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Kinetics and Mechanism of the Oxidation of Phenols by the Oxochromium(IV) Ion

Ahmad Al-Ajlouni, Andreja Bakac,* and James H. Espenson*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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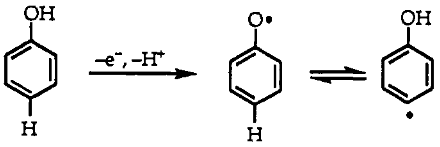
The oxidation of phenols by the pentaaquaoxochromium(IV) ion, $(H_2O)_5CrO^{2+}$, in acidic aqueous solutions yields *p*-benzoquinone as a major product. Small amounts of the unstable 4,4′-biphenoquinone were also produced, as evidenced by an increase (fast stage) and then a decrease (slow stage) in absorbance at 400 nm where there is an intense absorption band. The fast stage is first-order in CrO^{2+} and first-order in phenol. The slow stage follows a first-order exponential decay. There is a large kinetic isotope effect for the first stage, $k_H/k_D = 14.7$, on deuteration of the hydroxylic hydrogen. There is, however, no kinetic isotope effect of deuteration of the C–H hydrogen, $k_H/k_D \sim 1.0$. The rate constants for different meta-substituted phenols follow the Hammett relationship with $\rho = -1.7$. The activation parameters are $\Delta H^{\ddagger} = 15.2 \pm 1.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -144 \pm 15$ J mol^{-1} K^{-1}. We propose a mechanism according to which the phenols are first oxidized by one electron to the corresponding phenoxyl radicals; this occurs by hydrogen atom abstraction. The superoxochromium(III) ion, $(H_2O)_5CrO_2^{2+}$, which is also present in solution, then oxidizes the phenoxyl radical to benzoquinone. The rate constants for both stages increase with increasing ionic strength of the medium. The solution acidity was found to decrease the rate of the first stage and enhance the rate of the second, but both effects are relatively small. The activation parameters for the second stage are $\Delta H^{\ddagger} = 46 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -129 \pm 11$ J mol^{-1} K^{-1}.

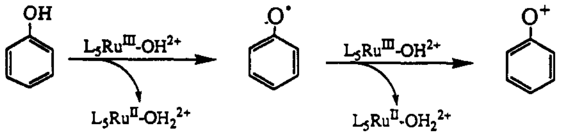
Introduction

Phenols serve as inhibitors of free radical autoxidations because they undergo facile reactions with alkyl peroxyl radicals.[1] The catalytic and noncatalytic activations of O_2 toward phenols by transition metals have therefore been studied extensively.[2,3] These reactions often take place by a radical mechanism wherein a hydrogen atom is transferred from the phenol to an oxidant, yielding a phenoxyl radical or its carbon-centered tautomer (eq 1).[4-6]



(1)

The oxidation of phenols by transition metal oxidants can take place by either inner-sphere or outer-sphere mechanisms. Inner-sphere reactions are prevalent for the substitutionally labile oxidants, whereas the inert ones, such as $Mn(acac)_3$ and $Co(acac)_3$, occur by the outer-sphere mechanism.[7] The oxidation of phenols by chromium(VI) in aqueous perchloric acid takes place by a hydride-transfer leading to the formation of an intermediate phenonium cation.[8] The hydroxoruthenium(III) complex $(bpy)_2(py)RuOH^{2+}$, on the other hand, has been found to oxidize phenol in one path by an inner-sphere mechanism and in another by an outer-sphere mechanism, eq 2.[9] The outer-sphere path leads to the formation of a phenonium cation which then reacts with water to produce hydroquinone.



(2)

A mechanism that involves electrophilic attack on the aromatic ring has been proposed for the oxidation of phenol to benzoquinone by the ruthenium(IV) reagent $(bpy)_2(py)Ru^{IV}{=}O^{2+}$. The oxidation of phenols produces primarily the corresponding benzoquinone; however, other products, such as biphenoquinone, biphenol, and dicarboxylic acids, may also be formed as intermediates or products.[5,6] The selectivity to a particular product depends upon the oxidant, the solvent, and the substituent(s) on the phenol.[5]

The chromyl or pentaaquaoxochromium(IV) ion, $(H_2O)_5CrO^{2+}$, is a strong oxidizing agent.[10] It can function as either a one-electron or a two-electron oxidant, and it has been shown to adopt different mechanisms in its reactions with organic materials: hydride abstraction occurs from alcohols and hydrogen peroxide, hydrogen atom abstraction from cyclobutanol, and O-atom transfer to PPh_3.[10,11]

Our continuing interest in the reactivity of CrO^{2+} is based on its versatility as an oxidant, the variety of mechanistic possibilities it presents, and in its role as a possible active species in catalytic reactions involving chromium and O_2.[10] From the point of view of the mechanistic chemist, CrO^{2+} offers the additional advantage over some other oxidants in that the presence or absence of the easily identifiable CrO_2^{2+} as a reaction product under aerobic conditions unequivocally shows that the reaction takes place in two- or one-electron steps, respectively.[10]

In this paper we present results of a kinetic and mechanistic study of the oxidation of several phenols by CrO^{2+}. The effects

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[®] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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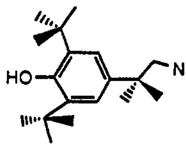
of the acidity, ionic strength, and isotopic substitution on the kinetics and products were determined. The rate constants for the meta-substituted phenols were correlated by the Hammett equation. The organic products were found to be mainly *p*-benzoquinones. In addition, the reaction yielded some 4,4′-biphenoquinone, which subsequently decomposed in aqueous acidic solution.

Experimental Section

Reagents. Water was purified by passing the laboratory distilled and deionized water through a Millipore water system. Phenol, *o*-cresol, 3-nitrophenol, 3-hydroxybenzoic acid, 3-aminophenol, 3-methoxyphenol, 3-(α,α,α-trifluoromethyl)cresol, and thallium sulfate were used without further purification. *m*-Cresol was purified by distillation. Deuterium oxide and 98 atom % phenol-d_6 were used as received. 2-Methyl-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylammonium chloride, ArOH, was synthesized by a published method.[12]



ArOH

The kinetic isotope effect, k_{PhOH}/k_{PhOD}, was determined by conducting experiments in H_2O and D_2O. The temperature was controlled by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature. The quartz cuvette in which the reaction was conducted was immersed in the water-filled holder throughout the experiment to ensure precise temperature control. The holder has quartz windows that allow the analyzing light of the spectrophotometer to pass through. The water bath creates a small but constant absorbance background.

Reactions. Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of Cr^{3+} with Zn/Hg. In a typical kinetic experiment CrO^{2+} was formed *in situ* by injecting 100 μL of 0.01 M Cr^{2+} into a spectrophotometric cell containing 5.0 mL of an O_2-saturated solution of the phenol. Under these conditions Cr^{2+} and O_2 react rapidly to produce 0.04 mM CrO^{2+} ($\sim$20% based on total Cr^{2+}), which then reacts with the phenol already present in solution. For anaerobic experiments the CrO^{2+} was prepared by injecting Cr^{2+} into a spectrophotometric cell that contained a 2–3-fold excess of air-free Tl^{3+} and the phenol (0.2–0.6 mM).

The acid concentration and the ionic strength were both kept at 0.10 M except in experiments designed to study the effects of these variables. The pH was maintained by perchloric acid, and the ionic strength, by lithium perchlorate. Solutions of CrO_2^{2+} were prepared by mixing Cr^{2+} and excess O_2 as previously described.[10]

Products. A 0.5-mL volume of 0.01 M Cr^{2+} was injected into 10 mL of O_2-saturated 0.1 M $HClO_4$ that contained 0.2 mM CrO_2^{2+} and 0.2 mM phenol. The procedure was repeated 10 times, and all the solutions were combined in a separatory funnel.[13] The organic product(s) were extracted by CH_2Cl_2 (2 × 10 mL) and dried over $MgSO_4$. Finally, the CH_2Cl_2 was evaporated at room temperature. The yield of benzoquinone was determined by a spectrophotometric titration with a standard solution of Cr^{2+}. The reaction occurs with a 2:1 stoichiometry and yields a binuclear chromium(III) quinone complex that can be easily identified and quantified by its UV–visible spectrum, λ_{max} 292 nm (ϵ 6.5×10^3 L mol^{-1} cm^{-1}) and 590 nm (ϵ 2.4×10^2 L mol^{-1} cm^{-1}).[14]

The UV–visible spectra were recorded with a Shimadzu spectrometer. The FT-IR spectra were determined in chloroform solution using NaCl plates. The ^{1}H-NMR spectra were recorded with $CDCl_3$ as solvent and referenced to tetramethylsilane.

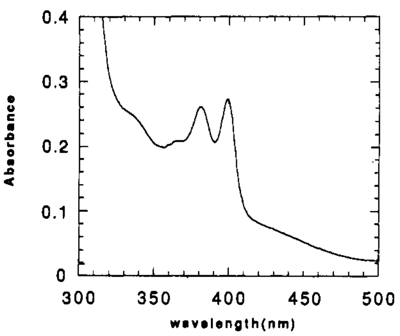


Figure 1. UV–vis spectrum of the phenoxyl radical (λ_{max} 381 and 399 nm) from reaction of 2-methyl-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylammonium chloride, ArOH (0.3 mM), with CrO^{2+} ($\sim$0.04 mM) in 0.1 M $HClO_4$ at 25 °C.

Kinetic Measurements. The kinetic data for the oxidation of phenols by CrO^{2+} were collected by following the absorbance changes at about 400 nm. The reactions were carried out with a large excess of phenol over CrO^{2+}. The sequential first-order rate constants were calculated by fitting the kinetic trace to a biexponential function (eq 3).[15]

$$A_t - A_\infty = \alpha \exp(-k_f t) + \beta \exp(-k_s t) \tag{3}$$

$$\alpha = \frac{(\epsilon_I - \epsilon_A)k_f - (\epsilon_A - \epsilon_P)k_s}{k_s - k_f}[CrO^{2+}]_0$$

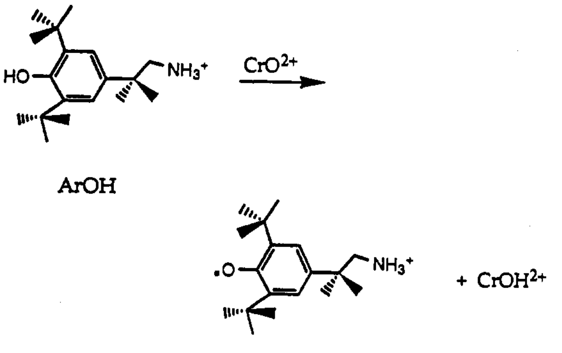
$$\beta = \frac{(\epsilon_P - \epsilon_I)k_f}{k_s - k_f}[CrO^{2+}]_0$$

In these expressions ϵ_A, ϵ_I, and ϵ_P are the molar absorptivities of the reactant, the intermediate, and the product, and k_f and k_s the rate constants for the fast and slow stages. Since the reactants and products have no significant absorption at 400 nm, *i.e.* $\epsilon_A \sim \epsilon_P \sim 0$, the expression simplifies to

$$\alpha = -\beta = \frac{\epsilon_I k_f}{k_s - k_f}[CrO^{2+}]_0$$

Results

The oxidation of ArOH leads to the formation of a stable, green-colored phenoxyl radical (eq 4), which was identified by its characteristic UV–visible spectrum (Figure 1).[12,16] This was taken as an indication that the other phenols, which do not give such an easily-recognized product, may react analogously. This is strongly supported by the observed kinetic isotope effects, by the correlation of the kinetic data to the Hammett equation (see later), and by the failure to observe the formation of CrO_2^{2+} in the presence of O_2, the product of a possible two-electron reaction.[10]



(4)

ArO•

In the oxidations of the other phenols by CrO^{2+}, the addition of Cr^{2+} causes the colorless solutions of phenol and oxygen to turn yellow rapidly and then to fade slowly, Figure 2a. The yellow

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[12] Traylor, T. G.; Lee, W. A.; Stynes, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 755.

[13] This procedure, utilizing the combination of several small preparations, resulted in better yields of products than an experiment based on a single preparation on a larger scale. The reason for this is the extreme sensitivity of the yields of CrO^{2+} on the reaction conditions, such as the local concentrations, mixing, and volumes of the reagents used.

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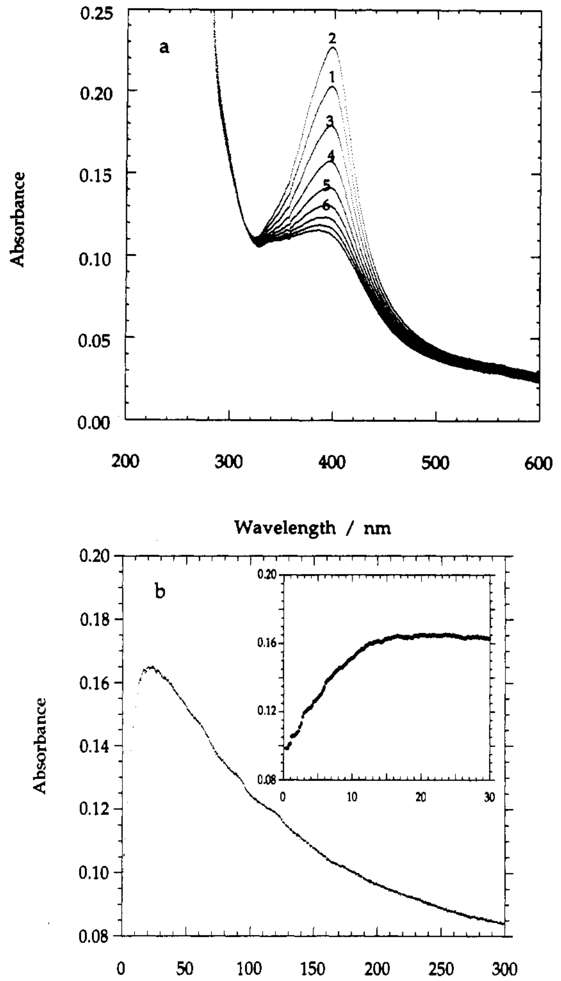
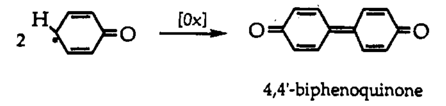


Figure 2. (a) Successive spectral changes at 30-s intervals during the oxidation of phenol (0.3 mM) by CrO^{2+} (~0.04 mM). (b) Absorbance change vs time at 400 nm. The inset shows the buildup of the intermediate in the first 30 s.

intermediate has a maximum absorption close to 400 nm (the exact value depends on the identity of the phenol), characterized by a high molar absorptivity.[17] This absorption band is typical for 4,4′-biphenoquinone, which is formed by the coupling of phenoxyl radicals followed by oxidation (eq 5).[18] In aqueous solutions this species hydrolyzes to other organic products.[19]



(5)

The UV–visible spectrum of the reaction mixture at the end of the reaction showed a strong absorption at 245 nm characteristic of *p*-benzoquinone ($\epsilon_{245} \sim 2 \times 10^4$ L mol^{-1} cm^{-1}). The product was also characterized by ^{1}H NMR and FT-IR spectra (Figure 3). The reaction of *p*-cresol with CrO^{2+} yielded the corresponding *o*-quinone ($\lambda_{wax} \sim 390$ nm). The second-order rate constant was about 900 L mol^{-1} s^{-1}.

The relative yields of the products obtained by the oxidation of phenol by CrO^{2+} were affected by added CrO_2^{2+}. The absorbance at 245 nm increased, and that at 400 nm decreased, with increasing concentrations of CrO_2^{2+}. In the presence of 0.2 mM CrO_2^{2+} the yield of *p*-benzoquinone was 83%, and in the absence of added CrO_2^{2+} (see the Experimental Section) the yield was 27%. The reaction rate, however, remained independent of both [CrO_2^{2+}] and [O_2]. In each experiment both *p*-benzoquinone and biphenoquinone were formed.

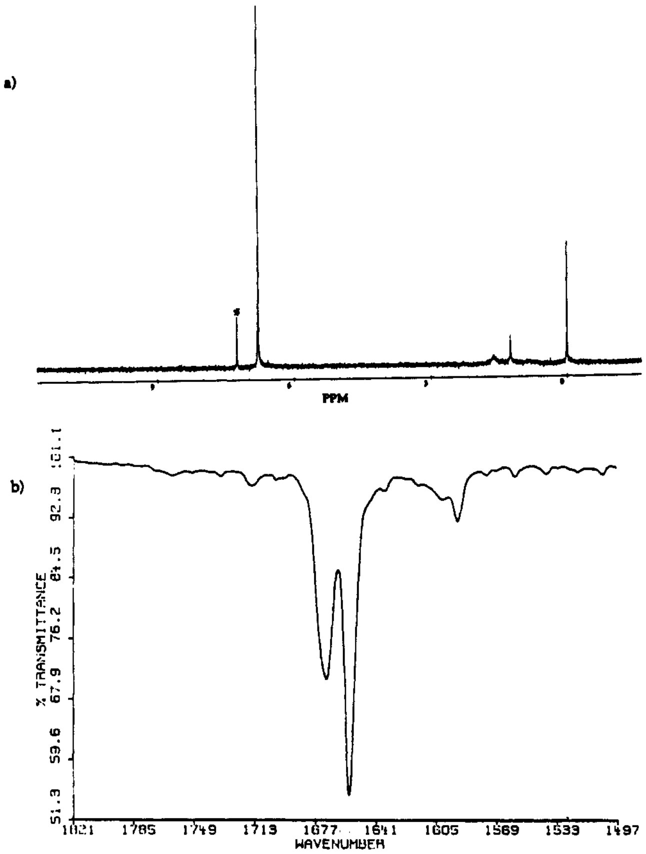


Figure 3. (a) ^{1}H NMR spectrum in $CDCl_3$ of the organic products of the oxidation of phenol by CrO^{2+} in the presence of O_2 after extraction with CH_2Cl_2. An asterisk indicates the $CDCl_3$ peak. (b) FT-IR spectrum of the same sample.

Kinetics. The reaction products, *p*-benzoquinone and 4,4′-biphenoquinone, are formed in rapid post-rate-controlling steps; see later. The rate constant for the disappearance of the reactants can thus be obtained by monitoring the buildup of either of the products. The kinetic data were collected at the maximum absorption of 4,4′-biphenoquinone, a relatively minor product that absorbs strongly at ~400 nm.

Figure 2 shows the spectral changes that occurred with time in a solution that initially contained 0.3 mM phenol and 0.04 mM CrO^{2+}. Similar absorption changes were observed for the other phenols used in this study. When the phenol was taken in a large excess over CrO^{2+}, the rate of the formation (fast stage) of 4,4′-biphenoquinone followed first-order kinetics. The subsequent absorbance decrease (slow stage) was found to depend on the concentration of the phenol RC_6H_4OH for R = H but not for R = alkyl.

The pseudo-first-order rate constants for the two steps were obtained by fitting the data to a biexponential equation (eq 3). The rate constants obtained for the fast stage at constant ionic strength and acidity varied linearly with the phenol concentration. The values of the second-order rate constants obtained from the slopes are shown in Table I. The intercepts of these plots, 0.002–0.04 s^{-1}, correspond to the decomposition of CrO^{2+}. This rate constant cannot be determined very accurately, however, since it is such a small component of the total reaction. Further comments on the decomposition of the oxochromium(IV) ion have been given before.[11]

Kinetic Isotope Effects. Large kinetic isotope effects (k_H/k_D

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Table I. Rate Constants[a] for the Oxidation of Phenols by CrO^{2+} (k_f) and for the Decomposition of 4,4′-Biphenoquinone Intermediates (k_s)

phenol	k_f/L mol^{-1} s^{-1}	k_s/10^{-3} s^{-1}	k_f^H/k_f^D	k_s^H/k_s^D
C_6H_5OH	471[a]	6.2[a]		
C_6H_5OD	32[b]	5.6[b]	14.7	1.1
C_6D_5OH	465[c]	4.6[c]	1.0	1.3
3-$CH_3C_6H_4OH$	645[a]	11[a]		
2-$CH_3C_6H_4OH$	1064[a]	5.5[a]		
2-$CH_3C_6H_4OD$	63[b]	3.5[b]	16.9	1.8
ArOH[d]	240[a]	5.0[a]		

[a] Oxidation of the phenol in H_2O (0.1 M $HClO_4$) at 25 °C in the presence of O_2 ($[CrO_2^{2+}] \sim 0.1$ mM). The standard deviation of the rate constants was estimated as ≤5%. [b] Oxidation of RC_6H_4OD in D_2O. [c] Oxidation of C_6D_5OH in H_2O. [d] 2-Methyl-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylammonium chloride.

Table II. Acidity and Ionic Strength Dependence of k_f and k_s at 25 °C

$[HClO_4]$/M	k_f/L mol^{-1} s^{-1}	k_s/10^{-3} s^{-1}
0.03	514[a]	4.1[a]
0.06	504[a]	5.0[a]
0.10	471[a]	6.2[a]
	635[b]	11.5[b]

[a] μ = 0.10 M. [b] μ = 1.0 M.

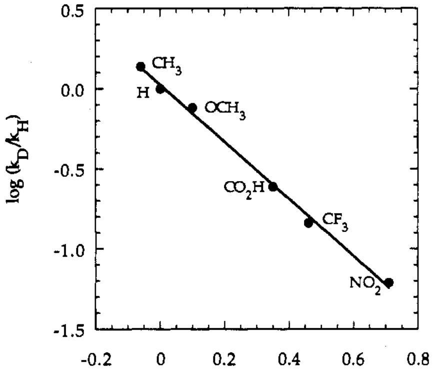


Figure 4. Plot of $\log(k_X/k_H)$ against σ for the reaction of meta-substituted phenols with CrO^{2+} in 0.1 M $HClO_4$ at 25 °C. The slope ρ is -1.7 ± 0.2.

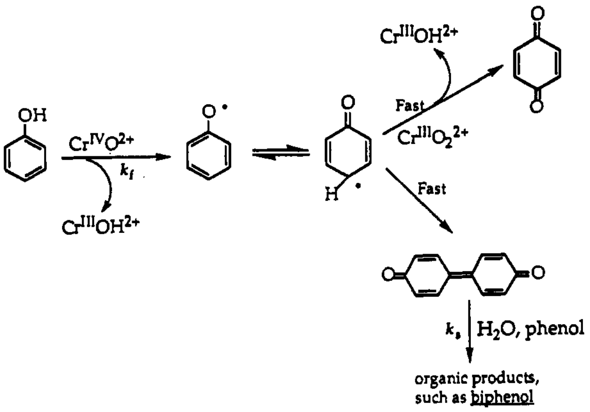
= 14.7 for C_6H_5OH) were observed upon changing the solvent from H_2O to D_2O. They relate the rate constants for the reactions of C_6H_5OH with $(H_2O)_5CrO^{2+}$ in H_2O to those for the reactions of C_6H_5OD with $(D_2O)_5CrO^{2+}$ in D_2O. The oxidation of C_6D_5OH and C_6H_5OH by $(H_2O)_5CrO^{2+}$ in H_2O showed no kinetic isotope effect, $k_H/k_D \sim 1.0$, Table I.

Acidity and Ionic Strength Effects. At constant ionic strength (0.1 M) the rate of the fast step decreased with increasing acidity of the solution. The rate of the slow stage, however, increased with acidity. Both of these effects are relatively small, however, as can be seen from the data in Table II. An increase in the ionic strength was found to enhance the rates of both stages of the reactions (Table II).

Hammett Correlation. The electronic effects of one substituent in the meta position of the phenol on the rate constants have been correlated by the Hammett equation, $\log(k_X/k_H) = \rho\sigma$.[20] The plot of $\log(k_X/k_H)$ against σ is linear (Figure 4), with a slope $\rho = -1.7 \pm 0.2$.

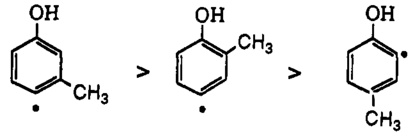
Activation Parameters. The effect of temperature in the range 4.5–32.2 °C on k_f and k_s for the oxidation of C_6H_5OH by CrO^{2+} yielded the activation parameters for the two stages. The values for the fast stage are $\Delta H^{\ddagger} = 15.2 \pm 1.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -144 \pm 15$ J mol^{-1} K^{-1} and for the slow stage $\Delta H^{\ddagger} = 46 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -129 \pm 11$ J mol^{-1} K^{-1}.

Scheme I



Discussion

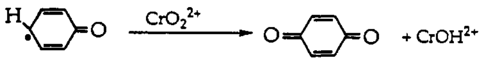
The results obtained in this study show that the oxidation of phenols by CrO^{2+} begins with the formation of the phenoxyl radical, Scheme I. Clear evidence for such one-electron process is provided by the direct observation of the stable phenoxyl radical in the reaction of CrO^{2+} with ArOH in that one reaction. We ask, does it apply to the other phenols? We note that the similarities in the second-order rate constants of the oxidation of *o*-cresol and *p*-cresol by CrO^{2+} and the result that the *m*-cresol oxidation is about 1.5 times slower support a scheme in which the hydrogen atom is abstracted from O–H and not C–H. The corresponding radical obtained from C–H abstraction in the case of *m*-cresol is expected to be the most stable relative to the other cresol isomer radicals as shown by the following stability trend:



The results obtained from this study, however, have indicated an opposite trend in the radical stabilities, which is consistent with the abstraction of hydrogen atom from O–H. The phenoxyl radicals undergo two rapid competitive reactions: oxidation to benzoquinone and coupling followed by oxidation to biphenols or biphenoquinones, Scheme I.

The biphenoquinones, we believe, are the observed yellow intermediates absorbing at 400 nm.[17] The biphenoquinone formed here is mostly the more stable isomer 4,4′-biphenoquinone. Formation of other isomers, such as 2,2′-biphenoquinone, is also possible, although the UV–visible spectra did not show any other absorption bands close to 400 nm. Perhaps the broad band absorption at 400 nm may include small absorption of other isomers. The literature contains no reports of the UV–visible spectra for any of these possible isomers that would enable us to compare it with that of 4,4′-biphenoquinone. Consistent with this assignment is an increase in the decay rate of the 400-nm absorbance with increasing acid and phenol concentrations.[21] The reaction with phenol produces biphenol.[21]

Most of the three-electron oxidation of phenoxyl radicals to the major product, benzoquinone, seems to be carried out by CrO_2^{2+}, a natural impurity in solutions of CrO^{2+} prepared from Cr^{2+} and O_2. The role of CrO_2^{2+} in the product-forming step(s) of eq 6 is demonstrated clearly by the decrease in the yield of



(6)

benzoquinone with a decrease in $[CrO_2^{2+}]$. We infer that the

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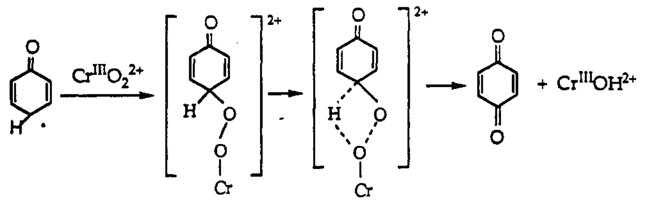
[20] Carey, F. A.; Sundberg, R. *Advanced Organic Chemistry*; Plenum Press: New York, 1984; Part A, p 179.

[21] Hay, A. S. *J. Org. Chem.* **1969**, *34* (4), 1160.

Scheme II

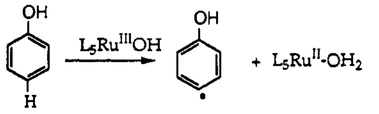


oxidation of the phenoxyl radical by CrO_2^{2+} is rapid, since the observed rate constants showed no dependence on the CrO_2^{2+} concentration. In the absence of CrO_2^{2+}, the oxidation of the radical was presumably carried out by CrO^{2+} itself and, in air-free experiments, also by the Tl^{3+} left over from the CrO^{2+} preparation step.

The oxidation of the phenoxyl radicals by CrO_2^{2+} probably occurs by the coupling of phenoxyl radicals with CrO_2^{2+}, resulting in the one-electron reduction of the coordinated superoxide to peroxide, Scheme II. The reaction is then completed by oxygen transfer from the new peroxo ligand to the ring. A similar mechanism has been proposed for the oxidation of phenols by $L_5Co^{III}O_2$ (L_5 = bis(3-(salicylideneamino)propyl)methylamine).[22]

The oxidations of phenols that are not substituted in the ortho position might be expected to yield some 2,2′-biphenoquinone and *o*-benzoquinone in addition to the thermodynamically more stable 4,4′-biphenoquinone and *p*-benzoquinone. The UV–visible spectra showed that CrO^{2+} yields only the second pair of products. Also, the ^1H NMR spectrum of the products showed only one singlet, as expected for *p*-benzoquinone. No signal corresponding to *o*-benzoquinone was observed. The IR absorptions at 1671 and 1657 cm^{-1} ($\nu_{C=O}$) of the same sample are also characteristic of *p*-benzoquinone (Figure 3). This selectivity of CrO_2^{2+} for the para position of the phenoxyl radical may be caused by the unfavorable steric effects of the C=O π-system in the ortho position.

The large kinetic isotope effects found for the reaction between CrO^{2+} and C_6H_5OH in H_2O versus C_6H_5OD in D_2O (k_H/k_D = 14.7), and the absence of a kinetic isotope effect for C_6H_5OH in H_2O versus C_6D_5OH in H_2O, provide convincing evidence that O–H but not C–H bond breaking is involved in the rate-controlling step. Hydrogen atom abstraction from O–H has also been observed in the oxidation of phenols by (salen)$Co^{III}O_2$[5] and of hydroquinone by $[(py)(bpy)_2Ru^{IV}{=}O]^{2+}$.[23] On the other hand, oxidations of phenols by $[(py)(bpy)_2Ru^{III}OH]^{2+}$ showed primary isotope effects of C–H but not O–H hydrogens, indicating hydrogen atom abstraction from C–H in the rate-controlling step, eq 7.[9]



(7)

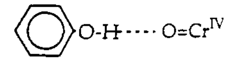
Hammett Correlation. The rate of the reaction is enhanced by the electron-donating power of the group in the meta position of the phenol, as shown in Table III. The linear correlation between the rate constants and the Hammett substituent constant σ_m (Figure 4) indicates that all the phenols react with CrO^{2+} by the same mechanism. The negative value of the reaction constant (ρ = −1.7 ± 0.2) calculated from the slope in Figure 4 is further evidence for the formation of the electron-deficient phenoxyl radical intermediate. The ρ value obtained from this work is consistent with the values were obtained for the oxidation of phenols by one electron in the rate-controlling step (RCS) yielding the phenoxyl radical intermediate; for example, $Fe(bpy)_2^{3+}$ has ρ = −1.4.[24] Reactions in which the RCS consists of two-electron transfer are characterized by much more negative reaction constants; for example $Tl(OAc)_3$ has ρ −6.6, V(V) has ρ −4.3, and Cr(VI) has ρ −4.1.[25]

Table III. Relative Rate Constants for Meta-Substituted Phenols

X	k_X/k_H	σ[a]	X	k_X/k_H	σ[a]
H	1.0	0.0	CO_2H	0.244	0.35
CH_3	1.37	−0.06	CF_3	0.145	0.46
OCH_3	0.760	0.10	NO_2	0.060	0.71

[a] Hammett substituent constants for X.

The enthalpy of activation for the first stage is low (15.2 ± 1.5 kJ mol^{-1}) suggesting the formation of a hydrogen bond between the oxo ligand of CrO^{2+} and the acidic hydrogen of phenol prior to the proton-coupled electron-transfer step:



The idea of hydrogen bond formation is supported by the large kinetic isotope effect on the O–H bond, since the isotopic change here is expected to affect the acidity, the hydrogen bond strength, and the O–H bond strength. Also, the slight decrease in the rate constant k_f with increasing acidity supports this suggestion. The relatively large negative entropy of activation ($\Delta S^{\ddagger}$ = −144 ± 15 J mol^{-1} K^{-1}) agrees with the entropies of activation determined for the oxidation of hydroquinone by other oxidants.[23] This is typical of a bimolecular reaction in the rate-controlling step. The decomposition of 4,4′-biphenoquinone has an enthalpy of activation of $\Delta H^{\ddagger}$ = 46 ± 4 kJ mol^{-1}. Bond breaking, most probably of the C=C bond between the two rings, may be involved in this stage.

The decomposition of 4,4′-biphenoquinone under these conditions arises from its self-decomposition (acid-catalyzed) and from a reaction with phenols.[21] Biphenoquinones with electron-donating groups, such as CH_3 or $C(CH_3)_3$, are expected to be less stable than unsubstituted biphenoquinones owing to steric and electronic factors. Also, substituted phenols are less likely to react with substituted biphenoquinones on steric grounds. Thus the presence of a substituent may enhance the self-decomposition of biphenoquinones and reduce the rate of the reaction with phenol. Consistent with this, we find that the disappearance of the substituted biphenoquinones does not depend on the concentration of the phenol.

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