

Kinetics and Mechanism of the Oxidation of a Substituted Phenol by a Superoxochromium(III) Ion

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A superoxochromium(III) ion, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, abstracts the hydrogen atom from the hydroxylic group of a substituted, cationic phenol (ArOH), $k_{\text{CrOO}} = 1.24 \text{ M}^{-1} \text{ s}^{-1}$ in acidic aqueous solution at 25°C . The reaction has a large kinetic isotope effect, $k_{\text{ArOH}}/k_{\text{ArOD}} \approx 12$ and produces ArO^\bullet , which also reacts with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in a rapid second step, $k_{\text{ArO}} = 1.26 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The final oxidation product is an *o*-quinone, which was identified by its behavior on a cation-exchange resin, UV–visible spectrum, and reaction with iodide ions. This work has extended to three the types of element–hydrogen bonds that react with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ about 10^2 times more slowly than with $\text{Cr}_{\text{aq}}\text{O}^{2+}$. The mechanistic implications of these findings are discussed.

Introduction

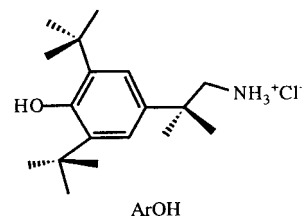
The interest in the chemistry of phenols and phenoxyl radicals is derived from their involvement in a large number of processes in natural systems. Tyrosyl radicals, for example, are involved in the function of a number of enzymes and in oxygen-evolving complex of photosystem II.^{1–5} α -Tocopherol and other phenolic compounds play their protective roles in biological systems by removing harmful radicals and interrupting damaging chain reactions.^{6–8} A crucial step in this chemistry is hydrogen atom transfer and the generation of phenoxyl radicals, a process that is fast and efficient because of the low O–H bond dissociation energy in phenols.⁹

This same characteristic should make phenols reasonably reactive toward superoxometal complexes, including $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, which has been shown to engage in hydrogen atom transfer with such diverse classes of compounds as aldehydes¹⁰ and rhodium hydrides.¹¹ In that earlier work we have shown that the reactivities of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and $\text{Cr}_{\text{aq}}\text{O}^{2+}$ are much more similar than those of their organic counterparts, *tert*-BuOO \bullet and *tert*-BuO \bullet . These findings were rationalized in terms of the thermodynamics of the O–H bonds formed in the process of hydrogen transfer.¹⁰

We have now extended this work and examined the kinetics of the reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ with a phenolic O–H bond. By

adding the third example of an element–hydrogen bond to our roster, we hoped to probe further the validity and limits of our earlier hypothesis.¹⁰

Because the primary purpose of this work was to determine the precise kinetics of hydrogen atom abstraction, we chose to work with a water-soluble, cationic phenol 2-methyl-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylammonium chloride (ArOH) that produces a stable phenoxyl radical. We were thus



able to avoid some of the complexities and intermediates that usually¹² accompany the reactions of phenols. The reaction of ArOH with the chromyl ion, $\text{Cr}_{\text{aq}}\text{O}^{2+}$, was examined earlier.¹²

Experimental Section

Materials. 2-Methyl-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylammonium chloride (ArOH) was synthesized by a published method¹³ and recrystallized from water. Stock solutions were prepared in 0.10 M HClO_4 containing 7% acetonitrile. Solutions of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ were prepared by injecting a small volume of dilute $\text{Cr}_{\text{aq}}^{2+}$ into an ice-cold, dioxygen-saturated solution of 0.10 M HClO_4 containing 0.10 M methanol, as described previously.¹⁰ These solutions were used within 2 h of preparation. Solutions of ArO^\bullet were prepared by oxidizing ArOH with $\text{Cr}_{\text{aq}}\text{O}^{2+}$. Water was purified by passing the in-house distilled and deionized water through a Millipore water system.

Kinetics. For the reaction of $\text{Cr}_{\text{aq}}\text{O}^{2+}$ with ArOH , an air-saturated solution containing 0.10 M HClO_4 and the desired concentration of ArOH were placed in a spectrophotometric cell and thermostated at 25°C inside the cell compartment of a Shimadzu 3101 PC spectrophotometer. A small volume of $\text{Cr}_{\text{aq}}^{2+}$ was added to generate $\text{Cr}_{\text{aq}}\text{O}^{2+}$, and the reaction was monitored at the 400 nm maximum of ArO^\bullet . The

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kinetics of the reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and ArOH were monitored at 295 nm, which provided the best absorbance change. Measurements were conducted under pseudo-first-order conditions using ArOH (0.3–5.0 mM) in large excess over $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ (~ 0.015 mM). Kinetic solutions typically contained 0.10 M HClO_4 , 0.10 M methanol to stabilize stock solutions of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$,¹⁴ and 5% acetonitrile to increase the solubility of ArOH . The kinetics of the reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and ArO^\bullet were measured by use of a stopped-flow spectrophotometer (Applied Photophysics). All the kinetic determinations were carried out at 25°C.

Products. After completion of the reaction between 0.22 mM $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and 1.8 mM ArOH in 0.1 M HClO_4 (total volume, 50 mL), the mixture was loaded onto a column of Sephadex C-25 cation-exchange resin that had been pretreated with 1 M H_2O_2 in 1 M HClO_4 . Elution with 0.10 M HClO_4 removed a yellow fraction, which already had begun to migrate during the loading process. An increase in the concentration of HClO_4 produced no other major fractions except $\text{Cr}_{\text{aq}}^{3+}$, which was eluted with 1 M HClO_4 . The number of oxidizing equivalents in the yellow fraction was determined iodometrically. The reaction with excess iodide (0.033 M) in 0.10 M HClO_4 was complete in about 2 min.

Molar Absorptivity of ArO^\bullet . A spectrum was recorded on a fresh sample of ArO^\bullet that was prepared by oxidation of ArOH with $\text{Cr}_{\text{aq}}\text{O}^{2+}$. A solution of sodium iodide was then added and the formation of triiodide monitored at 350 nm ($\epsilon = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Two kinetic stages were observed. One, believed to correspond to the reaction with ArO^\bullet , was completed in the mixing time. The oxidizing equivalents determined in this stage were used in the calculations of the molar absorptivity of ArO^\bullet , taking into account the stoichiometry, $[\text{ArO}^\bullet]_0/[\text{I}_3^-]_\infty = 2$. An average value of $\epsilon_{400} = (2.6 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ was obtained. The kinetics of the second stage were almost identical with those observed for the oxidation of iodide by the product of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArOH}$ reaction, which we believe to be an *o*-quinone (see later).

Results and Discussion

The iodometric titrations of the products formed in the $\text{Cr}_{\text{aq}}\text{O}^{2+}/\text{ArOH}$ reaction (see Experimental Section) yielded a molar absorptivity of $(2.6 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for ArO^\bullet at the 400 nm maximum. This value is larger than the one obtained earlier¹⁵ but close to that for the closely related 2,4,6-tri-*tert*-butylphenoxy radical in ethanol, $\epsilon = 2.45 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁶ Our old value in aqueous solution, $1.44 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$,¹⁵ was based on the $\text{VO}^{2+}/\text{H}_2\text{O}_2/\text{ArOH}$ reaction and the assumption that HO^\bullet is converted quantitatively to ArO^\bullet at low $[\text{H}_2\text{O}_2]$. We have now carried out iodometric titrations on spent solutions after completion of the $\text{VO}^{2+}/\text{H}_2\text{O}_2/\text{ArOH}$ reaction and found that the yield of ArO^\bullet is only $\sim 60\%$. Under the experimental conditions, at least some HO^\bullet reacts with VO^{2+} .¹⁷ The rest of the “missing” HO^\bullet may have reacted with ArOH by addition to the ring¹⁷ or hydrogen abstraction from the alkyl C–H groups to give products that are not converted to ArO^\bullet .

Kinetics. The disappearance of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in the reaction with ArOH ,



was monitored at 295 nm. The mixed second-order behavior was observed:

$$-d[\text{CrOO}^{2+}]/dt = k_{\text{app}}[\text{CrOO}^{2+}][\text{ArOH}] \quad (2)$$

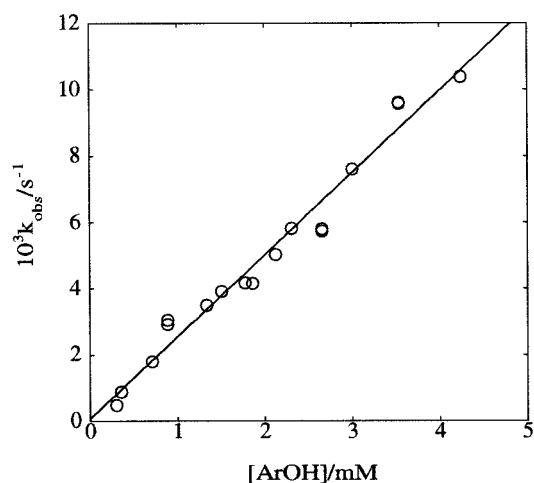


Figure 1. Plot of the observed rate constants for the reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ (0.015 mM) with ArOH against the average concentration of ArOH .

The slope of the straight line obtained by plotting the measured rate constants against the concentration of ArOH (Figure 1) yielded $k_{\text{app}} = 2.48 \pm 0.12 \text{ M}^{-1} \text{ s}^{-1}$. As shown later, the overall stoichiometry of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArOH}$ reaction is 2:1, which results in $k_{\text{CrOO}} = k_{\text{app}}/2 = 1.24 \text{ M}^{-1} \text{ s}^{-1}$. The observed rate constants were unaffected by the presence of 3 mM Mn^{2+} or by varying the concentration of methanol in the range 0–0.4 M, showing that $\text{Cr}_{\text{aq}}\text{O}^{2+}$ is not an important intermediate in this reaction.¹⁰

As expected for a reaction between two ions of like charges, the rate constant increased with an increase in the ionic strength. The effect was the same for the two electrolytes used, LiClO_4 and HClO_4 , showing that there are no $[\text{H}^+]$ -dependent terms in the rate law. At $[\text{ArOH}] = 1.77$ mM, the increase in k_{obs} was from 0.00354 s^{-1} ($\mu = 0.051$ M) to 0.0182 s^{-1} ($\mu = 0.740$ M). The data at the lower end of the ionic strength used (0.051–0.249 M) were fitted to an equation for the effect of electrolytes on rates,¹⁸

$$\log k = \log k_0 + \frac{2\alpha z_{\text{CrOO}} z_{\text{ArOH}} \mu^{1/2}}{1 + \mu^{1/2}} \quad (3)$$

where α is 0.509 and μ is the ionic strength. The fit provided the charge product $z_{\text{CrOO}} z_{\text{ArOH}} = 1.9$ (Figure S1 of Supporting Information),¹⁹ in good agreement with the calculated value of 2.0 for a reaction between a monocation and dication.

A single experiment was carried out in D_2O (final deuterium content, 98%). At $[\text{CrOO}^{2+}] = 0.017$ mM and $[\text{ArOH}] = 4.2$ mM, the observed rate constant was $9.8 \times 10^{-4} \text{ s}^{-1}$, ~ 12 times smaller than that observed in H_2O under otherwise identical conditions. The phenolic proton exchanges rapidly in D_2O , and we interpret the observed kinetic isotope effect as $k_{\text{ArOH}}/k_{\text{ArOD}}$. Our earlier work has shown that the change in solvent per se has no effect on the rates of hydrogen atom transfer from rhodium hydrides to $\text{Cr}_{\text{aq}}\text{OO}^{2+}$.¹¹ The replacement of coordinated molecules of H_2O by D_2O thus does not alter the hydrogen-atom abstracting ability of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The observed kie in the reaction with ArOH and the lack of involvement of $\text{Cr}_{\text{aq}}\text{O}^{2+}$ strongly support hydrogen atom abstraction in this case

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(19) Supporting Information.

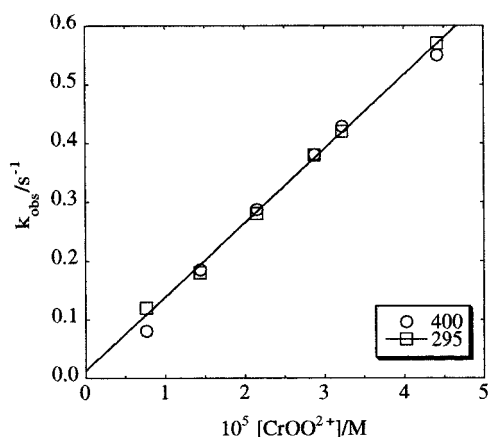
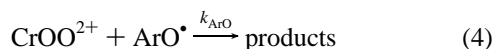


Figure 2. Plot of the observed rate constants for the stopped-flow reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ with ArO^* (8–16 μM) against the average concentration of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The reaction was monitored at 295 nm (squares) and 400 nm (circles).

as well (eq 1). The value of k_{ie} is difficult to discuss, other than to note that it is “large.” It is almost certainly affected by hydrogen bonding between the hydroxylic group and both the solvent^{20–22} and incoming $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, as proposed earlier in the corresponding reaction of $\text{Cr}_{\text{aq}}\text{O}^{2+}$.¹²

The $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArOH}$ reaction produced no absorbance increase at 400 nm, a maximum in the spectrum of ArO^* , suggesting that ArO^* , produced in eq 1, disappears rapidly in a followup reaction with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. Attempts to generate ArO^* more rapidly to observe it prior to its suspected reaction with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ were thwarted by the limited solubility (<5 mM) of ArOH in aqueous 0.1 M HClO_4 . An experiment was then conducted in DMSO, where the solubility of ArOH is much greater. A reaction between 0.013 mM $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and 0.03 M ArOH generated 0.010 mM ArO^* , which was identified by its characteristic visible spectrum. The less than quantitative yield of ArO^* suggests a competition between ArOH and ArO^* for $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ even in DMSO at the high concentration of ArOH used.

An independent study of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArO}^*$ reaction was then carried out. Solutions of ArO^* were prepared by oxidizing ArOH with less than stoichiometric amounts of $\text{Cr}_{\text{aq}}\text{O}^{2+}$. The kinetics were monitored by stopped-flow spectrophotometry at 400 and 295 nm under the conditions of excess $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in 0.10 M HClO_4 . Identical kinetic results were obtained at the two wavelengths, as shown in Figure 2, where k_{obs} is plotted against the average concentration of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The reaction took place with a 1:1 stoichiometry and obeyed mixed second-order kinetics with a rate constant $k_{\text{ArO}} = (1.26 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$:



It is now clear that ArO^* could not be detected in the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArOH}$ reaction in aqueous solutions at the low, solubility-limited concentrations of ArOH because of the rapid disappearance of ArO^* in reaction 4.

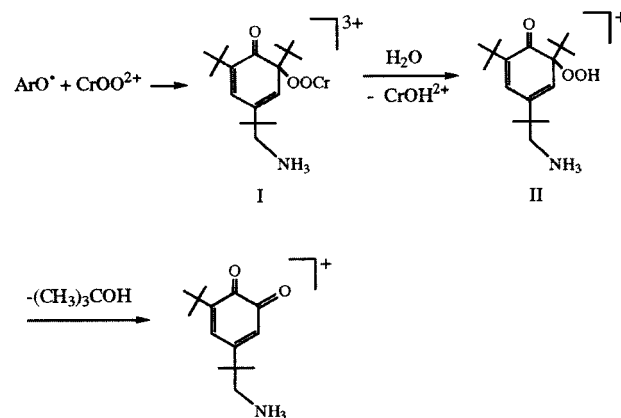
The reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and ArOH was studied previously.¹² In the present work the kinetics were redetermined

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Scheme 1



under the conditions that matched precisely those in the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{ArOH}$ reaction. The value obtained, $k_{\text{CrO}} = 194 \pm 27 \text{ M}^{-1} \text{ s}^{-1}$, is in acceptable agreement with our old value of $240 \text{ M}^{-1} \text{ s}^{-1}$.

Products. The behavior of the intensely colored yellow fraction on the ion-exchange resin was consistent with a +1 charge. The visible spectrum of this species is shown in Figure S2 of Supporting Information.¹⁹ The absorbance and titration data, see Experimental Section, yielded the molar absorptivity $\epsilon_{\text{max}} = 2.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm. These calculations used the stoichiometric ratio $[\text{product}]_0/[\text{I}_3^-]_{\infty} = 1$.

All the results are consistent with the product being the *o*-quinone shown in Scheme 1. In particular, the molar absorptivities of *o*-quinones at their maxima in the 300–400 nm range ($>10^3 \text{ M}^{-1} \text{ cm}^{-1}$) are much higher than those of the para analogues (typically $<10^2 \text{ M}^{-1} \text{ cm}^{-1}$).^{23,24} The ortho geometry is also consistent with the observed +1 charge. Had the *tert*-butylammonium group in the para position been removed, the resulting molecule would bear no ionic charge.

The combined yield of the quinone was $\sim 3 \times 10^{-3}$ mmol, or $\sim 60\%$ of the expected yield calculated on the basis of eqs 1 and 4 and Scheme 1. Possibly the conversion of the peroxochromium intermediate to *o*-quinone in Scheme 1 is less than quantitative, similar to the reactions of some superoxocobalt complexes with substituted phenols, which produced both *o*- and *p*-hydroperoxy quinols.²⁵ Any *p*-quinone that was possibly produced in the present work probably would not be detected because of the small absorptivity at 400 nm and the lack of ionic charge.

According to Scheme 1, the formation of the quinone is initiated by the attack of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ at the phenyl ring of ArO^* to produce a peroxochromium intermediate (I). The conjugative delocalization of electron density onto the aromatic ring in phenoxyl radicals has been discussed recently.⁹ More to the point, the chemistry analogous to that in Scheme 1 has been observed earlier with several superoxocobalt complexes in aprotic solvents,^{25–28} and a peroxo-*p*-quinolatocobalt(III) complex has been isolated and structurally characterized.²⁹ No such

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species was observed in the present work in aqueous solutions, where intermediate **I** would be expected to hydrolyze rapidly to hydroperoxide **II**.

Literature precedents for the next step include the rapid conversion of both *o*- and *p*-hydroperoxoquinols to the corresponding quinones in CH₂Cl₂.^{30,31} We are not aware of any kinetic data on these reactions in water, but in methanol the formation of quinones is substantially slower than in CH₂Cl₂.³⁰ We also cannot rule out the possibility that intermediate **I** in Scheme 1 yields the quinone directly without the involvement of intermediate **II**.

The reactivities of Cr_{aq}O²⁺ and Cr_{aq}OO²⁺ toward ArOH again differ by about 2 orders of magnitude, $k_{\text{CrO}}/k_{\text{CrOO}} = 159$, following the pattern established earlier in the reactions of rhodium hydrides¹¹ and trimethylacetaldehyde¹⁰ (Table 1). The similarity between the relative rates for hydrogen atom abstraction from Rh–H, C–H, and O–H bonds strongly supports our suggestion¹⁰ that the energetics of the O–H bonds formed (Cr_{aq}O–H and Cr_{aq}OO–H) are a crucial factor in determining

Table 1. Summary of Kinetic Data for Hydrogen Abstraction by Cr_{aq}O²⁺ (k_{CrO}) and Cr_{aq}OO²⁺ (k_{CrOO}) at 25 °C

reductant	$k_{\text{CrO}}/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{CrOO}}/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{CrO}}/k_{\text{CrOO}}$
L ¹ Rh–H ²⁺ ^{a,b}	$\sim 1 \times 10^4$	129	~ 80
L ² Rh–H ²⁺ ^{b,c}	1.12×10^3	24	47
ArO–H	194	1.24	156
(CH ₃) ₃ CC(O)–H ^d	23	0.16	144

^a L¹ = cyclam. ^b Reference 11. ^c L² = Me₆-cyclam. ^d Reference 10.

the kinetics of these reactions. This argument is especially convincing in view of the constancy of relative rates to within a factor of 3, despite the 10³-fold variations in absolute rate constants for both oxidants (Table 1). The kinetics of oxidation of organic materials with CrO₂Cl₂ and MnO₄[–] have also been shown to correlate strongly with the energies of O–H bonds formed.³²

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Supporting Information Available: Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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