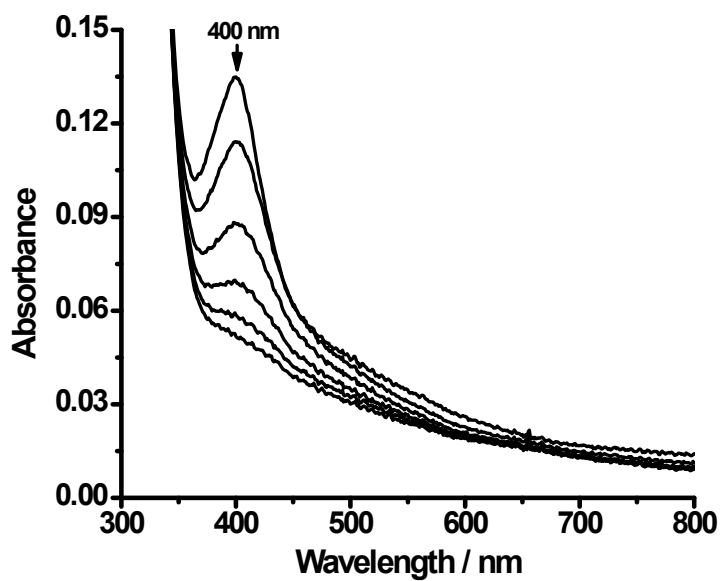


Figure S2 Spectral changes at 4s intervals during the second step of the oxidation of phenol (1.80×10^{-2} M) by ferrate(VI) (3.00×10^{-4} M) at 298.0K ($I = 0.3$ M; pH = 8.4).

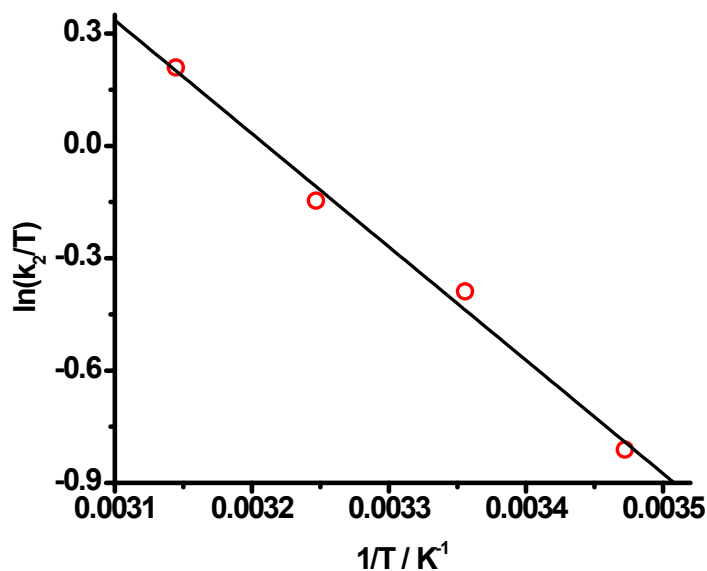


Figure S3 Plot of $\ln(k_2/T)$ vs $1/T$ for the oxidation of phenol by ferrate(VI) (3.00×10^{-4} M) at 298.0 K ($I = 0.3$ M; pH = 6.2). [Slope = $-(3.03 \pm 0.19) \times 10^3$; y-intercept = (9.72 ± 0.63) ; $r^2 = 0.99$]

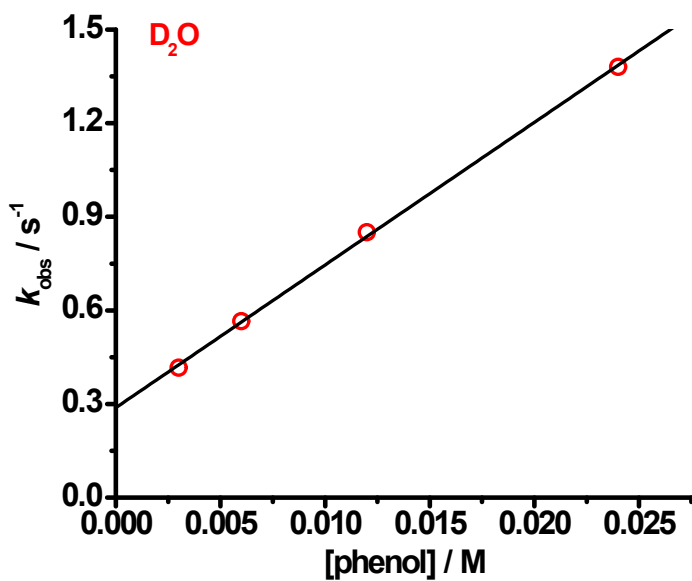


Figure S4 Plot of k_{obs} vs [phenol] for the oxidation of phenol by ferrate (3.00×10^{-4} M) at 298.0 K, pD = 6.2 and $I = 0.3$ M. (Slope = $(4.58 \pm 0.08 \times 10^1)$; y-intercept = $(2.88 \pm 0.10) \times 10^{-1}$; $r^2 = 0.999$)

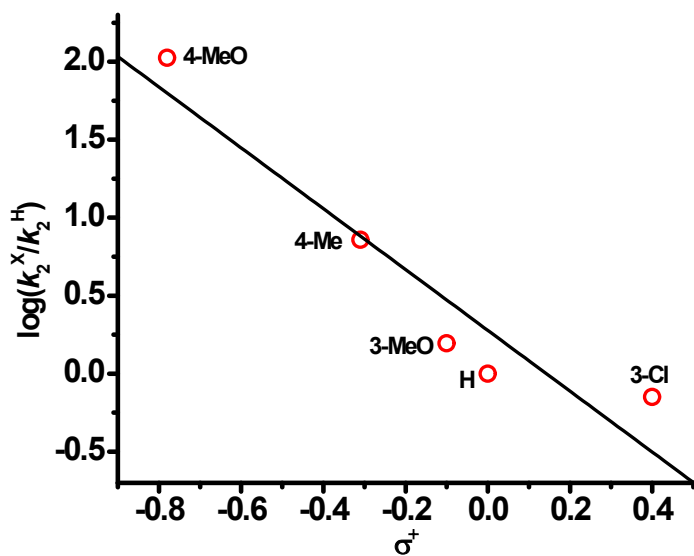


Figure S5 Hammett plot of $\log(k_2^x/k_2^H)$ vs σ^+ for the oxidation of phenols by ferrate(VI) at 298.0 K in H₂O (pH = 6.2; $I = 0.3$ M). [Slope = $-(2.0 \pm 0.4)$; y-intercept = $-(3.0 \pm 1.0) \times 10^{-1}$; $r^2 = 0.86$]

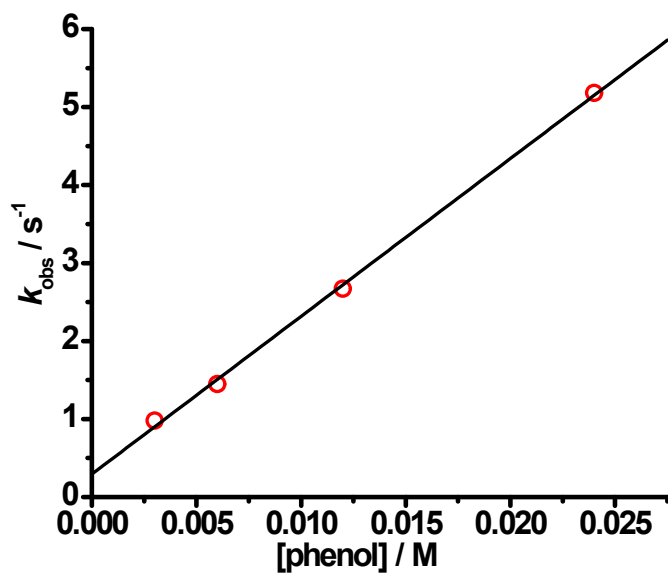


Figure S6 Plot of k_{obs} vs $[\text{phenol}]$ for the oxidation of phenol by ferrate (3.00×10^{-4} M) at 298.0 K, pH = 5.3 and $I = 0.3$ M. (Slope = $(2.02 \pm 0.05) \times 10^3$; y-intercept = $(2.93 \pm 0.70) \times 10^{-1}$; $r^2 = 0.998$)

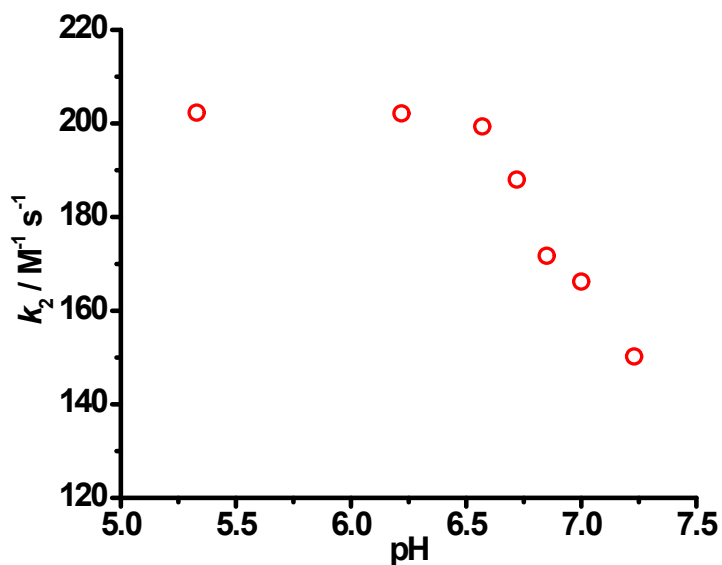


Figure S7 Plot of k_2 vs pH for the oxidation of phenol by ferrate (3.00×10^{-4} M) at 298.0 K and $I = 0.3$ M.

References

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- 6 J. P. Roth, J. C. Yoder, T. J. Won and J. M. Mayer, *Science*, 2001, **294**, 2524. According this reference, the H-atom self-exchange rates of H_2Q are $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in CCl_4 and $1.72 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in CH_3CN , respectively. Therefore, $\alpha_2^{\text{H}}(\text{H}_2\text{Q})$ is estimated to be 0.34 based on equation (16) and $\beta_2^{\text{H}}(\text{CH}_3\text{CN}) = 0.44$ from ref 4.