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Proton-Coupled Electron Transfer from an Interfacial Phenol Monolayer

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Highlights

- The pH-dependent mechanism and dynamics of proton coupled redox reactions from an alkane thiol monolayer with phenol head groups is revealed.
- A novel, non-pre-equilibrium model (Steady-state model) accurately describes the kinetics of proton coupled redox reactions and the scan-rate dependent current response in cyclic voltammetry.
- The presented model presents an alternative approach to describing surface confined proton coupled electron transfer reactions where proton transfer reactions are cannot be assumed to be fast in relation to the electron transfer reactions.

Graphical Abstract

Abstract

A tert-butyl protected phenol is covalently link to a mixed self-assembled monolayer on a gold or platinum electrode. The phenol reduction potential shows the expected pH-dependence of a one-electron, one-proton couple with a decrease in formal reduction potential of 59 ± 5 mV per pH. A titration of the phenol is observed with a pK_a of 13.2 and the reduction potential for the phenolate is 0.11 V vs. NHE. The kinetic behavior of the proton-coupled oxidation deviates substantially from the commonly used models for a step-wise reaction that assume the proton transfer reactions are in equilibrium throughout the reaction. A novel model for step-wise proton-coupled reactions is presented that fully accounts for the pH dependent kinetics and allows the formal rate constants and the transfer coefficients to be determined.

KEYWORDS: Phenol-terminated alkane-thiol monolayer, Proton-coupled electron transfer, pH dependence, Kinetic models.

1 Introduction

Proton-coupled electron transfer reactions are of great importance in a variety of biological and chemical processes. [1-4] The coupled reaction can proceed either in a stepwise or a concerted fashion. In the stepwise case, the proton-transfer occurs either prior to, or after the electron transfer reaction while in the concerted reaction the two processes share a unique transition state and are thus simultaneous. Recently, significant attention has been devoted to the relative importance of these reaction mechanisms and experimental tools for mechanistic discrimination have been developed and debated. [5-9]

In this report we have used a redox active phenol moiety as model to study proton-coupled electron transfer by electrochemical means. Due to its structural homology with tyrosine,

which is known to be important as a redox intermediate in several radical proteins including Photosystem II[10], DNA photolyase[11], ribonucleotide reductase[1] and cytochrome c oxidase[12], this model compound is of particular interest. The phenol radical was stabilized by tert-butyl substituents in ortho-position and a carboxylate functionality in the para-position was used to covalently attach the phenol onto an amine terminated alkane thiol layer on platinum or gold using a peptide linkage. The phenols were diluted with alcohol terminated thiols to form the system depicted in Figure 1. Immobilizing the phenol avoids mass transfer limitations which simplifies the kinetic analyses. The use of alkane thiol linkers for surface attachment makes it possible to tune the rates of the redox reaction by varying the length of the thiol spacer. With the densely packed alkane thiol monolayer, double layer effects are also minimized and the low capacitance of these layers reduces the response time of the electrochemical set-up. [13]

Figure 1. Schematic illustration of monolayers of 2,6-Di-tert-butyl-phenol attached to a metal substrate via an amide link to a alkane thiol. The phenol monolayer was diluted 20 fold with 6-mercapto-1-hexanol. Gold or platinum was used as substrate electrode.

The proton-coupled electron transfer reaction from the phenol is schematically depicted in Scheme 1. Two step-wise reactions that convert the protonated phenol to the deprotonated phenol radical can be envisioned, one in which the phenol first deprotonates forming a phenolate ion that is subsequently oxidized and another path where the primary step is the oxidation of the phenol forming the protonated phenol radical that deprotonates as a consequence of the oxidation. The first of these reaction paths is expected to dominate the kinetics at high pH where a significant fraction of phenolates are accessible, whilst the second reaction path dominates at low pH.

To treat the kinetics of electrochemically-driven, surface-confined proton-coupled electron transfers, and specifically the pH dependence of the reaction, a model is often adopted in which it is assumed that the proton transfer reactions are rapid compared to the electron transfer reactions. This model was originally developed by Laviron[14-18] and it has been used to successfully model the kinetics of proton-coupled electron transfer reactions in a variety of systems. [19-22] The model has also been extended by the work of Finklea et.al. to include the influence of a potential-dependent transfer coefficient as predicted from the Marcus density-of-states model. [23-25] Within this model, the overall rate constant is given by the fraction of the intermediate species, the phenolate and the protonated radical, relative to its proton equilibrium counterpart, multiplied by the rate constant for the relevant redox reaction. The apparent exchange rate constant at the formal potential shows a deep minimum at pHs between the pK_a -values for the reduced and the oxidized species. At pH values above the minimum, the reaction is dominated by the phenolate path and at pH values below the minimum it is dominated by the protonated radical route. The steepness of the pH response is controlled by both the pH dependent species present and the dependence of the electron transfer rate constant on pH.

Scheme 1. Reaction Scheme for proton-coupled redox reaction of phenol monolayers

Although the proton equilibrium model has been highly successful in interpreting surface-confined proton-coupled redox reactions, the assumption that proton transfer reactions are fast compared to the electron transfer reactions, is often questionable. For the proton transfer reactions two equilibria need to be considered as depicted in Scheme 1. At low pH the phenol dissociation equilibrium is dominated by deprotonation to H_2O and protonation by H_3O^+ (left panel Scheme 1) and the dissociation constant (K_a) is given by Equation 1 where k_{2d} is the rate constant for deprotonation to H_2O and k_{-2d} the protonation by H_3O^+ .

$$K_a = k_{2d}/k_{-2d} \quad (1)$$

For an exergonic proton transfer between two Eigen-acids with sufficiently different pK_a values, typically one pH unit, the rate of proton transfer non-activated and the reaction is diffusion controlled. [26-28] Consider for instance the protonation of a phenolate, for which the corresponding phenol typically has a pK_a value around 10 [29], by H_3O^+ , which has a pK_a value of -1.7 [27] (k_{-2d} in Scheme 1). This reaction is expected to be diffusion controlled. Given the high mobility of the proton, the rate constant (k_{-2d}) is on the order of $10^{11} \text{ M}^{-1}\text{s}^{-1}$.

From Equation 1 the corresponding deprotonation rate constant (k_{2d}) is 10s^{-1} which is readily exceeded by the observed rate constant in many electrochemical measurements.

At high pH, the phenol dissociation reaction is instead dominated by deprotonation to OH^- and protonation by H_2O (right panel Scheme 1). In this case the deprotonation reaction is expected to be diffusion controlled given that the pK_a value for water is 15.7. [27] The lower mobility of OH^- compared to H_3O^+ gives an order of magnitude lower diffusion controlled rate constant and k_{2d}' is expected to be on the order of $1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. At pH 7, for instance, the concentration of OH^- is 10^{-7} M and the rate of deprotonation by OH^- can be estimated to 10^3 s^{-1} . Also this rate is often surpassed by surface-confined redox reactions. From the equilibrium condition (Equation 2) the rate constant for protonation by water (k_{-2d}') is expected to be on the order of $1 \times 10^6 \text{ s}^{-1}$ for a phenol with a pK_a of 10. In Equation 2 K_w is the auto-protolysis constant for water.

$$K_a/K_w = k_{2d}' / k_{-2d}' \quad (2)$$

From the discussion above it is clear that the proton-equilibrium model does not apply at all pH values in proton-coupled redox systems, in particular where reactants with high pK_a -values are involved. We have therefore adopted a steady-state approach to rationalize the kinetics of proton-coupled electron transfers in the phenol monolayers depicted in Figure 1. In this model, the assumption is that in a kinetically controlled reaction the concentration of the intermediate species in Scheme 1 is never built up, i.e., the rate of intermediate state production is always less than the rate of reactions consuming it. With this assumption, analytical expressions for electrochemical responses have been derived and used in the kinetic analysis. For comparative reasons kinetic data have also been analyzed using the proton equilibrium model.

2 Experimental Section

All chemicals were purchased and used as received. For all solutions distilled deionized water with a resistivity above 18 MΩcm or anhydrous ethanol (Sigma Aldrich) was used.

2.1 Electrode fabrication

Platinum or gold disc electrodes were prepared by sealing a 100 μm radius platinum wire (Goodfellow) or a 125 μm radius gold wire (Goodfellow) in a soft glass tube. The end of the glass tube was first melted to give a small opening at one end of the tube. After sonicating the tube in acetone for 10 min and evaporation of the acetone from the tube the metal wire, attached to a 1 mm copper substrate wire, was fit into the melted end of the glass tube and was sealed into the glass by melting the glass around the metal. The open end of the glass tube, where the substrate copper wire was protruding, was sealed using a plastic cap and epoxy glue. The metal disc electrodes were exposed by sanding on 500 grit paper followed by successive polishing with 1, 0.3 and 0.05-μm alumina (Buehler) water slurry.

2.2 Monolayer preparation

Electrodes were first polished with 0.05 μm alumina, rinsed with water and sonicated for one minute in water. The electrodes were then electrochemically cleaned in 0.5 M H₂SO₄ (Sigma-Aldrich 99.999 %) by cycling the potential between -0.2 V and 1.45 V for platinum electrodes and between -0.25 and 1.5 V vs. Ag/AgCl saturated with KCl for gold electrodes. The reference electrode was kept in a compartment separated from the cleaning solution by a porous glass frit. Estimates of the real surface areas of the electrodes were made from the metal oxide reduction wave from voltammetric scans between -0.15 and 1.35 for platinum

electrodes and -0.25 and 1.45 for gold electrodes. The roughness factor was typically between 1.5 and 2.5. [30]

Immediately after the electrochemical cleaning, the electrodes were rinsed with water then ethanol and were immersed into 10 mM thiol deposition solution. The deposition solution was either a 1:20 mixture of 8-Amino-1-octanethiol and 6-mercapto-1-hexanol or pure 6-mercapto-1-hexanol. The 6-mercapto-1-hexanol covered electrodes served as backgrounds and one background electrode was prepared for each electrode with mixed thiol composition.

After at least 3 hours of coupling the mixed composition electrodes were rinsed with ethanol and were transferred to a peptide linkage solution composed of 40 mM 3,5-Di-tert-butyl-4-hydroxyphenylacetic acid (Alfa Aesar) and 1.8 M N-(3-Dimethylaminopropyl)-N'-Ethylcarbodiimide (Sigma-Aldrich) in ethanol. To one mL of this solution 1 drop 1M KOH_{aq} was added. The addition of KOH_{aq} was found to enhance the reaction yield and to speed up the reaction significantly. The peptide reaction was left to proceed for 3 hours, the electrodes were then rinsed with ethanol and transferred to a 10 mM 6-mercapto-1-hexanol solution and left overnight to improve packing of the monolayer. Also the background electrodes were left overnight in the coupling solution.

2.3 Electrochemical measurements

All electrochemical measurements were made in 0.1 M K₂SO₄ solution buffered with 10 mM H₃BO₃ (Sigma Aldrich) and 10 mM Na₂HPO₄ (Sigma-Aldrich). The pH was adjusted using concentrated sulfuric acid or potassium hydroxide. To remove dissolved oxygen the electrolyte solution was purged with argon prior to measurement and was kept under an argon atmosphere throughout the measurement.

A conventional three electrode system was used in a single compartment. An Ag/AgCl electrode with saturated KCl was used as reference. To facilitate comparison, all reported

potentials were converted to the normal hydrogen electrode scale by adding 0.197 V to the measured potential. The phenol covered platinum or gold disc electrodes and the corresponding 6-mercapto-1-hexanol covered electrodes (see above) constituted the working electrodes and a platinum wire served as the counter electrode. To correct for uncompensated resistance in the cell, AC impedance measurements between 10 and 10 000 Hz were made and the resistance were typically evaluated to be around 300 Ω . All potentials applied to the phenol monolayer were corrected for uncompensated resistance and the same correction was used for the 6-mercapto-1-hexanol layers to enable subtraction of capacitive currents. Since the 6-mercapto-1-hexanol layers gave a rather flat baseline for subtraction the error introduced by this procedure should be minor.

All data were collected using a CHI660C Electrochemical workstation (CH-Instruments) and CVs were collected at scan rates between 0.1 and 20000 Vs^{-1} with typically 1000 data points per CV. The lower scan rates were used to characterize the phenol monolayer while higher scan rates were used to get kinetic information on the phenol oxidation. All kinetic CVs were corrected for uncompensated resistance, the capacitive current was subtracted and the resulting voltammograms were analyzed in Origin by fitting the CVs to the models described below while the low scan rate CVs were analyzed in the software provided by CH-Instruments. The reported data are from fully reproducible voltammograms from multiple consecutive scans centred on the recorded redox process.

3 Results and discussion

3.1 Monolayer Characterization

Figure 2. Cyclic voltammetry at 1 Vs^{-1} of a gold electrode covered with phenol monolayer (black), 6-mercapto-1-hexanol monolayer (grey) and the background subtracted response (red) in $0.1 \text{ M K}_2\text{SO}_4$ buffered with $10 \text{ mM Na}_2\text{HPO}_4$ and H_3BO_3 and adjusted to pH 10.3 with KOH_{aq} . The surface coverage was evaluated from the peak area and the microscopic electrode area ($1.2 \times 10^{-3} \text{ cm}^2$) as $1.9 \times 10^{-11} \text{ mol cm}^{-2}$.

Figure 2 shows a typical cyclic voltammogram at 1 Vs^{-1} of the phenol monolayer depicted in Figure 1 on a gold electrode together with a voltammograms from a 6-mercapto-1-hexanol covered electrode at pH 10.3. Subtraction of the response from the 6-mercapto-1-hexanol layer removes a significant fraction of the background capacitance. (The somewhat higher capacitance of the phenol layer might be due to a decreased monolayer packing due to the

introduction of the phenol-functionalized thiols). At this scan rate the peak separation between the oxidation and the reduction wave is close to 0 (7mV) and is reduced to zero at even lower scan rates (0.1 Vs^{-1}) as expected for fully reversible redox reactions. The full width at half maximum for both the oxidation wave and the reduction wave was significantly larger than the expected 90.6 mV for a fully reversible one-electron reaction. This was found at all scan rates and pH values investigated and it suggests thermodynamic heterogeneity, interaction between the redox centers or double layer effects.[13] The origin of this non-ideal behavior has however not been pursued further in this work.

From the peak area and the estimated real electrode area the surface coverage of the phenol was estimated to $1.9 \times 10^{-11} \text{ mol cm}^{-2}$. By reductive desorption of the thiol layer in 0.1 M KOH the total amount of thiols on the surface was estimated to $9.1 \times 10^{-10} \text{ mol cm}^{-2}$. [31] 2% of the thiols on the surface are thus functionalized with phenols. Since the 8-Amino-1-octanethiol and the diluting 6-mercapto-1-hexanol are of similar size and are expected to have similar diffusion constants an approximate estimate of the surface composition can be made from the composition of the coupling solution, i.e. 8-Amino-1-octanethiol:6-mercapto-1-hexanol 1:20. [32, 33] The maximum phenol surface coverage is therefore $4.55 \times 10^{-11} \text{ mol cm}^{-2}$ and hence the peptide reaction yield is about 40 %. This is however an underestimation of the yield since the thiol monolayers are known to exchange slowly with thiols in solution and therefore, when the phenol covered electrodes are immersed in the 6-mercapto-1-hexanol solution for improved packing, some losses of phenols are expected. [34]

Figure 3. Absolute peak current normalized to the peak area as function of the logarithm of the scan rate between 0.1 and 100 Vs⁻¹. The conditions were the same as in Figure 2. Black squares correspond to the phenol oxidation and red triangles to the reduction. The solid lines are linear fits to the data and the evaluated slopes were 0.98 and 0.97 for the oxidative data and the reductive data respectively.

At scan rates below 10 Vs⁻¹ loss of surface coverage was observed indicating instability of the phenol radical. Below 1Vs⁻¹ this loss was severe and the effect was also more pronounced at low pH thus limiting the useful pH range. To account for the loss of surface coverage the peak currents in Figure 3 have been normalized to the peak area. With this correction made the logarithm of the peak currents show a linear increase with the logarithm of the scan rate up to 100 Vs⁻¹ and the slope was close to 1 at all pH investigated as expected for a surface confined redox reaction. By changing the scan rate, the relative influences of the rates of

electron and proton can be changed. At higher scan rates this linear increase in peak current with scan rate was no longer observed and at lower pH the onset of non-linearity occurred at lower scan rates. The origin of the non-linear dependence of the peak current with scan rate is discussed below.

3.2 pH dependence of the formal reduction potential

Figure 4. pH dependence of the formal potentials evaluated from cyclic voltammograms of a phenol monolayer together with a fit to Equation 3. The inset shows background subtracted cyclic voltammograms from phenol monolayers at pH 13.4 (red), 12.4 (green), 11.3 (black), 10.4 (blue), 9.3 (purple), 8.2 (orange) and 6.7 (grey) recorded at 50 Vs^{-1} in 0.1 M K_2SO_4 buffered with 10 mM Na_2HPO_4 and H_3BO_3 .

Figure 4 illustrates the effect of pH on the phenol redox chemistry. As the pH is decreased, the redox wave moves towards higher potentials. Also, the peak separation between the oxidation wave and the reduction wave increases, indicating that the rate constant for the redox reaction decreases, and the redox wave becomes broader at lower pH.

$$E^{0'} = E_1^0 + \frac{RT \ln 10}{nF} \log \frac{1 + 10^{pH - pK_{a2}}}{1 + 10^{pH - pK_{a1}}} \quad (3)$$

For a one-proton, one-electron proton-coupled redox reaction, the formal reduction potential is expected to depend on pH according to Equation 3, [35] where the symbols are as defined in Scheme 1. In the pH region between the pK_a -values for the oxidized and the reduced form the formal potential decreases linearly with pH with a slope of 59 mV per pH. At pH values above the pK_a -value for the reduced form and below the pK_a value for the oxidized state the potential becomes pH independent as the redox reaction is no longer coupled to proton transfer. By fitting the redox data in Figure 4 to Equation 3, the pK_a value for the reduced phenol-form was estimated to be 13.2. (In the fit, pK_{a1} was set to 0). No indication of a low-pH plateau was observed in the pH-range investigated. This was not unexpected since the phenol radical is known to be very acidic.[36, 37] The reduction potential for phenolate oxidation (E_2^0) was evaluated to 0.11 V vs. NHE and the standard potential for phenol oxidation was evaluated to 0.89 V vs. NHE from extrapolation of the formal potential to pH 0, i.e. when the proton activity is 1 and hence at standard state.

3.3 Evaluation of kinetic parameters using a pre-equilibrium approach

For proton-coupled redox reactions it is often assumed that the proton transfer reactions depicted in Scheme 1 are at equilibrium at all times during the redox conversion and this model has been very successful in evaluating kinetic data for these types of reactions. Since the protonation and deprotonation reactions are assumed to be fast compared to the electron

transfer reactions, equilibrium constants rather than rate constants can be used for the proton transfer steps. This has the advantage that the equilibrium constants are often known from the pK_a values of the species involved. Table 1 lists the analytical expressions for the peak current and for the peak over-potential as function of scan rate for a kinetically controlled surface-confined proton-coupled redox reaction. An experimental criterion for a kinetically controlled reaction has previously been identified as being scan rates at which the peak over-potential is more than 100 mV [38] and this criterion has been used throughout the analysis in the present study. The expression for the peak over-potential, given in Table 1, predicts a linear dependence on the peak over-potential with the logarithm of the scan rate and can be used to evaluate kinetic parameters for the proton-coupled redox reaction. Note that in this Equation $k^{0'}$ is the pH-dependent formal exchange rate constant and not the standard rate constants k_2^0 or k_1^0 depicted in Scheme 1 for the non-proton-coupled redox reaction. Within the pre-equilibrium model, these constants are however related by Equation 4 where α_1 and α_2 are the transfer coefficients for the redox reaction between fully protonated species and fully deprotonated species respectively and k_1^0 and k_2^0 are the corresponding standard rate constants.

$$k^{0'} = \frac{k_1^0 \left(\frac{1+10^{pH-pK_{a2}}}{1+10^{pH-pK_{a1}}} \right)^{1-\alpha_1} + k_2^0 \left(\frac{1+10^{pK_{a2}-pH}}{1+10^{pH-pH}} \right)^{1-\alpha_2} 10^{pH-pK_{a2}}}{1+10^{pH-pK_{a2}}} \quad 4$$

In the phenol system studied here, the pK_a value for the phenol radical (pK_{a1}) is expected to be very low. In this case Equation 4 can be simplified to Equation 5 since the first term can be neglected and the numerator in the second term simplified.

$$k^{0'} = \frac{k_2^0}{(1+10^{pK_{a2}-pH})^{\alpha_2}} \quad 5$$

Table 1. Analytical expressions for the peak current and the peak over-potential for the pre-equilibrium model and for the steady state model describing the cyclic voltammetry responses for a kinetically controlled, surface-confined proton-coupled redox reaction. In the Equations Γ is the surface coverage, A the electrode area, v the scan rate, $k^{0'}$ the formal exchange rate constant k_2^0 the standard rate constant, k_{2d} the deprotonation rate constant, and k_{-2d} is the protonation rate constant. Other parameters have their usual meaning.

	Peak Current (A)	$E_p - E^{0'} (V)$
Pre-Equilibrium model (Oxidative Scan)	$\frac{(1 - \alpha)nAF^2\Gamma v}{2.718RT}$	$\frac{RT}{(1 - \alpha)nF} \ln \frac{(1 - \alpha)nF}{RTk^{0'}} - \frac{RT}{(1 - \alpha)nF} \ln v$
Pre-Equilibrium model (Reductive Scan)	$-\frac{\alpha nAF^2\Gamma v}{2.718RT}$	$-\frac{RT}{\alpha nF} \ln \frac{\alpha nF}{RTk^{0'}} - \frac{RT}{\alpha nF} \ln v$
Steady State model (Oxidative scan)	$\frac{FA\Gamma_{Red}^0 k_{2d}(1 - \alpha)Fv}{RTk_{2d} + (1 - \alpha)Fv} \left[1 + \frac{(1 - \alpha)Fv}{RTk_{2d}} \right]^{-\frac{RTk_{2d}}{(1 - \alpha)Fv}}$	$E_2^0 - \frac{RT}{(1 - \alpha)F} \ln \frac{k_2^0 RTk_{2d}}{(1 - \alpha)Fv k_{2d} 10^{pK_{a_2} - pH}} + \frac{RT}{(1 - \alpha)F} \ln v$

Figure 5. Scan rate dependence of the background-subtracted voltammetric response from a platinum electrode covered with phenol monolayer at pH 9.6 in 0.1 M K_2SO_4 buffered with 10 mM Na_2HPO_4 and H_3BO_3 . The current response has been normalized to the scan rate for clarity and the data shown are from scan rates 100, 303, 500, 1000, 1600, 2500, 4000 and 6400 10000 Vs^{-1} . The red lines are fits to the Equation derived from a steady state model (see text).

Figure 6. Peak over-potentials evaluated from cyclic voltammetry as a function of scan rate for the oxidative scan (solid circles) and the reductive scan (open circles). The conditions were the same as in Figure 5. The solid lines are linear fits to the high scan-rate data.

Figure 5 shows typical scan rate dependence data for the phenol monolayer deposited on platinum at pH 9.6 for scan rates between 100 Vs^{-1} and 10000 Vs^{-1} . From the voltammograms, the peak over-potential was determined and the corresponding data are shown in Figure 6 as function of the logarithm of the scan rate. The data at scan rates where the peak over-potential was more than 100 mV was fitted to a straight line and the formal rate constants were evaluated from the intercept with the x-axis using the relevant Equation in Table 1. This was done for both the oxidative scan and the reductive scan at different pH values in the range between 8.5 and 11. At all pH-values the evaluated rate constant from the

oxidative scan was slightly higher than the rate constants evaluated from the reductive scan (Figure 7). This could possibly be due to difficulties in defining the peak potential in the oxidative case. As can be seen in Figure 5, the oxidation peak becomes broad and ill-defined at high scan rates. This could also explain the large scattering in the evaluated peak over potentials in Figure 6.

Figure 7. Evaluated formal rate constants from the oxidative scan (solid circles), the reductive scan (open circles) and the average of the two (solid squares) as a function of pH. Error bars have been included for the data from the oxidative and the reductive scan and corresponds to 99 % confidence interval as evaluated from the linear regression analysis of scan rate dependence data (Figure 6). The thick line shows a fit to Equation 5 of the average formal rate constant and the thin lines are the corresponding fit of the data from the reductive and the oxidative scans. The inset shows a simulation of Equation 4 using the data from the fit at an extended pH range together with

experimentally determined rate constants and the corresponding α -values (triangles). In the simulation k^0_1 has been set equal to k^0_2 and pK_{a1} has been set to zero.

The pH-dependence of the average formal rate constant gave good agreement with Equation 5 and a fit to this function (solid line Figure 7) resulted in a standard rate constant for the tyrosinate redox reaction (k^0_2) of $1.7 \cdot 10^5 \text{ s}^{-1}$. In the fit the pK_a value was locked to the pK_a value determined from the pH-dependence of the formal potential (Figure 4). From the scan-rate dependence data the transfer coefficient at the formal potential was evaluated from the ratio between the intercepts of the linear fit for the oxidative and the reductive reaction according to the procedure described in ref. [38]. The resulting α -values were at all pH values above 0.5 and showed a marked pH dependence with a maximum around pH 9.5 (inset Figure 7). It is interesting to note that the inclusion of a potential-dependent transfer coefficient predicts a pH-dependence of the transfer coefficient at the formal potential that is quantitatively similar to the observed pH dependence. [23-25] For completeness the inset in Figure 7 shows a simulation of the expected pH dependence of the formal potential at an extended pH range using Equation 4. In this simulation the determined standard rate constant for k^0_2 was used for both k^0_2 and for k^0_1 since no data are available to determine the standard rate constant for the fully protonated species. The pK_a -value for the phenol radical has been arbitrarily set to zero. The formal rate constant shows a deep minimum mid-way between the pK_a -values for the oxidized and the reduced species.

3.4 Evaluation of kinetic parameters using a steady state approach

Although the pre-equilibrium model does seem to account well for the observed formal rate constants evaluated from the scan rate dependence of the peak over potential, this model cannot account for the shape of the voltammograms. From Figure 5 it is evident that the

electrochemistry is more complicated than the pre-equilibrium model predicts. Firstly, the normalized peak current decreases as the scan rate increases (Figure 5) in clear contradiction with the expression for the peak current given for the pre-equilibrium model in Table 1. This effect is particularly evident at low pH but was observed at all values. Secondly, at scan rates where the reaction is kinetically controlled the peaks become much broader than anticipated from the pre-equilibrium model. We have therefore derived equations to evaluate cyclic voltammetry data using a steady state model in order to better model the data. Since, at pH values below the phenol pK_a , the deprotonation rate must be less than the rate of protonation and the rate constant for oxidation of the phenolate is higher than the rate constant for its reduction, a steady-state treatment of the phenolate is always valid under these conditions. For the oxidative scan the following also applies: Since the reaction is kinetically controlled at high scan rates the reduction rate must be negligible compared to the oxidation and can therefore be fully ignored in the kinetic analysis. The observed rate constant is then given by Equation 6 and the current response for an oxidative voltammetric scan is given by Equation 7 (See supporting information for the derivation of the functions). (For the re-reduction scan a corresponding current response function could not be derived since in this case both the reduction and the oxidation reaction have to be taken into account).

$$k_{Ox} = \frac{k_2^0 e^{\frac{(1-\alpha)F}{RT}(E-E_2^0)} k_{2d}}{k_{-2d} 10^{-pH} + k_2^0 e^{\frac{(1-\alpha)F}{RT}(E-E_2^0)}} \quad 6$$

$$i(E) = \frac{FA\Gamma_{Red}^0 k_{2d} k_2^0 e^{\frac{(1-\alpha)F}{RT}(E-E_2^0)}}{k_{-2d} 10^{-pH} + k_2^0 e^{\frac{(1-\alpha)F}{RT}(E-E_2^0)}} \left[\frac{k_{-2d} 10^{-pH} + k_2^0 e^{\frac{(1-\alpha)F}{RT}(E-E_2^0)}}{k_{-2d} 10^{-pH}} \right]^{-\left(\frac{RTk_{2d}}{(1-\alpha)Fv}\right)} \quad 7$$

With this function the voltammetric response for the oxidation scan could be fully reproduced at all pH-values used and at all scan-rates above 100 Vs^{-1} . This is exemplified at

pH 9.6 in Figure 5 where the solid red lines are fits of the voltammograms to Equation 7. In the fit the value for E_2^0 was fixed to the value obtained from the data in Figure 4 and the term k_{-2d} was replaced by k_{2d}/K_a from the proton equilibrium requirement to reduce the number of free parameters. An additional, constant term was added to Equation 7 in the fit to account for any capacitive currents uncompensated by the background subtraction procedure. From the fit the rate constants for deprotonation (k_{d2}), the standard rate constant for tyrosinate oxidation (k_2^0) and the transfer coefficients were evaluated (Table S1). The protonation rate constant (k_{2d}) was determined from the evaluated deprotonation rate-constant and the pKa-value for the phenol. All data reported below are average values evaluated from fits to voltammograms at several scan rates where the peak over-potential is more than 100 mV.

Figure 8 shows the standard rate constants for phenolate oxidation evaluated at different pH values together with the corresponding transfer coefficients. The exchange rate constant shows no statistically verified trend at 95 % confidence with pH, although the high pH data seem to give lower values, but scatters between $5 \cdot 10^4 \text{ s}^{-1}$ and $6 \cdot 10^5 \text{ s}^{-1}$ with an average value of $3 \cdot 10^5 \text{ s}^{-1}$. A large scattering of the data is probably due to the extrapolation from the formal potential to the standard potential for phenolate redox reaction involved in the fit. This is particularly true for the low-pH data as the extrapolation is longer at these values of pH. Also the transfer coefficients show a pH-dependence that followed the same trend as the rate constants. The pH dependence of the transfer coefficient was however not statistically significant at 95 % confidence and the average value was 0.6.

Figure 8. Standard rate constants for tyrosinate oxidation evaluated from fitting cyclic voltammograms to the steady state model (see text) as function of pH (solid circles) together with the corresponding transfer coefficient (open circles).

When comparing these results with the standard rate constant for tyrosinate oxidation evaluated from the steady state model, the agreement is fairly good, $k_2^0 = 3 \times 10^5 \text{ s}^{-1}$ for the steady state model and $1.7 \times 10^5 \text{ s}^{-1}$ for the pre-equilibrium model. As in the pre-equilibrium model the expected scan rate dependence of the peak over-potential is a linear increase with scan rate and the scan rate dependence is identical with $k^{0'} = k_2^0 k_{2d} / k_{-d} 10^{-\text{pH}}$. This is however in contradiction to Equation 5 and the pH-dependence of the formal exchange rate constant does not agree with the steady state model. This model predicts a much stronger pH-dependence of the rate constant evaluated from the scan rate dependence of the peak over-potential as outlined above, with a one decade increase per pH unit. From Figure 5 it is

evident that the peak at high scan rates becomes broad and ill-defined and hence that the peak potential is a blunt tool to evaluate kinetic data. This is also apparent from the scattering of the peak over-potentials for the oxidation process in Figure 6. We therefore believe that the apparent agreement to the pre-equilibrium model that is shown by the pH-dependence of the formal rate constants is erroneous and that the seemingly reasonable agreement to this model is not sufficient for evaluating its aptness.

Figure 9. Peak currents for the oxidative wave as a function of scan rate at pH 9.6. The solid black line is a fit to the expected scan rate dependence of the peak current using the steady state model (see text) and the solid red line is the expected variation of the peak current based on the pre-equilibrium model. The inset shows the scan rate dependence of the peak current normalized to the scan rate.

As seen in Figure 5 the peak current does not increase linearly with scan rate at high scan rates as the pre-equilibrium model predicts (Figure 5, solid red line). (Note that the peak current for the pre-equilibrium model is expected to decrease with scan rate if a potential dependent transfer coefficient is included. This deviation from linearity is, however, much weaker than the observed deviation). Instead a clear deviation from linearity is observed (Figure 9). The deviation from the pre-equilibrium model can be seen more clearly in the inset of Figure 9 which shows the peak current normalized to the scan rate. A clear decrease in normalized peak current is observed as the scan rate is increased. Similar behavior has previously been reported for the proton coupled electron transfer in an Osmium-aqua complex studied by Finklea et.al. [39] Such scan rate dependence cannot be accounted for by pre-equilibrium models that predict a constant normalized peak current. At lower scan rates a constant normalized peak current is observed however (data not shown) possibly indicating that the pre-equilibrium model is valid at lower over-potentials. In contrast to the pre-equilibrium model, the steady-state model predicts that the scan rate dependence of the peak current carries kinetic information (Table 1). By fitting the peak current to the equation given in Table 1 (Figure 9 solid line) the deprotonation rate constant could be determined and the resulting rate constants are presented in Figure 10 as function of pH together with the corresponding rate constants evaluated from fitting the voltammograms as described above. In both cases the logarithm of the deprotonation rate constant increases linearly with pH and the two procedures for evaluating the rate constant give excellent agreement.

Figure 10. Evaluated rate constants for the proton transfer reactions as function of pH. Circles correspond to the deprotonation rate constant (k_{2d}) and the squares to the protonation rate constant (k_{-2d}). The solid circles were evaluated from fitting voltammograms at different scan rates and the open circles from fits of the peak current as function of scan rate.

From the pH dependence of the deprotonation constant it is clear that the reaction is dominated by deprotonation by OH^- (right panel Figure 1). The evaluated deprotonation rate constant is thus a pseudo first order rate constant with respect to $[\text{OH}^-]$. It is important to note here that the derived Equations for the steady-state model are valid irrespective of the dominating deprotonation path (see supporting information). The true deprotonation rate constant (k_{2d}^0) was extracted from the slope of the fit of the data in Figure 10 to a straight line. From the data extracted from fitting the voltammograms the deprotonation rate constant

was $9.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and from the peak current data the corresponding value was $9.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This is orders of magnitudes less than diffusion controlled which might be due to the steric hindrance of the bulky tert-butyl groups around the phenol OH-group. Since deprotonation is dominated by proton extraction by OH^- the protonation reaction is dominated by the pH independent protonation by water. The rate constant for this reaction was determined from the pseudo first order deprotonation rate constants to $k_{-2d}' = 1.5 \times 10^7 \text{ s}^{-1}$ (Figure 10).

With all involved rate constants at hand we are now in a position to judge the validity of the two models presented. In the pre-equilibrium model the assumption is that all proton transfer reactions are fast compared to the electron transfer reactions ($k_{2d} \gg k_2$ and $k_{-2d} \gg k_2$), whilst in the steady state model it is assumed that the reactions forming the intermediate state, in this case the phenolate, is slower than its consumption, i.e. $k_{-2d} + k_2 \gg k_{2d}$. Since at all values of pH investigated the pseudo first order deprotonation rate constant k_{2d} is less than the exchange rate constant (k_2), the requirement for the pre-equilibrium model is clearly not met. On the other hand, since both the protonation and the oxidation reaction at all pH values investigated are faster than the rate of deprotonation, the steady state approach is valid. A major drawback with this model is that analytical expressions describing the cyclic voltammetry of the re-reduction process cannot be attained. Other methods of investigation must therefore be used to get more information on the proton-coupled electron transfer reaction from the phenol monolayers investigated in this study.

4 Conclusions

Tert-butyl protected phenols have been covalently attached to self-assembled thiol monolayers and the thermodynamics and kinetics of the proton-coupled electron transfer from these layers have been investigated in water solution as function of pH. The results are consistent with a 1e1H redox system and the kinetics has been modeled using two different

approaches, a pre-equilibrium approach and a steady state approach. In the pre-equilibrium model rapid proton transfer reactions ensures that acid-base equilibrium is at all times established and in the steady state approach it is instead assumed that the concentration of intermediate species in the reaction are never built up. We have shown that the behavior of the phenol monolayer is inconsistent with the pre-equilibrium model, which has been extensively used in the literature, although apparent and misleading agreement with this model is observed. For the steady state model Equations to describe voltammetric responses have been derived and the behavior of the phenol monolayers was accurately described using this model.

5 Supporting Information Available

Derivation of cyclic voltammetry response with the steady state model and Table S1 with fit parameters.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

	Peak Current (A)	$E_p - E^{0'}$ (V)
Pre-Equilibrium model (Oxidative Scan)	$\frac{(1 - \alpha)nAF^2 \Gamma v}{2.718RT}$	$\frac{RT}{(1 - \alpha)nF} \ln \frac{(1 - \alpha)nF}{RTk^{0'}} - \frac{RT}{(1 - \alpha)nF} \ln v$
Pre-Equilibrium model (Reductive Scan)	$-\frac{\alpha nAF^2 \Gamma v}{2.718RT}$	$-\frac{RT}{\alpha nF} \ln \frac{\alpha nF}{RTk^{0'}} - \frac{RT}{\alpha nF} \ln v$
Steady State model (Oxidative scan)	$\frac{FA\Gamma_{Red}^0 k_{2d}(1 - \alpha)Fv}{RTk_{2d} + (1 - \alpha)Fv} \left[1 + \frac{(1 - \alpha)Fv}{RTk_{2d}} \right]^{\frac{RTk_{2d}}{(1 - \alpha)Fv}}$	$E_2^0 - \frac{RT}{(1 - \alpha)F} \ln \frac{k_2^0 RT k_{2d}}{(1 - \alpha)Fv k_{2d} 10^{pK_{a2} - pH}} + \frac{RT}{(1 - \alpha)F} \ln v$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10