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Oxidation of Phenol by Tris(1,10-phenanthroline)osmium(III)

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Supporting Information

ABSTRACT: Outer-sphere oxidation of phenols is under intense scrutiny because of questions related to the dynamics of proton-coupled electron transfer (PCET). Oxidation by cationic transition-metal complexes in aqueous solution presents special challenges because of the potential participation of the solvent as a proton acceptor and of the buffers as general base catalysts. Here we report that oxidation of phenol by a deficiency of $[Os(phen)_3]^{3+}$, as determined by stopped-flow spectrophotometry, yields a unique rate law that is second order in [osmium(III)] and [phenol] and inverse second order in [osmium(II)] and $[H^+]$. A mechanism is inferred in which the phenoxyl radical is produced through a rapid PCET preequilibrium, followed by rate-limiting phenoxyl radical coupling. Marcus theory predicts that the rate of electron transfer from phenoxide to osmium(III) is fast enough to account for the rapid PCET preequilibrium, but it does not rule out the intervention of other pathways such as concerted proton–electron transfer or general base catalysis.

One-electron oxidation of phenols in aqueous solution generally involves the production of phenoxyl radicals and the attendant release of phenolic protons. Recent studies of such reactions with substitution-inert transition-metal complexes have shown that proton and electron transfer can be concerted, and these studies have highlighted the importance of the proton acceptor. Some studies have focused on the role of extrinsic bases such as phosphate and pyridine, while others have considered the solvent water as the proton acceptor. Direct measurements of the reaction kinetics have been performed for $[IrCl_6]^{2-}$, $[Ru(bpy)_3]^{3+}$, and two $[Ru(bpy)_3]^{3+}$ derivatives, and the rate laws obtained have included terms first order in both [oxidant] and [phenol] and independent of [base].[1−4] On the other hand, electrocatalytic studies of the oxidation of tyrosine by $[Os(bpy)_3]^{3+}$, $[Fe(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{3+}$, and $[Ru(dmb)_2(bpy)]^{3+}$ have revealed rates that are directly dependent on the base concentration.[5] The origins of these disparate results are unclear.

The present report describes the results of stopped-flow kinetic studies on the oxidation of phenol by $[Os(phen)_3]^{3+}$. This oxidant has redox properties quite similar to those of $[Os(bpy)_3]^{3+}$, but it lacks the potential complications that could arise from rotations about the C−C bond in bpy. The use of phenol rather than tyrosine limits the acidic site to the phenolic proton. Finally, the use of stopped-flow methodology avoids the possible effects of base adsorption that might occur with electrochemical methods.

$[Os(phen)_3]Cl_2$ was prepared as described previously.[6,7] Solutions of $[Os(phen)_3]^{3+}$ (Os^{III}) were prepared immediately prior to use by using Br_2/CH_3CN solutions to oxidize solutions of $[Os(phen)_3]Cl_2$ (Os^{II}) in 0.01 M HCl.[6,7] Care was taken to add only a deficiency of Br_2 so as to avoid overoxidation of the osmium reagent, and solutions were protected from room light at all times.

Figure S-1 in the Supporting Information displays the characteristic UV−vis spectra of Os^{III} and Os^{II} solutions in 0.01 M HCl. It also shows that the oxidation of phenol by Os^{III} at pH 4.7 leads to full recovery of the initial Os^{II}. Additionally, the spectra show an absorbance feature around 400 nm in the product solution that is typical of the biphenoquinone phenolic oxidation products in such reactions.[8] These results indicate that the overall reaction can be represented as

$$4Os^{III} + 2\text{phenol} \rightarrow 4Os^{II} + \text{biphenoquinones} + 4H^+ \quad (1)$$

Stopped-flow measurements were performed at 25.0 ± 0.1 °C, as described previously,[4] mixing equal volumes of the Os/HCl with a large molar excess of the phenol/buffer solutions. The ionic strength in both reactant solutions was maintained at 0.1 M (NaCl). Kinetic traces were monitored at 480 nm when the initial concentrations of Os^{II} were low and at 550 nm for high Os^{II} concentrations. In either case, the traces show a monophasic absorbance rise due to the formation of Os^{II}.

Under all conditions of pH, [phenol], $[Os^{III}]_0$, and $[Os^{II}]_0$ investigated, the kinetic traces failed to yield good pseudo-first-order fits. On the other hand, the half-lives showed a strong dependence on the initial Os^{III} and Os^{II} concentrations. For example, in a pair of reactions at 5 mM phenol and pH 4.7 (acetate buffer), the first half-life was 40 ms at 12.3 μM Os^{III} and 7.6 μM Os^{II}, but it increased to 180 ms at 4.7 Os^{III} and 15.1 μM Os^{II}. Because of this sensitivity to the Os^{II} concentration, all further experiments were performed with a large (flooding) excess of Os^{II}. Even with this constraint, the reaction traces still failed to give good pseudo-first-order fits. Pseudo-*second*-order fits, however, were of excellent quality, as shown in Figure 1.

This pseudo-second-order dependence on $[Os^{III}]$ was confirmed in a series of experiments at 135 μM Os^{II} with 2.0 mM phenol at pH 5.1 (acetate buffer): varying the initial Os^{III} concentration from 4.9 to 11.5 μM gave reaction half-lives that were inversely dependent on $[Os^{III}]_0$, as is required for second-order kinetics.

The dependence of k_{obs} on $[Os^{II}]$ was probed at pH 4.7 (acetate buffer) at 5 mM phenol. Under these conditions, k_{obs} showed an inverse second-order dependence on $[Os^{II}]$.

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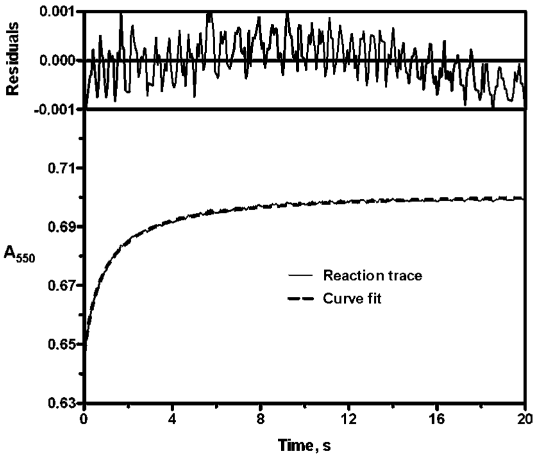

Figure 1. Second-order kinetic trace of phenol oxidation by Os^{III} at 550 nm. μ = 0.1 M (NaCl); T = 25 °C. The lower box shows the experimental trace (solid line) and the pseudo-second-order fit (dashed line). The upper box shows the residuals in the fit. $[Os^{III}]_0$ = 12.1 μM; $[Os^{II}]_0$ = 124 μM; [phenol] = 2 mM; p[H^+] = 5.4 (0.02 M acetate buffer).

The phenol concentration dependence was investigated at pH 5.4 (0.02 M acetate buffer) with 124 μM Os^{II} and $[Os^{III}]_0$ = 12 μM. Over the range of 2–20 mM phenol, the values of k_{obs} obeyed a second-order dependence on [phenol].

Finally, the pH dependence of k_{obs} was studied from pH 4.05 to 6.34 with 0.02 M acetate and cacodylate buffers. These experiments were performed with $[Os^{II}]_0$ = 16 μM and $[Os^{III}]_0$ = 4 μM and [phenol] ranging from 0.2 to 20 mM. From these results, an inverse second-order dependence on [H^+] is deduced.

Overall, the rate law is

$$-\frac{d[Os^{III}]}{dt} = \frac{k[Os^{III}]^2[\text{phenol}]_{tot}^{\,2}}{[Os^{II}]^2[H^+]^2} \qquad (2)$$

with k = (3.7 ± 0.2) × 10^{-9} M s^{-1}. Details of the kinetic methods and tables and figures showing the kinetic data are included in the Supporting Information. Rate law (2) is consistent with the following mechanism:

$$Os^{III} + \text{phenol} \rightleftharpoons Os^{II} + \text{phenoxyl}^\bullet + H^+ \qquad K_{PCET} \qquad (3)$$

$$2\text{phenoxyl}^\bullet \rightarrow \text{coupling products} \qquad k_{dim} \qquad (4)$$

This mechanism leads to the observed rate law (2) when the first step, oxidation of phenol to the phenoxyl radical, is a rapidly established preequilibrium and the second step, radical coupling, is rate-limiting. These approximations imply that $k = 2K_{PCET}^{\ 2}k_{dim}$ (PCET = proton-coupled electron transfer). Further conversion of the coupling products to biphenoquinones, as indicated in eq 1, probably occurs through the overoxidation mechanisms described elsewhere.[8]

Support for this mechanism is provided by consideration of the known constants in eqs 3 and 4. A value for K_{PCET} of 6.1 × 10^{-10} M can be calculated from $E_f(Os^{III}/Os^{II})$ = 0.835 V vs NHE at μ = 0.1 M and [7] E_f(phenoxyl,H^+/phenol) = 1.38 V vs NHE at μ = 0.1 M.[4] A value of 2.3 × 10^9 M^{-1} s^{-1} has been reported for k_{dim}.[9] Thus, a value of 1.7 × 10^{-9} M s^{-1} is obtained for k in eq 2, which is in excellent agreement with the observed result.

Although the rate law in eq 2 is unprecedented in phenol chemistry, there is good precedent for the mechanism that leads to it. Hints of rate law (2) were reported previously for the oxidation of phenol by $[IrCl_6]^{2-}$, where kinetic inhibition by $[IrCl_6]^{3-}$ was observed at low pH.[4] An analogous mechanism was inferred, although the redox step was partially rate-limiting; phenoxyl radical scavenging by dibromonitrosobenzenesulfonate (DBNBS) was used to make the redox step fully rate-limiting, thus revealing the kinetics of the K_{PCET} step. Moreover, Costentin et al. observed rate-limiting phenoxyl radical dimerization in the electrochemical oxidation of phenol, which implies a mechanism analogous to that in eqs 3 and 4.[10,11]

DBNBS has a significant effect in the current reaction (Table S-6 and Figure S-6 in the Supporting Information). With 10 mM DBNBS at pH 4.7, 2.5 mM phenol, 7.1 μM Os^{II}, and 13 μM Os^{III}, the reaction becomes pseudo-*first*-order and substantially faster than that in the absence of DBNBS. These results can be understood by adding the following steps to the reaction mechanism, in strict analogy with the $[IrCl_6]^{2-}$ mechanism:[4]

$$C_6H_6O^\bullet + \text{DBNBS} \rightarrow \text{adduct}^\bullet \qquad k_{DBNBS} \qquad (5)$$

$$Os^{III} + \text{adduct}^\bullet \rightarrow Os^{II} + \text{adduct}^+ \qquad k_{adduct} \qquad (6)$$

$$(\text{DBNBS})_2 \rightleftharpoons 2\text{DBNBS} \qquad K_{dimDBNBS} \qquad (7)$$

Apparently, under the above conditions, scavenging of the phenoxyl radical by DBNBS is rate-limiting, so that the rate law becomes

$$-\frac{d[Os^{III}]}{dt} = \frac{k_{DBNBS}K_{PCET}[\text{DBNBS}][Os^{III}][\text{phenol}]_{tot}}{[Os^{II}][H^+]} \qquad (8)$$

This model can be tested with no adjustable parameters because the requisite value for K_{PCET} is given above and the value for k_{DBNBS} (=2.0 × 10^5 M^{-1} s^{-1}) has been determined previously.[8] The results of kinetic simulations based on these parameters provide an excellent match to the experimental results, as shown in Table S-7 in the Supporting Information. Unfortunately, even with the highest concentration of DBNBS investigated, the rate of phenoxyl radical scavenging was not high enough to shift the rate-limiting step to the PCET oxidation of phenol (reaction 3).

Although our data are insufficient to define the full mechanism of the PCET process in eq 3, at a minimum, it should include the outer-sphere sequential proton transfer–electron transfer (PTET) pathway:

$$\text{phenol} \rightleftharpoons \text{phenoxide}^- + H^+ \qquad K_a \qquad (9)$$

$$Os^{III} + \text{phenoxide}^- \rightarrow Os^{II} + \text{phenoxyl}^\bullet \qquad k_{et} \qquad (10)$$

An estimate of k_{et} (2 × 10^9 M^{-1} s^{-1}) can be made based on the formulation of Marcus theory that we have used previously,[8] along with several supporting parameters: $k_{11}(Os^{III/II})$ = 3 × 10^8 M^{-1} s^{-1},[12] k_{22}(phenoxyl/phenoxide), from electron-spin resonance = 1.9 × 10^8 M^{-1} s^{-1},[13] r(Os) = 6.7 Å,[7] and r(phenoxide) = 4.8 Å.[8] Alternatively, if we use k_{22} = 2.3 × 10^6 M^{-1} s^{-1} as derived from the reaction of phenoxide with $[IrCl_6]^{2-}$,[8] then a somewhat lower estimate of 4 × 10^8 M^{-1} s^{-1} is obtained for k_{et}. In either case, kinetic calculations described in the Supporting Information show that this PTET pathway is fast enough for the PCET process in eq 3 to reach equilibrium irrespective of whether the fate of the phenoxyl radical is to undergo coupling as in eq 4 or scavenging by DBNBS. In contrast, when the oxidant is $[IrCl_6]^{2-}$, the rate of electron transfer is much slower ($k_{et} = 8 \times 10^6$ M^{-1} s^{-1}), which makes it possible to use scavenging by DBNBS to make the electron-transfer step rate-limiting. The lower rate constant for $[IrCl_6]^{2-}$ is due to its lower self-exchange rate constant and to its negative charge.

On the basis of electrochemical experiments, Fecenko et al. have reported that the oxidation of tyrosine by $[Os(bpy)_3]^{3+}$ is catalyzed by buffers.[5,14] Similarly, the PCET oxidation of phenol by $[Ru(bpy)_3]^{3+}$ is buffer-catalyzed.[2,15] Buffer catalysis of the electrochemical PCET oxidation of phenol has also been reported by Costentin et al.[10,11] An analogous catalysis may be operative in the current study, but our data do not afford any insight on this matter.

Another potential concern is that deprotonation of phenol could be rate-limiting, as has been reported for the photoinduced intramolecular oxidation of phenols by Ru^{III}.[16] However, the form of the rate laws in the current study clearly is inconsistent with rate-limiting proton transfer. This is understandable because the rates reported here are orders of magnitude slower than those encountered in the intramolecular studies.

In summary, when the overall oxidation of phenol by $[Os(phen)_3]^{3+}$ is monitored by stopped-flow spectrophotometry, the rate-limiting step is phenoxyl radical coupling. This leads to a qualitatively different rate law than when the oxidant is $[IrCl_6]^{2-}$, even though both reactions probably have the same mechanism. These results underscore the challenges in probing endothermic PCET reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details regarding the collection and fitting of kinetic data, table of spectroscopic data, tables and figures of experimental kinetic data, table of simulated kinetic data, and details demonstrating the competence of the PTET mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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