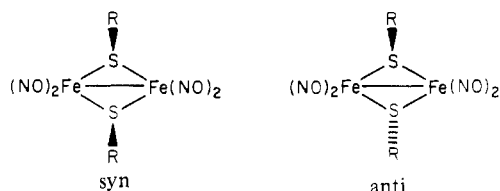


The ^1H NMR spectra of the alkyl thioesters $\text{Fe}_2(\mu\text{-SET})_2(\text{NO})_4$, $\text{Fe}_2(\mu\text{-SCH}_2\text{Ph})_2(\text{NO})_4$, and $\text{Fe}_2(\mu\text{-SCH}_2\text{Ph})(\mu\text{-SePh})(\text{NO})_4$ show a doubling of the alkyl signals, indicating that there exist equal quantities of the syn and anti isomers in solution. The X-ray structure of the ethyl ester revealed a planar Fe_2S_2 core with the alkyl groups disposed in the anti configuration;⁵ apparently in solution both isomers coexist, and their rate of inversion is slow on the ^1H NMR time scale. In the case of the esters of $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6^{2-}$, the tetrahedral Fe_2S_2 core geometry gives rise to three possible geometric isomers, depending on whether the substituents occupy axial or equatorial sites on the sulfur atoms. For $\text{Fe}_2(\mu\text{-SMe})_2(\text{CO})_6$, King has chromatographically separated two of these isomers.²³ Due to the long S...S distance in $\text{Fe}_2(\mu\text{-SET})_2(\text{NO})_4$ ($r_{\text{SS}} = 3.63 \text{ \AA}^5$) compared with that for $\text{Fe}_2(\mu\text{-SMe})_2(\text{CO})_6$ ($r_{\text{SS}} = 2.93 \text{ \AA}^{24}$), there is little steric interaction between the organic substituents attached to the planar Fe_2S_2 core. For this reason the two isomers coexist in solution in equal populations. ^1H NMR spectroscopy revealed a splitting of the phenyl proton resonances for the PhS and PhSe esters. Since the organic chalcogenide precursors do not show this behavior, this observation is consistent with syn-anti isomerism.



$\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6^{2-}$ is known to undergo metalation to afford stable $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S})_2\text{ML}_n$ cluster compounds. We find, however, that **1** is considerably less reactive toward transition-metal electrophiles. Thus treatment of **1** with *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$ afforded an unstable solid, which by ^1H NMR and IR contained the anticipated $\text{Fe}_2\text{S}_2\text{Pt}$ cluster; we have previously shown that $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6^{2-}$ reacts with the same platinum(II) complex to afford robust $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S})_2\text{Pt}(\text{PPh}_3)_2$.^{8,26} An unstable cluster formulated as $(\text{NO})_4\text{Fe}_2(\mu_3\text{-S})_2\text{Ni}(\text{dppe})$ was isolated from the reaction of **1** and $\text{NiCl}_2(\text{dppe})$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$). The instability of this compound is understandable in view of the tendency of other metal complexes containing *cis* mercaptides to reductively eliminate their sulfur-containing ligands.²⁵

Summary

In comparison with $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6^{2-}$, Roussin's nitrosyl anion is considerably more stable and is reactive toward a narrower range of electrophiles. These observations are consistent with the view that nitric oxide is a more effective π -acid ligand than carbon monoxide. The net result is that the nucleophilicity of metal nitrosyl complexes is attenuated relative to the analogous carbonyls. An additional finding of this study relates to the synthetic utility of $\text{Fe}_2(\mu\text{-I})_2(\text{NO})_4$. This diiron reagent allows one to prepare anhydrous solutions of $\text{Fe}_2(\mu\text{-E})_2(\text{NO})_4^{2-}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$). These intermediates permit the assembly of organochalcogenide ligands *in situ*, thus obviating the need for noxious and unstable ligand precursors.

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Registry No. **2**, 15002-08-1; $\text{Fe}_2(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{Br})_2(\text{NO})_4$, 79919-42-9; $\text{Fe}_2(\mu\text{-SPh})_2(\text{NO})_4$, 15696-38-5; $\text{Fe}_2(\mu\text{-SePh})_2(\text{NO})_4$, 79919-43-0; $\text{Fe}_2(\mu\text{-SeCH}_2\text{Ph})_2(\text{NO})_4$, 79919-44-1; $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$, 79919-45-2; $\text{Fe}_2(\mu\text{-TeCH}_2\text{Ph})_2(\text{NO})_4$, 79919-46-3; $\text{Fe}_2(\text{NO})_4(\mu_3\text{-S})_2\text{Ni}(\text{dppe})$, 79919-47-4; $\text{Fe}_2(\mu\text{-SCH}_2\text{Ph})(\mu\text{-SePh})(\text{NO})_4$, 79933-10-1; $(\text{NO})_4\text{Fe}_2(\mu_3\text{-S})_2\text{Pt}(\text{PPh}_3)_2$, 79919-48-5; $\text{Fe}_2(\mu\text{-SCH}_2\text{Ph})_2(\text{NO})_4$, 79827-00-2; $\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{NO})_4$, 14917-04-5; $\text{K}_2[\text{Fe}_2\text{S}_2(\text{NO})_4]$, 79919-49-6; $\text{NiCl}_2(\text{dppe})$, 14647-23-5; Ph_2Se_2 , 1666-13-3; Ph_2Te_2 , 32294-60-3; benzyl chloride, 100-44-7; polystyrene, 9003-53-6.

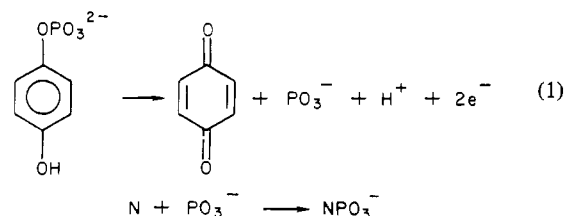
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Oxidation of Hydroquinone Esters and Substituted Hydroquinones by Cerium(IV) in 1 N Sulfuric Acid

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Phosphorylation of nucleophiles (N) may accompany the oxidation of hydroquinone phosphates,¹ i.e.



where $\text{N} = \text{H}_2\text{O}, \text{ROH}, \text{PO}_4^{3-}, \text{ADP}$, etc.

Although P-O bond cleavage predominates in the simple hydrolysis of phosphate monoesters in their mono- and dianion forms,² the efficiency of oxidative phosphorylation achieved with hydroquinone phosphates typically is quite low.¹ Tracer studies with H_2^{18}O showed that only 35% of the orthophosphate product of the reaction of Br_2 with 4-hydroxy-2,3-dimethyl-1-naphthyl dihydrogen phosphate in 1 N HClO_4 resulted from P-O bond cleavage.³ The dominant pathway evidently involves unproductive C-O bond breaking, induced by nucleophilic displacement of H_2PO_4^- by water. Similarly, oxidation of hydroquinone phosphate with ceric ion in methanol gives a 95% yield of the product expected from C-O bond cleavage, the dimethyl ketal of 1,4-benzoquinone.⁴

While hydroquinone phosphates probably are not involved in biological oxidative phosphorylation, these compounds nevertheless are useful in understanding how phosphorylation may be efficiently coupled to a two-electron oxidation process. Our ultimate goal is to determine the effect of transition-metal ions on the mechanism of reactions having the potential for coupled electron and group transfer, i.e., the oxidative hydrolysis of hydroquinone esters. In this note we report kinetic studies of the oxidation of (4-hydroxyphenyl)phosphoric acid (HQ-P) and (4-hydroxyphenyl)sulfuric acid (HQ-S) by cerium(IV) in 1 N sulfuric acid. To characterize further the reactivity of $\text{Ce}(\text{IV})$ with phenolic substrates under these conditions, we report rate constants for the oxidation of several substituted hydroquinones ($\text{H}_2\text{Q-X}$). The dependence of rate on thermodynamic driving force is examined to determine whether an outer-sphere mechanism pertains in the reaction

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Table II. Rate Parameters for the Oxidation of Hydroquinone Esters and Substituted Hydroquinones by Ce(IV) in 1 N H₂SO₄^a

reductant	k_{12} , M ⁻¹ s ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	ΔG_{12}^* , kcal/mol ^b	ΔG_{12}° , kcal/mol ^c
HQ-P ^d	9.5 (0.2) × 10 ⁴	10.3 (0.6)	-1 (2)	8.2	
HQ-S ^d	5.9 (0.2) × 10 ⁴	8.9 (0.8)	-7 (3)	8.5	
H ₂ Q ^d	1.90 (0.08) × 10 ⁵	7.7 (0.3)	-9 (1)	7.81	+0.1
H ₂ Q-CH ₃	1.04 (0.05) × 10 ⁵			8.16	-0.7
H ₂ Q-SO ₃ H	1.42 (0.08) × 10 ⁵			7.98	+1.2
H ₂ Q-OCH ₃	1.80 (0.07) × 10 ⁵			7.84	-1.3
H ₂ Q-OH	2.87 (0.08) × 10 ⁵			7.56	-1.7
H ₂ Q-Br	1.37 (0.02) × 10 ⁵			8.00	-0.8

^a 25.0 ± 0.1 °C. Standard deviations shown in parentheses. ^b $\Delta G_{12}^* = -RT \ln(k_{12}/Z)$ where Z , the bimolecular collision frequency of uncharged species in aqueous solution, is taken to be 10¹¹ M⁻¹ s⁻¹.⁹ ^c $\Delta G_{12}^\circ = -RT \ln K_{12}$, where $K_{12} = (K_a K_{sq})^{1/2}$.⁶ Further details of this calculation are given in ref 6. K_a calculated using $E^\circ(\text{Ce(IV)/Ce(III)}) = 1.44$ V (Latimer, W. L. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1952; p 294). ^d Temperature dependence studies of HQ-P, HQ-S, and H₂Q covered the ranges 18.3–39.3, 17.7–37.3, and 6.7–32.6 °C, respectively.

of hydroquinone esters and substituted hydroquinones with Ce(IV) in 1 N H₂SO₄.

Experimental Section

Reagent grade chemicals were used throughout, and solutions were prepared with triply distilled water. A stock solution of cerium(IV) in 1 N H₂SO₄ was prepared from Ce(HSO₄)₄ (G. F. Smith), and was standardized against As₂O₃.⁵ Hydroquinone (H₂Q), methylhydroquinone (H₂Q-CH₃), hydroquinonesulfonic acid, potassium salt (H₂Q-SO₃K), methoxyhydroquinone (H₂Q-OCH₃), hydroxyhydroquinone (H₂Q-OH), and bromohydroquinone (H₂Q-Br) were obtained and purified as described by Clemmer et al.⁶ Barium 4-hydroxyphenyl phosphate hydrate, Ba(O₃POC₆H₄OH)·H₂O, was synthesized by a new method, to be described in a subsequent publication.⁷ The potassium salt of the sulfate monoester of hydroquinone, K(O₃SO-C₆H₄OH), was prepared by the method of Yamaguchi.⁸ The purity of these latter two compounds was confirmed by analytical data (% C, H).

Kinetic studies were carried out on a Durrum D-110 stopped-flow apparatus, with Ce(IV) being the limiting reagent. Loss of Ce(IV) (10 μM initial concentration) was followed at 350 nm (ϵ_{350} (1 N H₂SO₄) 4.1 × 10³ M⁻¹ cm⁻¹). Reductant and oxidant solutions were prepared in 1 N H₂SO₄ (except in hydrogen ion dependence studies) and were used on the same day as their preparation. Ultraviolet spectra (Cary 17 spectrophotometer) of hydroquinone phosphate and hydroquinone sulfate solutions in 1 N H₂SO₄ were found to be invariant within 8 h after preparation, indicating that these esters are quite stable toward hydrolysis at room temperature. Hydroquinone phosphate solutions were carefully filtered to remove a fine precipitate of BaSO₄.

Observed pseudo-first-order rate constants (k_{obsd}) were derived from the least-squares slopes of linear (for at least 3 half-lives) $\ln(A_t - A_\infty)$ vs. time plots, based on oscilloscope (Tektronix Model 564 B) traces. Reported rate constants generally are the average of three determinations.

Results and Discussion

Surveys of the dependence of k_{obsd} on reductant concentration are shown in Table I⁹ for the reactions of Ce(IV) with HQ-P, HQ-S, H₂Q, H₂Q-CH₃, H₂Q-SO₃H, H₂Q-OCH₃, H₂Q-OH, and H₂Q-Br. In each case, the data are consistent with the rate law

$$-d[\text{Ce(IV)}]/dt = k_{12}[\text{phenol}][\text{Ce(IV)}] \quad (2)$$

Temperature-dependence results on the oxidation of hydroquinone, hydroquinone phosphate, and hydroquinone sulfate also are given in Table I. Second-order rate constants, derived from the least-squares analysis of k_{obsd} vs. [phenol] plots, and activation parameters, based on Eyring plots of $\ln(k_{12}/T)$ vs.

Table III. Kinetic Hydrogen Ion Dependence of the H₂Q/Ce(IV) Reaction^a

[H ⁺], ^b M	k_{obsd} , ^c s ⁻¹	k_{12} , ^d M ⁻¹ s ⁻¹
0.10	18.5 (0.1)	7.40 × 10 ⁴
0.25	20.9 (0.5)	8.36 × 10 ⁴
0.50	24.8 (0.6)	9.92 × 10 ⁴
0.75	30.6 (0.4)	1.22 × 10 ⁵
1.00	42.6 (0.2)	1.70 × 10 ⁵
1.50	45.2 (0.1)	1.81 × 10 ⁵

^a 25.1 °C, $I = 2.0$ M, [H₂Q] = 0.250 mM. ^b Hydrogen ion concentration varied at constant ionic strength in H₂SO₄/(NH₄)₂SO₄ solutions. [H⁺] calculated with the assumption of 100% ionization of H₂SO₄ to HSO₄⁻ and with a second ionization constant of 0.375 ($I = 2.0$ M), extrapolated from a plot of K_2 vs. I (Tong, J. Y.-P.; King, E. J. *Am. Chem. Soc.* 1960, 82, 3805). ^c Average deviations from the mean shown in parentheses. ^d k_{12} calculated as $k_{\text{obsd}}/[\text{H}_2\text{Q}]$.

1/ T , are summarized in Table II. Finally, a study of the effect of hydrogen ion concentration on the rate of the H₂Q-Ce(IV) reaction at constant ionic strength (2.0 M) is presented in Table III.

Rate constants for the oxidation of substituted hydroquinones by Ce(IV) in 1 N H₂SO₄ are strikingly insensitive to variations in the substituent. Less than a threefold reactivity range is spanned by the six substrates examined. A comparison of activation free energies (ΔG_{12}^*) and standard free energy changes (ΔG_{12}°) for the redox step, set out in Table II, clearly shows that there is no simple relationship between rate and thermodynamic driving force in the H₂Q-X/Ce(IV) sulfate system. In calculating standard free energy changes, we have assumed that the electron-transfer process is



where H₂SQ-X⁺ represents the semiquinone cation radical.

For reactions with small driving force and negligible electrostatic work terms, the equation of relative Marcus theory for outer-sphere electron transfer is¹⁰ given in eq 4, where

$$\Delta G_{12}^* = 0.5(\Delta G_{11}^* + \Delta G_{22}^*) + 0.5\Delta G_{12}^\circ \quad (4)$$

ΔG_{11}^* and ΔG_{22}^* represent the activation free energies of the reactant self-exchange reactions. Free energy changes in the H₂Q-X/Ce(IV) reactions are not consistent with this equation, as a linear least-squares analysis of ΔG_{12}^* , ΔG_{12}° pairs yields a correlation coefficient of 0.42 and a slope of 0.08 ± 0.09 instead of the predicted value of 0.5. Looked at in another way, the rate constant of the H₂Q/Ce(IV) reaction is substantially larger than the value estimated from the Marcus relationship (1.4 × 10⁴ M⁻¹ s⁻¹; based on $k_{11}(\text{H}_2\text{Q}/\text{H}_2\text{SQ}^+) = 5 \times 10^7$ M⁻¹ s⁻¹,¹¹ $k_{22}(\text{Ce(IV)}/\text{Ce(III)}) = 4.4$ M⁻¹ s⁻¹,¹² K_{12}

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= 0.91). With consideration only of $\text{H}_2\text{Q-OH}$, $\text{H}_2\text{Q-OCH}_3$, $\text{H}_2\text{Q-Br}$, and $\text{H}_2\text{Q-CH}_3$, the fit to the Marcus equation is more satisfactory, with a correlation coefficient and slope of 0.98 and 0.54 ± 0.08 , respectively. A range of only 1.0 kcal/mol in ΔG°_{12} is spanned by the reactions of these four substrates with Ce(IV), however, making it impossible to conclude safely that these reactions are outer-sphere or follow a different mechanism from the oxidations of H_2Q and $\text{H}_2\text{Q-SO}_3\text{H}$.

Excellent conformity to the Marcus relationship has been demonstrated in the reactions of substituted hydroquinones with numerous outer-sphere oxidants.⁶ Free energy correlations based on reactions of ceric sulfate with outer-sphere reductants (i.e., iron(II)¹³ and ruthenium(II)¹⁴ phenanthroline complexes, $\text{Fe}(\text{CN})_6^{4-}$,¹⁵ $\text{Mo}(\text{CN})_8^{4-}$,¹⁵ $\text{W}(\text{CN})_8^{4-}$)¹⁵ also accord well with Marcus theory. It appears likely, therefore, that an inner-sphere mechanism is employed in the reactions of $\text{H}_2\text{Q-X}$ with cerium(IV) sulfate. A zeroth order hydroquinone dependence has been reported in the reaction with Ce(IV) in perchlorate media, suggesting the presence of a stable inner-sphere intermediate complex.¹⁶ The first-order reductant dependences reported here also are consistent with an inner-sphere mechanism, considering the attenuation in precursor complex formation constants expected in sulfate media, where SO_4^{2-} competes strongly for positions in the first coordination sphere of cerium (ca. 93% of the Ce(IV) in 1 N H_2SO_4 is present as $\text{Ce}(\text{SO}_4)_3^{2-}$, 7% as $\text{Ce}(\text{SO}_4)_2$).¹⁷ The activation enthalpy of the hydroquinone-ceric sulfate reaction must reflect, for the most part, substitution of SO_4^{2-} by H_2Q in the first coordination sphere of cerium, as the rate of electron transfer within the $\text{H}_2\text{Q-cerium(IV)}$ perchlorate inner-sphere complex is independent of temperature ($\Delta H^\ddagger \approx 0$ kcal/mol).¹⁶

Rate constants for the one-electron oxidation of hydroquinone phosphate and hydroquinone sulfate by ceric sulfate are comparable to $k_{12}(\text{H}_2\text{Q})$, being smaller by factors of only 2 and 3, respectively, at 25 °C. By contrast, the oxidations of HQ-P and HQ-S by periodic acid, a two-electron acceptor, in strongly acidic solution are much slower, by factors of 3×10^2 ¹⁸ and 2×10^3 ,¹⁹ respectively, than the analogous oxidation of hydroquinone. Both of these substrates, $\text{HOC}_6\text{H}_4\text{OPO}_3\text{H}_2$ ($\text{p}K_1 = 1.5$)²⁰ and $\text{HOC}_6\text{H}_4\text{OSO}_3\text{H}$ ($\text{p}K_1 = 2.9$),²⁰ are fully protonated to the free acid forms in 1 N H_2SO_4 . Irreversible two-electron oxidation waves have been reported in cyclic voltammetric studies of HQ-P and HQ-S in 1 M H_2SO_4 .²⁰ An ECEC mechanism pertains in each case, with ester hydrolysis occurring only after loss of the second electron. The similarity of rate constants for reactions of ceric sulfate with hydroquinone, (4-hydroxyphenyl)phosphoric acid, and (4-hydroxyphenyl)sulfuric acid may be partially understood on this basis, as little stretching of the C-O (or P-O, S-O) bonds presumably is required in converting these reductants to the corresponding semiquinones. Substantial rate discrimination between hydroquinone and its esters (and among individual esters) will be observed only when ester hydrolysis accompanies the (two-electron) redox process.

The hydroquinone-ceric sulfate reaction exhibits a modest 2.5-fold rate increase as the hydrogen ion concentration is increased from 0.10 to 1.5 M at 25 °C, while the rate of the $\text{H}_2\text{Q-Ce(IV)}$ reaction in perchlorate media is independent of acidity in the interval $0.2 \leq [\text{H}^+] \leq 2.0$ M.¹⁶ Protonation of hydroquinone, as monitored by proton NMR spectroscopy, is detected only in superacid media,²¹ ruling this possibility out as a source of the kinetic hydrogen ion dependence. A plot of k_{12} vs. $[\text{H}^+]$ based on the data in Table III is sigmoidal, reminiscent of a titration curve with an inflection point corresponding to a $\text{p}K$ of ca. 0.1. The weak hydrogen ion dependence in the $\text{H}_2\text{Q-cerium(IV)}$ sulfate system may be linked to the protonation of SO_4^{2-} ions coordinated to Ce(IV) ($\text{p}K(\text{HSO}_4^-) = 0.43$, 25 °C, $I = 2.0$ M; see Table III).

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Registry No. HQ-P, 940-75-0; HQ-S, 17438-29-8; H_2Q , 123-31-9; $\text{H}_2\text{Q-CH}_3$, 95-71-6; $\text{H}_2\text{Q-SO}_3\text{H}$, 88-46-0; $\text{H}_2\text{Q-OCH}_3$, 824-46-4; $\text{H}_2\text{Q-OH}$, 533-73-3; $\text{H}_2\text{Q-Br}$, 583-69-7.

Supplementary Material Available: Table I, listing observed rate constants for the oxidation of hydroquinone esters and substituted hydroquinones by Ce(IV) (2 pages). Ordering information is given on any current masthead page.

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Magnetic Circular Dichroism of Cyclic π -Electron Systems. 22.^{1a} Derivatives of the Trisulfur Trinitride Anion

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Magnetic circular dichroism (MCD) of low-energy transitions in molecules derived from $(4N + 2)$ -electron cyclic conjugated perimeters can be interpreted simply by using the perimeter model.²⁻⁴ Of the three categories of parent perimeters [two π electrons, $N = 0$, two π holes, $N = (n/2) - 1$, and the rest, $N \neq 0$, $N \neq (n/2) - 1$], the third category is the largest and the predicted signs are a sensitive yet usually simply predictable function of molecular structure. The first two categories provide an interesting contrast to the third in that the MCD signs are predicted to be structure independent.

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