

Kinetics and Mechanisms of the Oxidation of Phenols by a *trans*-Dioxoruthenium(VI) Complex

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Received November 16, 2002

The kinetics of the oxidation of phenols by *trans*-[Ru^{VI}(L)(O)₂]²⁺ (L = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane) have been studied in aqueous acidic solutions and in acetonitrile. In H₂O the oxidation of phenol produces the unstable 4,4'-biphenoquinone, as evidenced by a rapid increase and then a slow decrease in absorbance at 398 nm. The first step is first-order in both Ru^{VI} and phenol, and rate constants are dependent on [H⁺] according to the relationship $k_t = k_x + (k_y K_a/[H^+])$, where k_x and k_y are the rate constants for the oxidation of PhOH and PhO⁻, respectively. At 298 K and $I = 0.1$ M, $k_x = 12.5$ M⁻¹ s⁻¹ and $k_y = 8.0 \times 10^8$ M⁻¹ s⁻¹. At $I = 0.1$ M and pH = 2.98, the kinetic isotope effects are $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 4.8$ and 0.74 for k_x and k_y , respectively, and $k(\text{C}_6\text{H}_5\text{OH})/k(\text{C}_6\text{D}_5\text{OH}) = 1.1$. It is proposed that the k_x step occurs by a hydrogen atom abstraction mechanism, while the k_y step occurs by an electron-transfer mechanism. In both steps the phenoxy radical is produced, which then undergoes two rapid concurrent reactions. The first is a further three-electron oxidation by Ru^{VI} and Ru^V to give *p*-benzoquinone and other organic products. The second is a coupling and oxidation process to give 4,4'-biphenoquinone, followed by the decay step, k_s . A similar mechanism is proposed for reactions in CH₃CN. A plot of log k_x vs O–H bond dissociation enthalpies (BDE) of the phenols separates those phenols with bulky *tert*-butyl substituents in the *ortho* positions from those with no 2,6-di-*tert*-butyl groups into two separate lines. This arises because there is steric crowding of the hydroxylic groups in 2,6-di-*tert*-butyl phenols, which react more slowly than phenols of similar O–H BDE but no 2,6-*tert*-butyl groups. This is as expected if hydrogen atom abstraction but not electron transfer is occurring.

Introduction

The oxidation of phenols has been extensively studied because of its relevance to a large number of biological processes.^{1–3} Among the various types of oxidants used, metal oxo species are of particular interest because a variety of mechanisms are apparently operating, depending on the nature of the metal oxo species. In the oxidation by chromium(VI) in perchloric acid, a hydride-transfer mechanism was suggested.⁴ In the case of [Ru^{IV}(bpy)₂(py)(O)]²⁺, a mechanism that involves electrophilic attack on the

aromatic ring was proposed.⁵ Evidence supporting this mechanism include a large kinetic isotope effect for the oxidation of C₆H₅OH versus C₆D₅OH in CH₃CN ($k_{\text{CH}}/k_{\text{CD}} = 5.5$), and ¹⁸O-labeling results. On the other hand, oxidation by [(H₂O)₅CrO]²⁺ occurs by a hydrogen-atom abstraction mechanism on the basis of the observation of 4,4'-biphenoquinone which arises from the coupling of phenoxy radicals and a large deuterium isotope effect ($k_{\text{C}_6\text{H}_5\text{OH}}/k_{\text{C}_6\text{H}_5\text{OD}} = 14.7$).⁶ For the oxidation by ferrate(VI), it was suggested that the reaction occurred by a one-electron transfer followed by deprotonation to produce phenoxy radicals.⁷

We report here results of a study on the kinetics and mechanisms of the oxidation of phenols in aqueous solutions and acetonitrile by a cationic *trans*-dioxoruthenium(VI)

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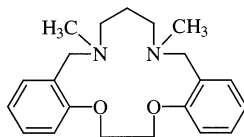


Figure 1. Structure of L.

complex, $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$, where L = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane, Figure 1, that was first synthesized by Che and co-workers.⁸ This complex contains a macrocyclic ligand that is resistant to oxidative degradation and ligand exchange. It is also a relatively strong oxidant with well-defined redox potentials, E° , for the $\text{Ru}^{\text{VI/V}}$ and $\text{Ru}^{\text{VI/IV}}$ couples of 0.94 and 1.14 V (pH = 1.1) vs NHE, respectively.⁸ The reduced oxidation states Ru^{V} , Ru^{IV} , and Ru^{III} have been isolated and/or characterized spectroscopically. The oxidation of aromatic hydrocarbons,⁹ alcohols,¹⁰ alkenes,¹¹ phosphites, and hypophosphites¹² by $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ have been reported.

Experimental Section

Materials. $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2][\text{PF}_6]_2$ was prepared by a literature method.⁸ (Anal. Found: C, 33.30; H, 3.90; N, 3.58. Calcd for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_4\text{P}_2\text{F}_{12}\text{Ru}$: C, 33.0; H, 3.7; N, 3.7%.) Phenol (Johnson and Matthey) was used as received and was standardized by iodometry.¹³ 4-Methoxyphenol (96%, Sigma) was purified by recrystallization from water.¹⁴ Other substituted phenols were purchased from Aldrich and were used as received. Water for kinetic experiments was distilled twice from alkaline permanganate. Ionic strength was maintained with sodium trifluoroacetate. Acetonitrile was stirred with KMnO_4 overnight and then distilled. It was further distilled over P_2O_5 under nitrogen. Phenol- d_6 (98+ atom %, Aldrich) and D_2O (99.8 atom % D, Acros) were used as received. For D_2O solutions the pD were determined either by direct titration with standard NaOH solutions and/or by using a pH meter using the relationship $\text{pD} = \text{pH}_{\text{meas}} + 0.4$.

Kinetics. Kinetic experiments were performed with the phenolic compound in >10-fold excess using either a Hi-Tech SF-61 stopped-flow spectrophotometer or a Hewlett-Packard 8452A diode-array spectrophotometer. The progress of the reaction was monitored by measuring absorbance changes at 398 nm. For reactions that occur in two steps the sequential pseudo-first-order rate constants were calculated by fitting the kinetic trace to a biexponential function.¹⁵

Products. The ruthenium product was determined by the following procedure. A known amount of $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ (1.0×10^{-4} M) was allowed to react with an excess of phenol (1.0×10^{-3} M) at 25 °C and pH = 2.0. The resulting solution was

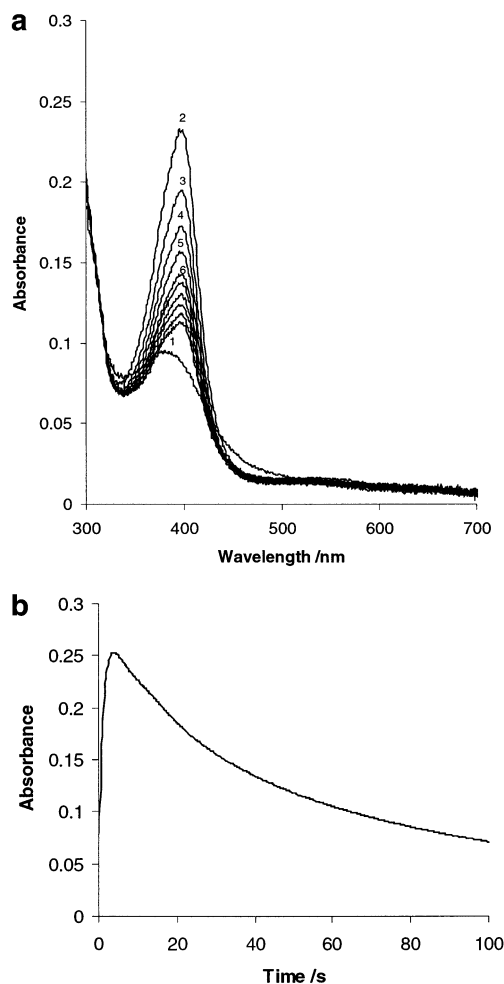


Figure 2. (a) Spectrophotometric changes at 10-s intervals during the oxidation of excess phenol (1.28×10^{-2} M) by $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ (4.0×10^{-5} M) at 298.2 K ($I = 0.1$ M; pH = 2.7). (b) Absorbance change versus time at 400 nm.

loaded onto a Sephadex-SP C-25 cation-exchange column. By elution with 0.2 M $\text{CF}_3\text{CO}_2\text{H}$ and examination of the UV-vis spectrum of the solution, $trans\text{-}[\text{Ru}^{\text{IV}}(\text{L})(\text{O})(\text{OH}_2)]^{2+}$ ($\lambda_{\text{max}} = 265$ nm, $\epsilon = 2400 \text{ M}^{-1} \text{ cm}^{-1}$)⁸ was found to be produced quantitatively.

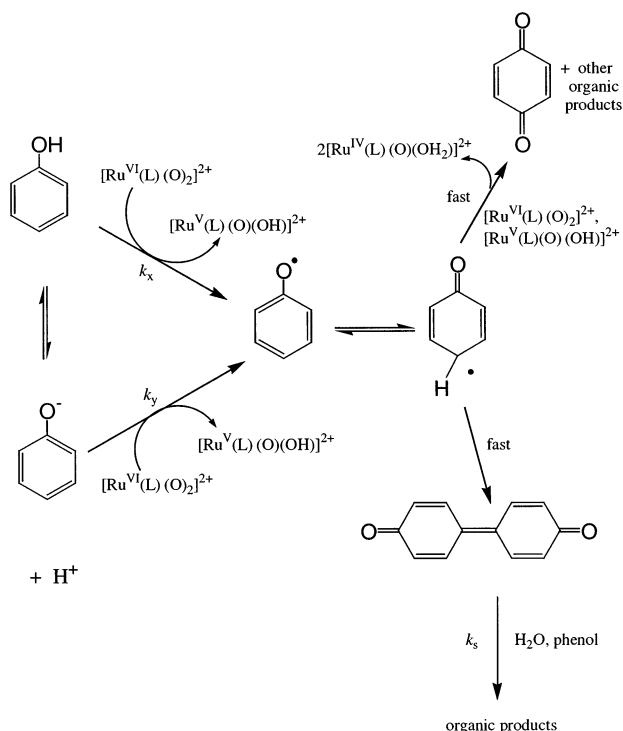
The organic products were determined by using an HP 6890 gas chromatograph with an Ultra2 capillary column. GC-MS measurements were carried out on an HP5890 gas chromatograph interfaced to a HP5970 mass selective detector. In a typical experiment 5.85×10^{-3} mmol of Ru^{VI} was mixed with 0.165 mmol of PhOH in 1.8 mL of H_2O (pH = 2.0) at room temperature. Analysis by GC and GC-MS after 1 h using cyclohexanone as the internal standard indicated that 1.93×10^{-3} mmol of *p*-benzoquinone was produced and no *o*-benzoquinone could be detected. The yield is 66% since 2 mol of Ru^{VI} is required to produce 1 mol of *p*-benzoquinone. In CH_3CN , again *p*-benzoquinone was the only organic product that could be detected by GC, but the yield was only 16%.

Results

Reactions in H_2O . Spectrophotometric Changes and Products. Figure 2 shows absorbance changes occurring for an aqueous solution initially containing 13.8 mM phenol and 0.06 mM $trans\text{-}[\text{Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ at pH = 2.7. The initial Ru^{VI} species has a λ_{max} of 385 nm ($\epsilon = 2510 \text{ M}^{-1} \text{ cm}^{-1}$).⁸ On mixing with excess phenol, there is rapid increase in

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Scheme 1



absorbance to give an intermediate with λ_{max} at 398 nm, which then slowly decays. This observation is very similar to that of the oxidation by $[\text{Cr}(\text{O})(\text{H}_2\text{O})_5]^{2+}$,⁶ and is consistent with the buildup and decay of 4,4'-biphenylquinone, a minor product that absorbs strongly with a peak at 398 nm ($\epsilon = 69\,000\text{ M}^{-1}\text{ cm}^{-1}$) in CHCl_3 .^{16,17} The intermediate is formed by rapid coupling of phenoxyl radicals and further oxidation, and in aqueous solutions it slowly decomposes to other organic products.^{18,19} Analysis of the reaction mixture by GC and GC-MS indicated that *p*-benzoquinone is formed, but *o*-benzoquinone detected. The ruthenium product was found to be *trans*- $[\text{Ru}^{\text{IV}}(\text{L})(\text{O})(\text{OH}_2)]^{2+}$.

Kinetics. The kinetics were followed at 398 nm, the absorption maximum of the 4,4'-biphenylquinone intermediate. With > 10-fold excess of phenol, first-order rate constants for the formation and decay of the intermediate were obtained using a biexponential fitting procedure.¹⁵ The formation step (k_f) was first-order in the phenol and Ru^{VI} oxidant. The first-order dependence on the phenol indicates that 4,4'-biphenylquinone is not a primary product and formation of a phenoxyl radical (which exists in rapidly equilibrating tautomeric forms) is proposed, Scheme 1. This gives *p*-benzoquinone and 4,4'-biphenylquinone in rapid competing steps. The second stage (k_s) corresponds to the decay of 4,4'-biphenylquinone in aqueous solutions and is also first-order in the phenol. Rate constants for both stages are independent of $[\text{O}_2]$.

Acidity and Ionic Strength Effects. The effects of acidity on both steps were studied over the pH range 1–3 at 25.0

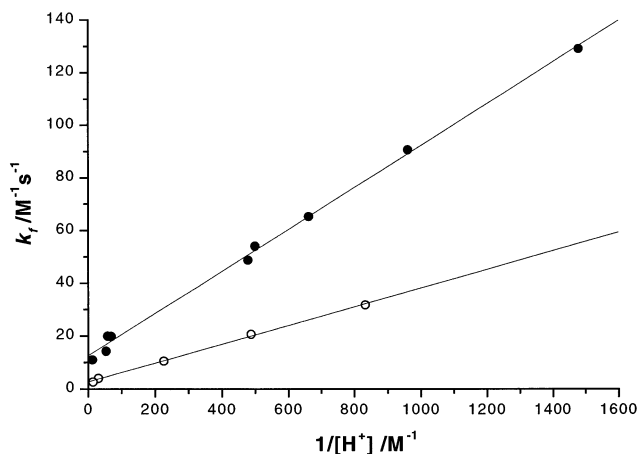


Figure 3. Plot of k_f vs $1/[\text{H}^+]$ (solid circle) and $1/[\text{D}^+]$ (open circle) for the oxidation of phenol by *trans*- $[\text{Ru}(\text{L})(\text{O})_2]^{2+}$ at $T = 298.0\text{ K}$ and $I = 0.1\text{ M}$.

$^\circ\text{C}$. At $\text{pH} > 3$ *trans*- $[\text{Ru}(\text{L})(\text{O})_2]^{2+}$ is not very stable. The rate of the fast step was found to decrease with an increase in $[\text{H}^+]$, and a plot of k_f against $1/[\text{H}^+]$ is linear (Figure 3). This is consistent with the following relationship:

$$k_f = k_x + (k_y K_a / [\text{H}^+]) \quad (1)$$

K_a is the acid dissociation constant of phenol and is taken as $1 \times 10^{-10}\text{ M}$ at $25\text{ }^\circ\text{C}$.²⁰ The rate constants k_x and k_y are for the oxidation of PhOH and PhO^- respectively. These rate constants were evaluated by nonlinear least-squares fits of the data to eq 1; at 298 K and $I = 0.1\text{ M}$, $k_x = (1.25 \pm 0.10) \times 10\text{ M}^{-1}\text{ s}^{-1}$ and $k_y = (7.96 \pm 0.16) \times 10^8\text{ M}^{-1}\text{ s}^{-1}$. Rate constants for the slow step were found to increase with acidity.

The effect of ionic strength on the rate of the fast step was investigated from 0.1 to 1.0 M. k_f was found to decrease with an increase in ionic strength, but the effect was rather small.

Activation Parameters. The effects of temperature were studied from 10.4 to 40.4 $^\circ\text{C}$ at $\text{pH} 1\text{--}3$ and $I = 0.1\text{ M}$. Activation parameters were obtained from plots of $\ln(k_x/T)$ or $\ln(k_y/T)$ versus $1/T$ according to the Eyring equation. For the k_x step, $\Delta H^\ddagger = (47.4 \pm 3.4)\text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = (-60 \pm 11)\text{ J mol}^{-1}\text{ K}^{-1}$. For the k_y step, $\Delta H^\ddagger = (41.7 \pm 2.2)\text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = (64 \pm 7)\text{ J mol}^{-1}\text{ K}^{-1}$.

Kinetic Isotope Effects. The kinetics were also carried out in D_2O at $\text{pD} 1\text{--}3$, and a similar dependence on acidity was obtained (Figure 3):

$$k_f' = k_x' + (k_y' K_a' / [\text{D}^+]) \quad (2)$$

Using a $\text{p}K_a'$ of 10.48 M for phenol in D_2O ,²⁰ $k_x' = (2.59 \pm 0.38)\text{ M}^{-1}\text{ s}^{-1}$ and $k_y' = (1.07 \pm 0.08) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ at 298 K and $I = 0.1\text{ M}$. The solvent kinetic isotope effect for the oxidation of the phenol molecule $k_x/k_x' = 4.8 \pm 0.4$, while that of the phenolate ion was $k_y/k_y' = 0.74 \pm 0.06$. On the other hand, the oxidation of $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{D}_5\text{OH}$ in H_2O

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Table 1. Second-Order Rate Constants for the Oxidation of Substituted Phenols (X-PhOH) by $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ in H_2O ($\text{pH} = 1.10$; $I = 0.1 \text{ M}$) and CH_3CN at $25.0 \text{ }^\circ\text{C}$

X	O-H BDE/ kcal mol ⁻¹	$k_x(\text{H}_2\text{O})/\text{M}^{-1} \text{ s}^{-1}$	$k_x(\text{CH}_3\text{CN})/\text{M}^{-1} \text{ s}^{-1}$
H	87.05	$(1.10 \pm 0.04) \times 10$	2.36 ± 0.09
2-Me	85.05	$(1.38 \pm 0.04) \times 10^2$	$(1.66 \pm 0.06) \times 10$
3-Me	86.65	$(2.32 \pm 0.05) \times 10$	9.46 ± 0.08
3-CF ₃	89.15	$(5.69 \pm 0.10) \times 10^{-1}$	$(4.17 \pm 0.11) \times 10^{-1}$
3-CN	89.75	$(2.00 \pm 0.07) \times 10^{-1}$	$(1.19 \pm 0.06) \times 10^{-1}$
4-MeO	80.95	$(8.94 \pm 0.22) \times 10^4$	$(3.06 \pm 0.06) \times 10^3$
4-Me	84.58	$(1.89 \pm 0.03) \times 10^2$	$(1.25 \pm 0.04) \times 10$
4- <i>t</i> -Bu	84.76	$(1.36 \pm 0.04) \times 10^2$	$(1.89 \pm 0.03) \times 10$
4-Cl	85.65	$(1.87 \pm 0.05) \times 10$	7.77 ± 0.20
4-CN	89.25	$(8.03 \pm 0.21) \times 10^{-2}$	$(2.23 \pm 0.07) \times 10^{-1}$
2-Cl-4-Me	85.55		$(1.84 \pm 0.05) \times 10$
2,4-di- <i>t</i> -Bu	81.85		$(1.35 \pm 0.02) \times 10^2$
3,5-di- <i>t</i> -Bu	85.68		7.54 ± 0.10
2,6-di- <i>t</i> -Bu	81.65		$(5.80 \pm 0.08) \times 10^{-1}$
2,6-di- <i>t</i> -Bu-4-Me	79.15		$(2.63 \pm 0.09) \times 10$
2,6-di- <i>t</i> -Bu-4-MeO	75.55		$(2.56 \pm 0.07) \times 10^{-4}$

shows little kinetic isotope effect, $k_f(\text{C}_6\text{H}_5\text{OH})/k_f(\text{C}_6\text{D}_5\text{OH}) = 1.1 \pm 0.1$ at $I = 0.1 \text{ M}$ and $\text{pH} = 2.98$.

Oxidation of Substituted Phenols. The oxidation of various substituted phenols was also investigated at $\text{pH} = 1.1$; at this pH the pathway involving oxidation of the phenolate anion is insignificant, and $k_f \approx k_x$. The spectrophotometric changes for the oxidation of *ortho*-substituted phenols showed the same biphasic behavior as for the parent phenol. However, for *meta*- and *para*-substituted phenols no intermediate formation of the highly absorbing 4,4'-biphenylquinone derivatives was observed. Instead the spectral changes revealed only decay of $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ ($\lambda_{\text{max}} = 385 \text{ nm}$) to $trans\text{-[Ru}^{\text{IV}}(\text{L})(\text{O})(\text{OH}_2)]^{2+}$. For the *meta*- and *para*-substituted phenols the decay at 385 nm followed first-order kinetics and the pseudo-first-order rate constants depended linearly on $[\text{PhOH}]$. Representative second-order rate constants are shown in Table 1.

Reactions in CH_3CN . The spectrophotometric changes during the oxidation of excess phenol ($1.06 \times 10^{-2} \text{ M}$) by $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ ($5.0 \times 10^{-5} \text{ M}$) in CH_3CN at 298 K reveal a rapid and large increase in absorbance at 385 nm , consistent with the formation of 4,4'-biphenylquinone. The subsequent decrease in absorbance is much slower than in H_2O , indicating that 4,4'-biphenylquinone is much more stable in CH_3CN than in H_2O . The increase in absorbance at 385 nm followed first-order kinetics and the pseudo-first-order rate constants depended linearly on $[\text{PhOH}]$. The second-order rate constants (k_2) are slower than that in H_2O by a factor of about 5. Oxidations of various substituted phenols were also studied, and more substrates could be investigated than in H_2O due to the more favorable solubility. The spectrophotometric changes for the oxidation of *ortho*-substituted phenols are similar to those of the parent phenol. However, as in the case of H_2O , no intermediate formation of 4,4'-biphenylquinone derivatives were observed for *meta*- and *para*-substituted phenols, and the spectral changes indicated the conversion of $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ ($\lambda_{\text{max}} = 385 \text{ nm}$) to $trans\text{-[Ru}^{\text{IV}}(\text{L})(\text{O})(\text{CH}_3\text{CN})]^{2+}$. For the *meta*- and *para*-substituted phenols, the decay at 385 nm followed first-order kinetics and the pseudo-first-order rate constants depended linearly on $[\text{PhOH}]$. Representative second-order

rate constants are shown in Table 1. As in H_2O , the oxidation of $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{D}_5\text{OH}$ in CH_3CN shows little kinetic isotope effect, $k_2(\text{C}_6\text{H}_5\text{OH})/k_2(\text{C}_6\text{D}_5\text{OH}) = 1.3 \pm 0.1$ at 298 K .

Discussion

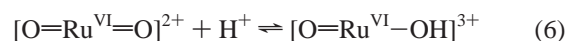
Overview of the Reactions. In the presence of excess phenol, $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ is rapidly reduced to $trans\text{-[Ru}^{\text{IV}}(\text{L})(\text{O})(\text{OH}_2)]^{2+}$ in H_2O and to $trans\text{-[Ru}^{\text{IV}}(\text{L})(\text{O})(\text{CH}_3\text{CN})]^{2+}$ in CH_3CN . No intermediate Ru^{V} species was observed, as in the oxidation of other substrates by $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$.⁹⁻¹² In acidic solutions Ru^{V} is a stronger oxidant than Ru^{VI} and is more rapidly reduced once it is formed.⁸

The results obtained in this study show that the oxidation of phenols by $trans\text{-[Ru}^{\text{VI}}(\text{L})(\text{O})_2]^{2+}$ begins with the formation of the phenoxyl radical, as evidenced by the observation of the strongly absorbing 4,4'-biphenylquinone intermediate at 398 nm for the parent and *ortho*-substituted phenols. Radical coupling was not the only reaction of the phenoxyl radical, since *p*-benzoquinone, which arises from further oxidation of the phenoxyl radical, was also produced. For *meta*- and *para*-substituted phenols, no such intermediates were observed, and the spectral changes were consistent with the direct conversion of Ru^{VI} to Ru^{IV} . This may be due to a slow of the radical coupling step due to steric effects, so that further oxidation of the phenoxyl radical by ruthenium oxo species becomes the predominant pathway.

The observed acid dependence of k_f is consistent with the following scheme:



Here k_x and k_y correspond to the rate constants for the reduction of Ru^{VI} by the neutral phenol molecule and the phenolate anion, respectively. The ratio of k_x/k_y is 4×10^8 at 298 K and $I = 0.1 \text{ M}$. The observed acid dependence may also be accounted for by a pathway that involves protonated Ru^{VI} species:



This pathway is, however, unlikely since no evidence of protonation of Ru^{VI} was observed in acid concentrations of up to 5 M , as monitored by UV-vis spectroscopy. Moreover, the rate of oxidation of $cis\text{-[Ru}(\text{NH}_3)_4(\text{isn})_2]^{2+}$ ($\text{isn} = \text{isonicotinamide}$) by Ru^{VI} was independent of acidity at $\text{pH} 1-3$.²¹

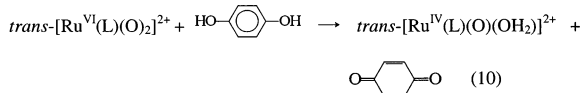
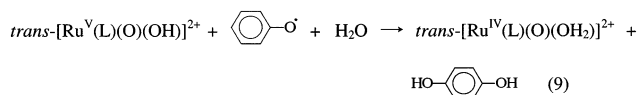
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Our results show that in aqueous solutions parallel pathways occur for the oxidation of the neutral phenol molecule ArOH and the phenoxide ion ArO⁻. The mechanisms for the oxidation of ArOH in H₂O and CH₃CN and of ArO⁻ in aqueous solutions are discussed below.

Mechanism of Oxidation of ArOH. In aqueous solutions the large kinetic isotopic effect for the oxidation of C₆H₅-OH in H₂O versus C₆H₅OD in D₂O ($k_x/k_x' = 4.8$) and the small kinetic isotope effect of 1.1 for the oxidation of C₆H₅-OH versus C₆D₅OH indicate that the rate-determining step involves O–H but not C–H cleavage. This is also supported by the result that the rate constants for the oxidation of *o*-cresol and *p*-cresol are similar but are larger than that of *m*-cresol.⁶ An opposite trend is expected for C–H cleavage since among the cresol isomers the most stable radical resulting from C–H abstraction is expected to come from *m*-cresol. A hydrogen atom abstraction mechanism for the oxidation of phenol by Ru^{VI}, similar to that by [(H₂O)₅-CrO]²⁺,⁶ is proposed in Scheme 1.

According to Scheme 1 the first step in the reaction between Ru^{VI} and phenol involves hydrogen atom abstraction by Ru^{VI} to form a phenoxyl radical that is in equilibrium with its carbon-centered tautomer. This then undergoes two rapid competitive reactions, a further three-electron oxidation by Ru^{VI} and Ru^V to benzoquinone and possibly other organic products²² and coupling followed by oxidation to 4,4'-biphenoquinone. The latter decays more slowly to give other organic products; this decomposition arises from acid-catalyzed self-decomposition and from a reaction with the phenol to produce products such as biphenol.^{6,18} The three-electron oxidation of the phenoxyl radical to benzoquinone is brought about by *trans*-[Ru^V(L)(O)(OH)]²⁺ as well as *trans*-[Ru^{VI}(L)(O)₂]²⁺ (eqs 9 and 10).²²

Independent experiments showed that the oxidation of hydroquinone by Ru^{VI} occurs much more rapidly than that of phenol.



In CH₃CN, the coupling product 4,4'-biphenoquinone was also observed for the parent phenol and *ortho*-substituted phenols. As in the case of H₂O, 4,4'-biphenoquinone was not observed for phenols with substituents in *meta* or *para* positions. The small kinetic isotope effect of 1.1 for the oxidation of C₆H₅OH versus C₆D₅OH and the reactivity order of *ortho* ≈ *para* > *meta* for the oxidation of methylphenols suggest that a similar hydrogen atom abstraction mechanism for the oxidation of phenols occurs in CH₃CN as in H₂O.

(22) Although *p*-benzoquinone was the only organic product detected by GC, oxidation of the phenoxyl radical to give other undetected products cannot be ruled out.

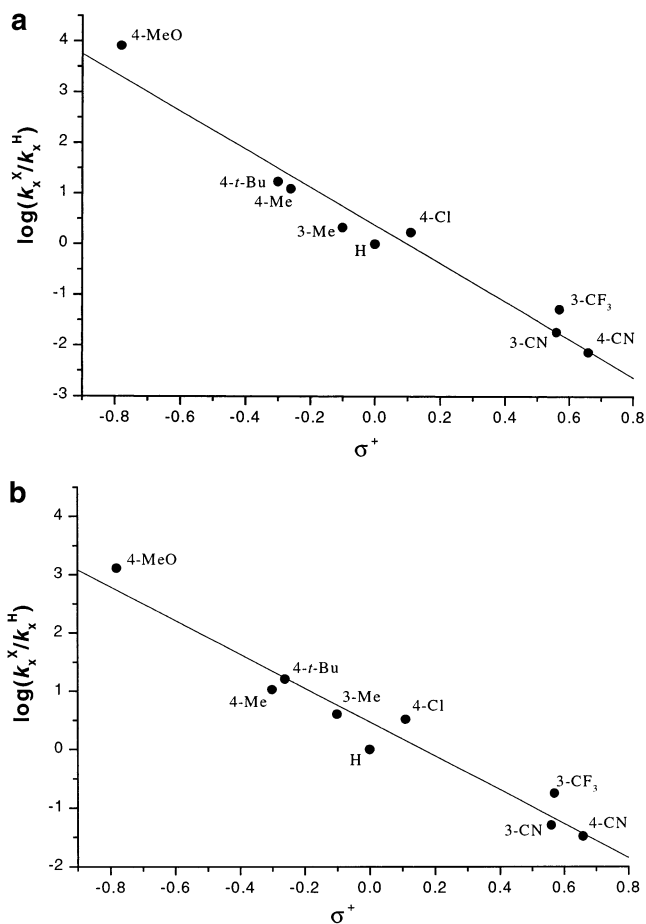


Figure 4. Hammett plot of $\log(k_x^X/k_x^H)$ vs σ^+ for the oxidation of substituted phenols by *trans*-[Ru(L)(O)₂]²⁺ at 298.0 K: (a) in H₂O (pH = 1.10; *I* = 0.1 M); (b) in CH₃CN.

The phenoxyl radical produced either undergoes coupling or is further oxidized by the ruthenium oxo species.²³

Hammett Correlation. The electronic effects of a substituent X in the *meta* or *para* position on the rate constant have been correlated by the Hammett equation, $\log(k_x^X/k_x^H) = \rho\sigma^+$.²⁴ The plot of $\log(k_x^X/k_x^H)$ against σ^+ is reasonably linear for reactions in H₂O as well as in CH₃CN (Figure 4), with the slopes $\rho = -3.76 \pm 0.30$ and -2.90 ± 0.25 , respectively. The negative reaction constants are consistent with the formation of the electron-deficient phenoxyl radical intermediate. A good correlation between rate constants and σ^+ has also been observed for hydrogen abstraction of phenols by *tert*-butyl radicals.²⁵

Correlation of Rates with Oxidation Potentials of Phenols. The oxidation potentials of a variety of phenols have been determined by cyclic voltammetry, which are irreversible for most phenols.²⁶ Figure 5 shows the plot of $\log k_x$ vs oxidation potentials of the phenols for reactions in both H₂O and CH₃CN. For an electron-transfer mechanism,

(23) The low yield of *p*-benzoquinone suggests that in CH₃CN the majority of the phenoxyl radicals were oxidized by the ruthenium oxo species to other undetected products.

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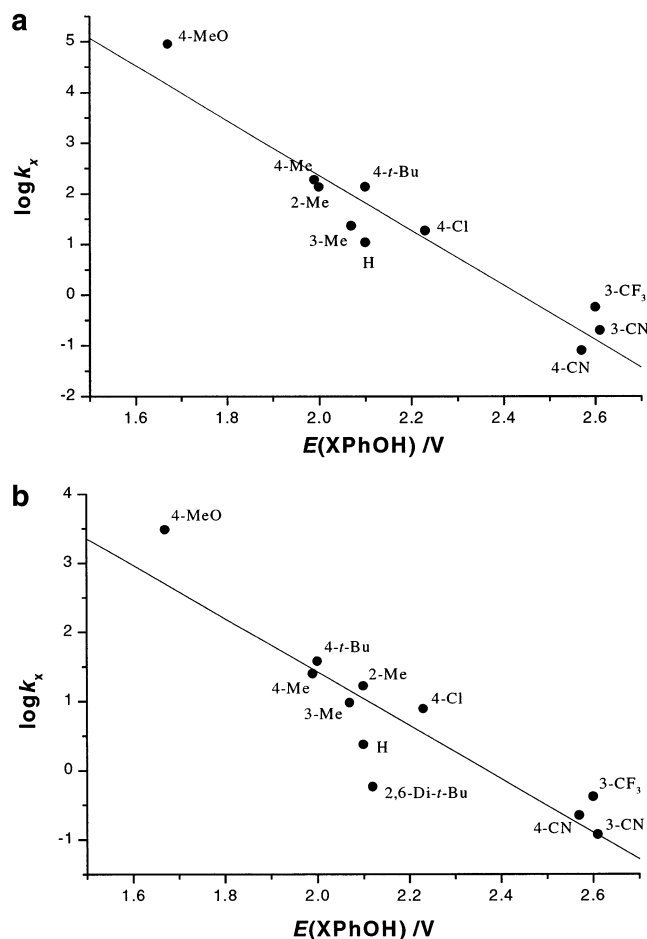


Figure 5. Plot of $\log k_x$ vs oxidation potentials (vs $\text{FeCp}_2^+/\text{FeCp}_2$) for the oxidation of phenols by $\text{trans-}[\text{Ru}(\text{L})(\text{O})_2]^{2+}$ at 298.0 K: (a) in H_2O ($\text{pH} = 1.10$; $I = 0.1 \text{ M}$); (b) in CH_3CN .

such a plot should be approximately linear or slightly curved since the reactions occur in the endergonic region. However, the points are rather scattered, which is not expected for an electron-transfer mechanism. No further attempts were made to fit these data to the Marcus equations, since accurate redox potentials values are not available.

Correlation of Rates with Phenolic O–H Bond Strengths. The rate constants (k_x) for the oxidation of the phenols were found to decrease with an increase in the O–H bond dissociation enthalpies (BDE) of the phenols as shown in Table 1.²⁷ In aqueous solutions a linear correlation was obtained when the logarithms of the rate constants at 298 K are plotted against the O–H BDE's of the phenols for a series of monosubstituted phenols that do not contain any bulky substituent in the *ortho* positions (Figure 6a). For the same plot in CH_3CN (Figure 6b), it was found that phenols without any bulky *tert*-butyl substituent in the *ortho* positions fall on one straight line. However, phenols that contain 2,6-di-*tert*-butyl groups react much more slowly than phenols of similar O–H BDE but with no such bulky groups. For example the rate constant for the oxidation of 2,6-di-*tert*-butyl phenol (O–H BDE = $81.65 \text{ kcal mol}^{-1}$) is slower than

(27) The gas-phase BDE values calculated by Wright et al. were used.²⁸ Although the O–H BDE of phenols are dependent on solvent, the relative O–H bond strength is essentially invariant with solvent.^{29,30}

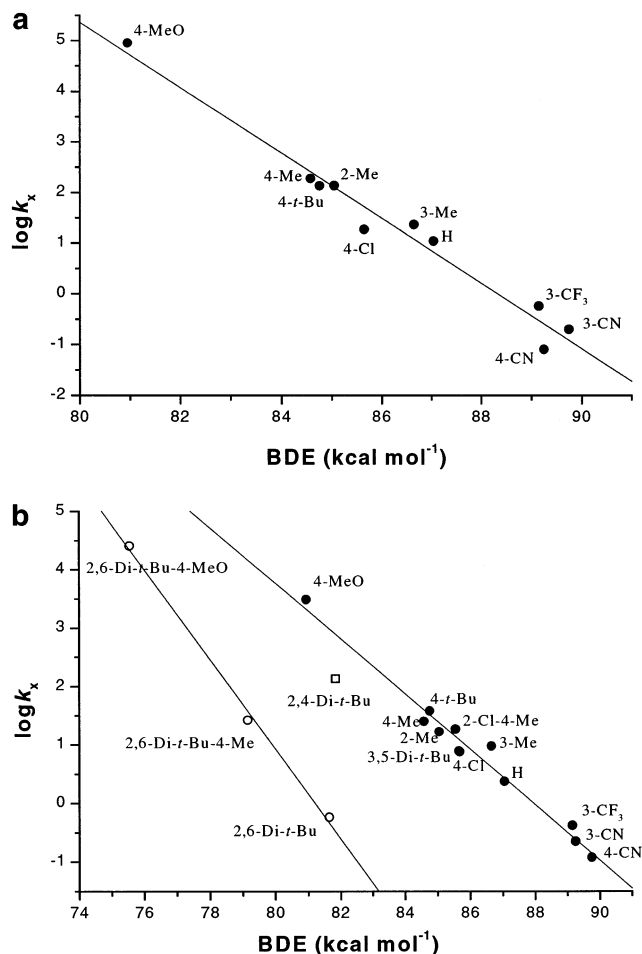


Figure 6. Plot of $\log k_x$ vs O–H BDE for the oxidation of phenols by $\text{trans-}[\text{Ru}(\text{L})(\text{O})_2]^{2+}$ at 298.0 K: (a) in H_2O ($\text{pH} = 1.10$; $I = 0.1 \text{ M}$); (b) in CH_3CN .

that of 4-methoxyphenol (O–H BDE = $80.95 \text{ kcal mol}^{-1}$) by a factor of 5×10^3 . The rate constant for the oxidation of 2,4-di-*tert*-butylphenol (O–H BDE = $81.85 \text{ kcal mol}^{-1}$), which has one *tert*-butyl group in the *ortho* position, is slower than that of 4-methoxyphenol by a factor of 20 but is faster than that of 2,6-di-*tert*-butyl phenol by a factor of 2×10^2 . In the plot of $\log k_x$ vs BDE, phenols with 2,6-di-*tert*-butyl groups fall on a separate line, while 2,4-di-*tert*-butylphenol lies between the two lines. Evidently steric crowding about the hydroxylic group is very important in decreasing the reactivity of the phenols, which is expected for a hydrogen atom abstraction mechanism but not for an electron-transfer mechanism. Similar steric effects have been observed in hydrogen atom abstraction from phenols by peroxy radicals³¹ and alkyl radicals.³² Correlations between rate constants and C–H BDE have also been observed in the oxidation of

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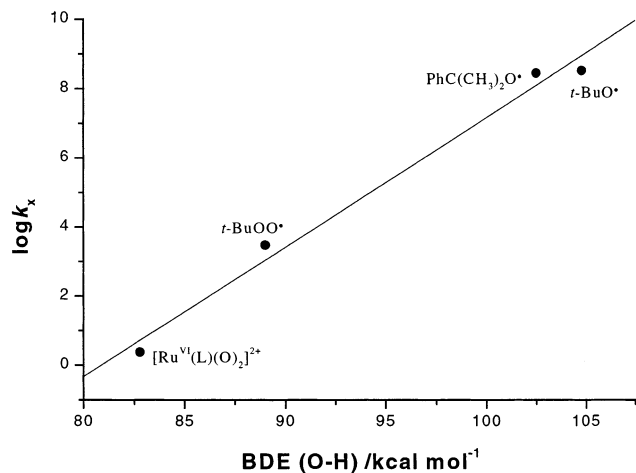


Figure 7. Plot of rate constants at 298 K for hydrogen atom abstraction of phenol by oxygen radicals and *trans*-[Ru(L)(O)₂]²⁺ vs the strength of the O–H bond.

alkylaromatics by metal–oxo species such as CrO₂Cl₂ and MnO₄[–].^{33–36}

Correlation with Hydrogen Atom Abstraction by Radical Species. The O–H bond strength (*D*) in [O=Ru^V(L)O–H]²⁺ can be calculated using the following equation, which is derived from a thermochemical cycle:^{35–40}

$$D(\text{O}=\text{Ru}^{\text{V}}-\text{O}-\text{H}) = 23.06E^{\circ} + 1.37\text{p}K_{\text{a}} + C \quad (11)$$

With use a value of 0.94 V (vs NHE) for *E*^o of the *trans*-[RuL(O)₂]²⁺/*trans*-[RuL(O)₂]⁺ couple,⁸ 1.19 for the p*K*_a of [O=Ru^V(L)O–H]²⁺,²¹ and 59.5 kcal/mol for the constant *C* in CH₃CN,⁴¹ *D*(O=Ru^V–O–H) is calculated to be 82.8 kcal/mol (assuming that the entropies of [Ru(L)(O)₂]²⁺ and [Ru(L)(O)(OH)]²⁺ are equal).

Figure 7 shows a plot of log *k*_x (the rate constant for hydrogen atom abstraction) vs the strength of the O–H bond formed for a number of oxygen radicals^{36,42} and [Ru^{VI}(L)(O)₂]²⁺. It should be noted that the rate constants for the oxygen radicals are measured in hydrocarbon solvents, and they should be lower if measured in CH₃CN,³⁰ the solvent for the reaction of [Ru^{VI}(L)(O)₂]²⁺. Nevertheless there is a reasonably good correlation, which is similar to those found for the oxidation of alkylaromatics by ⁿBu₄NMnO₄ and manganese phenanthroline *μ*-oxo dimers.^{35,36,43}

This is further evidence for a hydrogen atom abstraction mechanism in the oxidation of phenols by [Ru^{VI}(L)(O)₂]²⁺.

Mechanism of the Oxidation of PhO[–] to PhO•. The oxidation of the phenoxide ion to the phenoxyl radical in aqueous solutions probably occurs by a simple outer-sphere mechanism. This is supported by the agreement of the experimental rate constant *k*_y with the theoretical rate constant for outer-sphere electron transfer (*k*₁₂) using the Marcus cross-relation,⁴⁴ eqs 12 and 13 (neglecting work terms):

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (12)$$

$$\log f_{12} = (\log K_{12})^2/4 \log(k_{11}k_{22}/10^{22}) \quad (13)$$

The equilibrium constant for the reaction, *K*₁₂ = 2.5 × 10⁴, is calculated from the reduction potentials for the [Ru^{VI}(L)(O)₂]²⁺/[Ru^V(L)(O)₂]⁺ (0.94V vs NHE)⁸ and the PhO•/PhO[–] (0.68V vs NHE at pH = 3.0)⁴⁵ couples. A value of 1 × 10⁵ M^{–1} s^{–1} is used for *k*₁₁, the self-exchange rate for the [Ru^{VI}(L)(O)₂]²⁺/[Ru^V(L)(O)₂]⁺ couple;²¹ *k*₂₂, the self-exchange rate for PhO•/PhO[–], is taken as 1 × 10⁸ M^{–1} s^{–1}.^{46,47} Using these data *k*₁₂ is calculated to be 2.7 × 10⁸ M^{–1} s^{–1} at 298 K, which is in good agreement with the value of 7.1 × 10⁸ M^{–1} s^{–1} (*I* = 0.1 M) for *k*_y. The positive entropy of activation for this step can be accounted for by the release of solvated and hydrogen-bonded water molecules as a result of the combination of the oppositely charged ions ([Ru(L)(O)₂]²⁺ and PhO[–]) in the transition state.

Concluding Remarks

Our results indicate that, in both H₂O and CH₃CN, oxidation of the phenolic compounds ArOH by *trans*-[Ru^{VI}(L)(O)₂]²⁺ proceeds via a hydrogen atom abstraction mechanism. It should be noted that, on the basis of a large kinetic isotope effect alone, an alternative mechanism that involves initial electron transfer to produce ArOH⁺, followed by proton transfer to give ArO•, cannot be ruled out. For example, large deuterium isotope effects (*k*_{ArCH₃}/*k*_{ArCD₃}) have been observed in the oxidation of methylarenes by iron(III) complexes⁴⁸ and photoactivated quinones.⁴⁹ However, these reactions occur via initial electron transfer to produce ArCH₃⁺, followed by proton transfer, and the large kinetic isotope effects arise from proton transfer and not from hydrogen atom transfer. On the other hand, in the oxidation of ArOH by *trans*-[Ru^{VI}(L)(O)₂]²⁺, the observation of a correlation between rate constant and BDE is more consistent with a hydrogen atom abstraction mechanism. More importantly, the rates constants are subject to large steric effects by bulky groups in the *ortho* positions; such effects are not expected to occur for an electron-transfer process. It should

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also be noted that in the oxidation of phenols by IrCl_6^{2-} , where an outer-sphere electron transfer mechanism is most likely, only a small deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.7$ for the oxidation of 2,6-dimethylphenol) was observed.⁵⁰

Acknowledgment. The work described in this paper was supported by the Research Grants Council of Hong Kong

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(Grant CityU 1097/98P) and the City University of Hong Kong (Grant 7100195). We thank Prof. A. G. Sykes for helpful discussions.

Supporting Information Available: Kinetic data and spectral changes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC026184V