

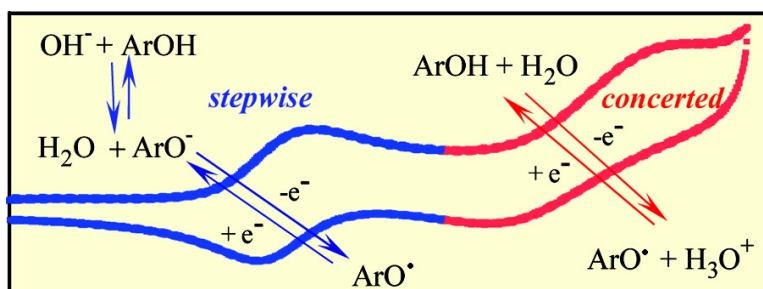
Communication

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J. Am. Chem. Soc., **2008**, 130 (47), 15817-15819 • DOI: 10.1021/ja8064914 • Publication Date (Web): 31 October 2008

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Evidence for Concerted Proton–Electron Transfer in the Electrochemical Oxidation of Phenols with Water As Proton Acceptor. Tri-*tert*-butylphenol.

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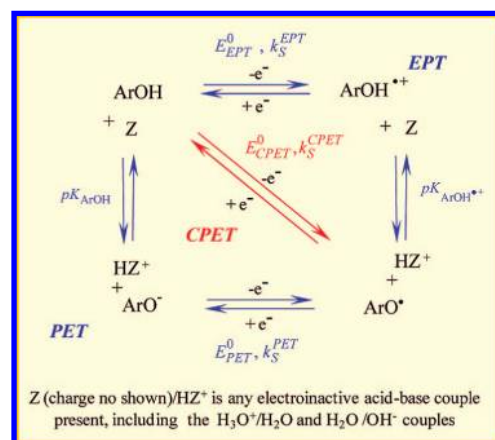
Association between single electron transfer and proton transfer in many reactions of electron transfer and radical chemistry is a well-recognized and largely spread phenomenon. Molecular electrochemists have dedicated an active attention to this possible association as a particular case of the coupling between electron transfer and acid–base reactions in a general sense. Until very recently, however, proton transfer and electrochemical electron transfer have been viewed as separate steps. This conception is rapidly changing as electrochemistry increasingly contributes to the interpretation of recently discovered clues that the two reactions may be concerted in several natural processes.¹ The most prominent of these involves photosystem II,² but evidence has been gathered that similar processes might be at work in the functioning of several other biochemical systems.³ Very likely, this is only the tip of the iceberg as electron transfer (and/or transport) and proton transfer (and/or transport) are associated in a considerable number of natural processes. One may even wonder if the remarkable efficiency of enzymatic systems in which proton and electron transfers are coupled is not the result of their acting in concert.

Coupling proton transfer to electron transfer entails an improvement of the driving force of the reaction. These Proton Coupled Electron Transfer (PCET) reactions may follow two types of mechanism (Scheme 1): a mechanism in which the two reactions occur in a stepwise manner (in blue), with proton transfer first, followed by electron transfer (PET) or, vice versa, electron transfer first, followed by proton transfer (EPT) and a mechanism in which proton and electron transfer occur in a concerted manner (CPET pathway, in red). Only in the latter case will the benefits of the additional driving force offered by the coupling with proton transfer be fully exploited, although there might be a kinetic price to pay for this advantage.

In view of the involvement of tyrosine oxidation in photosystem II, PCET oxidation of phenols currently attracts a particularly active attention. The oxidation of phenols with an amine present in a nonaqueous solution or bearing an amine attached to the structure as proton acceptor is a case of special interest, as a mimic of the role of the proximal histidine in photosystem II. These model systems have been investigated using molecular oxidants or by means of electrochemical oxidation.⁴ The advantages of the electrochemical approach, through techniques like cyclic voltammetry, are an easy determination of the standard potential of the CPET reaction and the possibility of observing the kinetics of the forward as well as reverse reaction as a function of a continuously varying driving force as provided by the electrode potential.

When these PCET oxidations of phenols take place in water, besides the base components of the buffer, another proton acceptor of obvious interest is water itself.⁵ So far, these reactions have been investigated using molecular oxidants in solution or attached to the phenol. Because of the advantages just mentioned and of the ongoing debate concerning the reactions that involve water as proton

Scheme 1



acceptor,⁵ we thought it interesting to examine the occurrence of CPET pathways and their competition with the stepwise pathways in the direct electrochemistry of phenols and in total absence of buffer, which is the best way to unambiguously assign water as a proton acceptor.

A first difficulty in this venture is related to the self-reactivity of the radical ArO• and of its reactivity toward the surface of the glassy carbon used as a working electrode. The introduction of three *tert*-butyl groups in the 2, 4, and 6 positions to the phenolic group prevents the occurrence of these reactions. We are left however with a scarce solubility of the ensuing ArO• radical in water, which then tends to accumulate at the electrode and may cause consequently a rise in undesired current inhibition.⁶ We have found that a 50/50 (volume) water–ethanol mixture leads to satisfactory results in this respect as already suggested by an early investigation of the electrochemical oxidation of 2,4,6-tri-*tert*-butylphenol (TTBP).⁷ The same study also showed the appearance of a one-electron reversible cyclic voltammetric wave in a basic buffered medium unambiguously assigned to the reversible fast interconversion between ArO⁻ and ArO•. A single irreversible two-electron wave was observed at low pH, where the oxidation of ArO• into ArO⁺ (followed by an irreversible reaction with water) is easier than its generation from ArOH.

We have found that the cyclic voltammetric observation of TTBP oxidation in nonbuffered media⁸ allows us to clearly identify for the first time the occurrence of a CPET pathway consisting in the one-step formation of a proton and a phenoxy radical (red pathway in Scheme 1) and to read directly on the cyclic voltammograms its competition with a PET pathway in which OH⁻ is the proton acceptor. Useful thermodynamic data were nevertheless derived from the reversible wave observed in basic buffered media in which the linear correlation between the apparent standard potential and the pH (“Pourbaix diagram”, red data points in Figure 1a) could

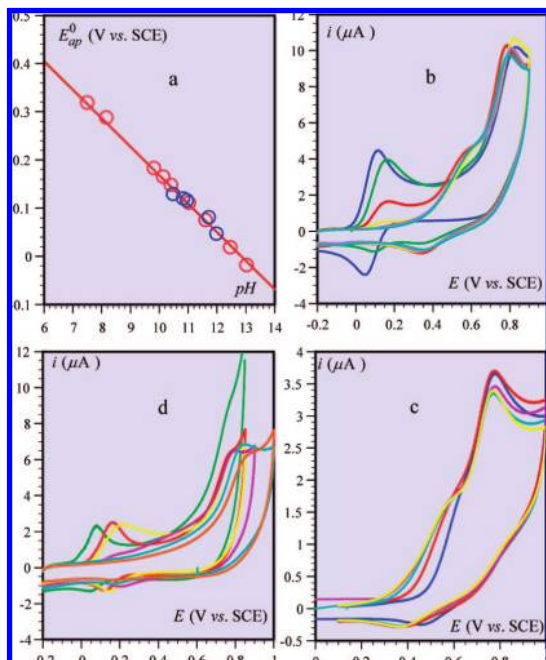


Figure 1. (a) Apparent standard potential vs pH obtained from the reversible cyclic voltammograms in buffered media (Britton–Robinson 0.05 M) (red circles) and in unbuffered media (blue circles). (b) Cyclic voltammograms at concentration $C^0 = 0.28$ mM in unbuffered water as a function of pH: 11.7 (blue), 11 (green), 10.5 (red), 10.1 (yellow), 9.6 (magenta), 8.2 (cyan). Scan rate: 0.1 V/s. (c) Cyclic voltammograms at concentration $C^0 = 0.28$ mM in unbuffered water as a function of pH: 7.5 (yellow), 6.9 (magenta), 5.0 (cyan), 4.1 (red), 3.0 (blue). Scan rate: 0.02 V/s. (d) Cyclic voltammograms at $C^0 = 0.14$ mM in unbuffered D_2O as a function of pH: 11 (green), 10.5 (red), 10 (yellow), 9 (magenta), 8 (cyan), 7 (brown). Scan rate: 0.1 V/s.

be obtained thanks to the constancy of pH and the fast establishment of the protonation–deprotonation equilibria. The Pourbaix diagram did not show a clear leveling off of the apparent standard potential at high pH corresponding to the zone of stability of the phenoxide ion that would allow precise determination of the TTBP pK_a . It appears as being equal or larger than 13, i.e., much larger than in the case of unsubstituted phenol ($pK_a = 10$). The small electron-donating effect of the *tert*-butyl substituents is not sufficient to account for such a large shift of the pK_a , which should rather be ascribed to steric hindrance by the two bulky *tert*-butyl groups of $-O^-$ solvation by water molecules.

The cyclic voltammogram obtained in very basic water (pH 11.7 in Figure 1b) shows two waves. The first of these corresponds to the PET mechanism sketched in Scheme 1: the phenoxide ion quickly generated from the phenol by reaction with OH^- is rapidly oxidized into the phenoxyl radical giving rise to a one-electron reversible Nernstian wave. The second wave is irreversible and corresponds to the oxidation of the phenoxyl radical produced at the first wave, generating the cation which then irreversibly reacts with water.⁷

As the pH is decreased a new (chemically) reversible wave progressively appears in between the two others. It increases at the expense of the first until this has completely disappeared. It may be assigned to the occurrence of a CPET oxidation (Scheme 1) of TTBP in which a water molecule serves as proton acceptor and H_3O^+ is formed concertedly with the phenoxyl radical. The location of the most positive wave remains the same as expected from the fact the same phenoxyl radical as in the PET process is the result of the CPET reaction.

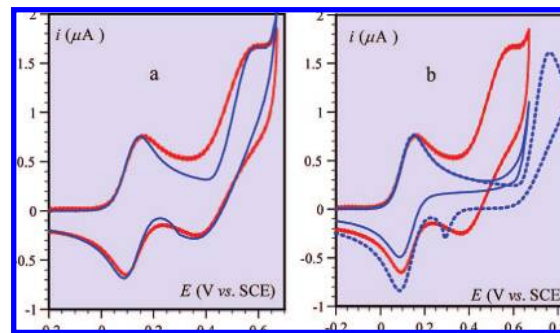


Figure 2. The two first cyclic voltammometric waves at pH = 10.5 ($C^0 = 0.28$ mM, scan rate: 0.1 V/s) in H_2O corrected from background (in red) and simulation¹¹ (in blue) for (a) a PET- OH^- -CPET mechanism with the following: $E_{PET}^0 = -0.028$ V vs SCE (implying that $pK_{ArOH} = 13$), $E_{CPET}^0 = 0.735$ V vs SCE; standard rate constants ($cm\ s^{-1}$) $k_{PET}^0 = 1$, $k_{CPET}^0 = 0.1$, $[H^+] = 8.3 \times 10^{-11}$ M, $[OH^-] = 1.9 \times 10^{-5}$ M; diffusion coefficients ($cm^2\ s^{-1}$) $D_{ArOH} = 2 \times 10^{-6}$, $D_{H_3O^+} = 10^{-4}$, $D_{OH^-} = 5 \times 10^{-5}$; protonation/deprotonation rate constants $10^{12}\ M^{-1}\ s^{-1}$ or s^{-1} in the downhill direction. Simulation of the beginning of the ArO^+/ArO^+ wave involves as parameters the following: $E_{ArO^+/ArO^+}^0 = 0.735$ V vs SCE; $k_{ArO^+/ArO^+}^0 = 0.05\ cm\ s^{-1}$; $k_{ArO^+ \rightarrow product} = 10^7\ s^{-1}$,¹² (b) a PET- OH^- -EPT mechanism with the same parameters and $E_{EPT}^0 = 1.035$ V vs SCE (implying that $pK_{ArOH} = -5$); standard rate constant $k_{EPT}^0 = 1\ cm\ s^{-1}$. To gauge the intrinsic response of the EPT process, the oxidation of ArO^+ has been omitted in the simulation represented by the dotted blue line.

At very high pH's, oxidation follows a PET pathway in which OH^- ions serve as proton acceptors. The rapid decrease of the first wave upon decreasing the pH in the absence of buffer—much more rapid than in buffered media—is caused by the elimination of the OH^- ions present by the protons produced by oxidation. The height of the wave is therefore a function of the balance between the initial amount of OH^- ions, $[OH^-]^0$, and the concentration of TTBP, C^0 , which is the main parameter of proton production. Then,⁹ if $[OH^-]^0 D_{OH^-} > C^0 D_{ArOH}$ (the D 's are the diffusion coefficients of the subscript species), i.e., for pH < 10.5, a wave of normal height (proportional to $C^0 \sqrt{D_{ArOH}}$) is expected, whereas, for $[OH^-]^0 D_{OH^-} < C^0 D_{ArOH}$, the prediction is a still reversible wave whose height is proportional to $[OH^-]^0 D_{OH^-} / \sqrt{D_{ArOH}}$ until it vanishes as the medium is made more and more acidic.¹⁰

The decrease and disappearance of the PET- OH^- wave provides space for the development of the CPET wave. One of the most striking features of the cyclic voltammetry of TTBP in H_2O is the curve recorded at pH 10.5 where the contributions of the PET- OH^- and CPET- H_2O pathways are about equal: the occurrence of the two competing routes is directly visualized in the cyclic voltammetry response. The curve is shown in more detail in Figure 2a, reversing the scan at the foot of the ArO^+/ArO^+ wave and subtracting the background current. Simulation¹¹ according to the competitive PET- OH^- and CPET- H_2O mechanism led to quite satisfactory results (the simulation parameters are detailed in the caption of Figure 2a), taking into account that the autoprotolysis constant is smaller (1.5×10^{-15}) in the water–ethanol mixture than in water.¹³ We also see that the standard rate constant of the concerted proton–electron transfer is somewhat lower than that of the simple outersphere electron transfer from the phenoxide ion. This is expected in terms of both reorganization energy and also pre-exponential factor as a reflection of proton tunneling through the activation barrier.^{4b}

In line with this mechanism is the observation (Figure 1b, c) that the location of the CPET wave is independent of the pH until⁹

$$pH < -\log(C^0 \sqrt{D_{ArOH}/D_{H^+}})$$

≈ 5 in our case. The wave indeed starts to shift in the positive direction at pH 4.2, and the shift continues for smaller pH's (Figure 1c). The above condition reflects the fact that, in nonbuffered basic medium, it is the production of protons by the CPET reaction itself that controls the backward reaction, leading to an apparent standard potential independent of the initial pH:⁹

$$E_{ap}^0 = E_{CPET}^0 + (RT/F) \ln(C^0 \sqrt{D_{ArOH}/D_{H^+}})$$

At lower pH's, E_{ap}^0 gradually reaches back to the Pourbaix variation:⁹

$$E_{ap}^0 = E_{CPET}^0 - (RT/F \ln 10) \text{pH}$$

Now that we have shown that the experimental data are compatible with a PET-OH⁻-CPET mechanism, the next question to be discussed is how can we be sure that a CPET mechanism is indeed operating? The only alternative is an EPT mechanism (Scheme 1) in which the initial formation of the cation radical is followed by its rapid deprotonation. We could then envisage a competition between this mechanism and the same PET-OH⁻ mechanism that has been discussed above through its competition with the CPET mechanism. Figure 2b shows the results of a simulation of the pH = 10.5 double wave for this PET-OH⁻-EPT mechanism in which the PET-OH⁻ parameters have the same values as in the simulation of the PET-OH⁻-CPET mechanism in Figure 2a. For simulation the EPT kinetics, we need an estimate of the dissociation constant of the cation radical, ArOH^{•+}. For unsubstituted phenol, the corresponding pK_a has been determined as being equal to -2.¹⁴ It has been seen earlier that steric hindrance to solvation destabilizes the phenoxide ion in the phenol/phenoxide couple by a factor of at least 10³ in terms of the equilibrium constant. A similar effect is expected to affect the stability of the cation radical, which can be then estimated as being smaller than 10⁻⁵ in terms of the dissociation constant. Using the Pourbaix diagram, the EPT standard potential can therefore be estimated as being more positive than $E_{EPT}^0 = 1.035$ V vs SCE. Electron transfer from TTBP, leading to the cation radical, is a fast outersphere process as is electron transfer from the phenoxide ion leading to the phenoxyl radical. This led us to take the same value of the standard rate constant for both reactions. However, since the follow-up deprotonation reaction is very fast, the whole process is kinetically controlled by the forward electron transfer step. It unambiguously appears that the PET-OH⁻-EPT mechanism is not compatible with the experimental data: the potential at which the EPT current appears (shown as a dotted curve in Figure 2b) is so positive that it merges with the phenoxyl radical oxidation current in the framework of an "ECE" mechanism.¹⁵

Observation of the wave system in a 50/50 D₂O-C₂D₅OD mixture is an additional source of mechanistic information. As seen in Figure 1c, the PET-OH⁻ wave shows a similar behavior as in H₂O. This is not the case with the intermediate wave, which is now merged with the ArO[•]/ArO⁺ wave. Using buffered solutions, we have found that the Pourbaix diagram is practically the same in D₂O and H₂O. It follows that the strong change in behavior is due to a significant decrease of the standard rate constant. Assuming a transfer coefficient of 0.5, the decrease is at least by a factor of 10. This very significant H/D isotopic effect is compatible with the CPET mechanism^{4b} but not with the EPT mechanism. Since

the EPT process is kinetically governed by the forward electron transfer, no significant H/D isotopic effect is indeed expected for this mechanism. The observation of a quite significant H/D isotopic effect thus confirms the ruling out of the EPT mechanism and therefore the concerted character of the reaction.

In summary, we have shown, with the example of 2,4,6-tri-*tert*-butylphenol in nonbuffered aqueous solutions, that the cyclic voltammetric observation of the electrochemical oxidation and reverse reaction has allowed the unambiguous identification of a reaction pathway in which the phenol is directly and reversibly converted into the phenoxyl radical while the generated proton is accepted by a water molecule in a concerted manner. In very basic media, a stepwise mechanism takes place in which the phenol is deprotonated by OH⁻ and the resulting phenoxide ion rapidly oxidized into the phenoxyl radical. As the pH decreases, this pathway progressively shuts down to the advantage of the concerted pathway. At intermediate pH's the contributions of the two pathways are about equal and the occurrence of the two competing routes is directly visualized in the cyclic voltammetry response.

Supporting Information Available: Detailed analysis of the PET-OH⁻ and CPET waves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) At a 3-mm-diameter glassy carbon electrode, carefully polished before each CV run, with 0.5 M KNO₃ as supporting electrolyte. The pH was adjusted by appropriate additions of NaOH or HCl.
- (9) See Supporting Information.
- (10) These two limiting regimes are also characterized by different expressions of the apparent standard potential, E_{ap}^0 , defined as the middle between the anodic and cathodic peaks. When $[\text{OH}^-]^0 D_{\text{OH}^-} > C^0 D_{\text{ArOH}}$: $E_{ap}^0 = E_{PET}^0 + (RT/F) \ln([\text{H}^+]^0 / K_{\text{ArOH}})$, which corresponds to the Pourbaix variation. When $[\text{OH}^-]^0 D_{\text{OH}^-} < C^0 D_{\text{ArOH}}$: $E_{ap}^0 = E_{PET}^0 + (RT/F) \ln(K_5 D_{\text{OH}^-} / K_{\text{ArOH}} C^0 D_{\text{ArOH}})$. K_5 : Solvent autoprotolysis constant. This is what is indeed observed in Figure 1a: the Pourbaix diagram is followed for most of the pH domain where the PET wave can be seen. It ended by a slight leveling off of E_{ap}^0 observed before the wave vanishes.
- (11) (a) Using the DigiElch software.^{11b} (b) Rudolph, M. *J. Electroanal. Chem.* **2003**, *543*, 23. (c) Taking into account that the current depression between the two waves is due to the lack of accuracy of the simulation technique for the very fast reactions involved.
- (12) These are not precisely determined values, but merely values that are just able to reproduce the current at the foot of the phenoxyl radical oxidation wave.
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JA8064914