Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2010 ; 114(19): 8938–8949. doi:10.1021/jp100079q.

The Effect of H-bonding and Proton Transfer on the Voltammetry of 2,3,5,6-Tetramethyl-p-phenylenediamine in Acetonitrile. An Unexpectedly Complex Mechanism for a Simple Redox Couple

Laurie A. Clare, Lydia E. Rojas-Sligh, Sonia M Maciejewski, Karina Kangas, Jessica E. Woods, L. Jay Deiner, Andrew Cooksy, and Diane K. Smith

Department of Chemistry and Biochemistry, San Diego State University, San Diego, CA 92182-1030

Abstract

The voltammetry of 2,3,5,6-tetramethyl-p-phenylenediamine, H₂PD, has been studied and compared to that of its isomer N,N,N',N'-tetramethyl-p-phenylenediamine, Me₂PD. Both undergo two reversible electron transfer processes in acetonitrile that nominally correspond to 1e⁻ oxidation to the radical cations, Me₂PD⁺ and H₂PD⁺, and a second 1e⁻ oxidation at more positive potentials to the quinonediimine dications, Me₂PD²⁺ and H₂PD²⁺. While the voltammetry of Me₂PD agrees with this simple mechanism, that of H₂PD does not. The second voltammetric wave is too small. UV/Vis spectroelectrochemical experiments indicate that the second wave does correspond to oxidation of H₂PD⁺ to H₂PD²⁺ in solution. The fact that the second wave is not present at all at the lowest concentrations (5 μM), and that it increases at longer times and higher concentrations, indicates that H₂PD⁺ is not the initial solution product of the first oxidation. A number of lines of evidence suggest instead that the initial product is a mixed valent, H-bonded dimer between one H₂PD in the the full reduced, fully protonated state, H₄PD²⁺, and another in the fully oxidized, fully deprotonated state, PD. A mechanism is proposed in which this dimer is formed on the electrode surface through proton transfer and H-bonding. Once desorbed into solution, it breaks apart via reaction with other H₂PD's, to give 2 H₂PD⁺, which is the thermodynamically favored species in solution.

Introduction

A very important current goal in organic electrochemistry is to develop a detailed mechanistic understanding of how electron transfer, proton transfer and hydrogen bonding work together in organic redox couples.¹ This is an important objective for numerous reasons, not the least of which is that these reactions are central to the major energy transduction processes in living organisms, including photosynthesis and mitochondrial ATP production. For this reason, along with the many industrial and commercial applications of these compounds, the electrochemistry of organic redox couples that are capable of

Correspondence to: Diane K. Smith.

Supporting Information Available: Diagram of the spectroelectrochemical cell. Additional examples of the experimental and simulated CV's for Me₂PD and H₂PD at higher concentrations. Examples of the DPV data used to generate Figure 7. CV's of 10 μM H₂PD from 0.5 to 15 V/s. This information is available free of charge via the Internet at <http://pubs.acs.org>.

undergoing overall $2\text{e}^-/2\text{H}^+$ transformations such as quinones, flavins and phenylenediamines have been studied for many years. From this work, the broad outlines of their redox chemistry are generally known, but there are still many mechanistic details that are not well understood, and, as this paper will show, these details may turn out to be rather surprising.

In this paper we focus our attention on the p-phenylenediamine redox couple, which is closely related to the biologically important quinone redox couple. Like quinones, p-phenylenediamines are generally expected to undergo a single $2\text{e}^-/2\text{H}^+$ redox reaction in buffered aqueous solutions² and two separate 1e^- reactions in aprotic solvents.^{3–12} Both have aromatic structures in their fully reduced forms and "quinoidal" structures in their fully oxidized forms. The difference is that the most stable form for the quinones is the fully oxidized "quinoidal" form, where for phenylenediamines it is the fully reduced aromatic form. So, in aprotic solvents quinones undergo two separate 1e^- reductions producing first a radical anion and then an aromatic dianion, reaction 1, whereas phenylenediamines are expected to undergo two 1e^- oxidations forming first a radical cation, then a quinonediimine dication, reaction 2. The acid-base properties differ as well. Quinones are essentially neutral in their fully oxidized form and become increasingly basic as they are reduced. Phenylenediamines, on the other hand, are weak bases to start and become increasingly acidic as they are oxidized.

(1)

(2)

The rationale for focusing on p-phenylenediamines is three-fold. First, the role of H-bonding and H^+ transfer has not yet been systematically investigated for this redox couple as it has been for the quinones.^{13,14} Second, with p-phenylenediamines a useful comparison can be

made between the N,N-dialkyl derivatives and the N-H derivatives because both have similar inherent redox chemistry in aprotic solvents. The difference is that the N-H analogues have the possibility of H-bonding and H^+ transfer between themselves and other bases, but the N,N-dialkyls do not. A similar type of comparison is not possible with quinones. Finally, there are obvious structural similarities between the phenylenediamines and quinones, yet also important differences. A comparison of the similarities and differences in their voltammetry in conjunction with their chemical properties should yield useful insights into the electrode mechanisms of both couples.

One complexity in studying H^+ transfer and H-bonding in the redox chemistry of phenylenediamines is the fact that the fully oxidized quinonediimine form is quite electrophilic and shows a strong tendency to form addition compounds with nucleophiles, including other phenylenediamines.¹⁵ This reactivity is the basis of the commercial applications of these types of compounds in color film processing and permanent hair dyes. It is also a common cause of electrode fouling problems in voltammetric studies of N-H phenylenediamines. In order to avoid this issue, we have focused our attention on 2,3,5,6-tetramethylphenylenediamine, which we are abbreviating as H_2PD to emphasize the two acidic H's in the dicationic quinonediimine state. This compound should not readily undergo addition reactions because the most common substitution positions are blocked by methyl groups. Accordingly, we have observed no electrode fouling problems with H_2PD . For comparison, we have also run parallel experiments with its isomer N,N,N',N'-tetramethylphenylenediamine. This compound is commonly abbreviated as TMPD, but to avoid confusion since both compounds are tetramethyl derivatives, we are abbreviating it as Me_2PD , to emphasize the difference between it and H_2PD .

Literature reports suggest that the electrochemistry of Me_2PD in organic solvents such as acetonitrile or DMF should follow the simple two step mechanism described by reaction 2 quite nicely.^{4,8,9} However, while the general expectation seems to be that p-phenylenediamines containing NH's, such as H_2PD , will show the same fundamental type of electrochemical behavior as the N,N-dialkylphenylenediamines in aprotic solvents,^{3,6,11} a couple of mechanistic studies have found a level of complexity that is not in accord with the simple picture outlined in reaction 2.^{7,10} The most obvious clue that something odd is happening in the electrochemistry of H_2PD is that the second voltammetry wave is considerably smaller than the first. Similar observations have been made with other NH phenylenediamines.^{4,10} Interestingly, similar behavior is often observed with quinones in

aprotic solvents (although, of course, not necessarily for the same reasons).^{13,16} In both cases, each CV wave should correspond to a 1 e⁻ reaction, and therefore should be close to the same size. This indeed is what is observed with Me₂PD. Leaving quinones out of the discussion for the present, given the structural differences between H₂PD and Me₂PD, it is reasonable to suspect that H⁺ transfer and/or H-bonding may be part of the explanation for the unusual voltammetry of H₂PD. The question is, in what way?

The different protonation and oxidation states possible for quinones are typically presented in a nine-membered square scheme. A similar type of organization for phenylenediamines gives the nine-membered parallelogram scheme shown in Scheme 1. In this presentation, the compounds in the same rows are the most likely oxidation states for a given protonation state, going from most reduced on the left to most oxidized on the right. The compounds in the same columns show the most likely protonation states going from the least protonated and least acidic on the top to the most protonated and most acidic on the bottom. Known or estimated aqueous pK_a values for p-phenylenediamine are also included in the scheme,¹⁷⁻¹⁹ along with our experimental E_{1/2} values for H₂PD. The other values are those calculated by taking into account that the sum of ΔG°s = 0 for a thermodynamic cycle.

To date, the most thorough mechanistic study of p-phenylenediamine oxidation in acetonitrile appears to be that of Solis et al in 1976.⁷ These authors observed two well separated voltammetric waves and confirmed by coulometry that the first oxidation corresponded to 1 e⁻ per phenylenediamine consistent with the mechanism outlined in reaction 2. However, rotating disk and chronopotentiometry experiments indicated kinetic complications in the first oxidation that were not consistent with a simple 1 e⁻ transfer. Based on these results, along with CV experiments in the presence of pyridine and acid, they suggested that the first voltammetric wave actually corresponds to formation of the doubly-oxidized, HPD⁺ (Scheme 1) through an "ECE" mechanism (electron transfer, chemical step, electron transfer), reactions 3–5. Specifically, they proposed that initial one electron oxidation produces the radical cation, H₂PD⁺, which then loses a H⁺ to another H₂PD. This gives the uncharged radical HPD, which is easier to oxidize than the starting H₂PD (Scheme 1), leading to the second electron being removed at the same potential as the first. Since the overall process, reaction 6, consumes two H₂PD's and two electrons, it still corresponds to 1 e⁻ per H₂PD in accord with the coulometry. The Authors then speculated that the second voltammetric wave could be due to oxidation of the protonated H₃PD⁺, reaction 7.

More recently, Klymenko et al¹⁰ reported a study of the oxidation of N,N-diethyl-p-phenylenediamine in DMF using microdisk electrodes under steady state conditions. They assumed a mechanism similar to that proposed by Solis et al, except they suggested that the second oxidation wave could be due to the oxidation of an addition product formed between the starting phenylenediamine and the diimine form. They found good agreement between the observed voltammograms and the theoretical model they developed for what would overall be a EC_{rev}ECE mechanism.

The problem with both of the above mechanisms is that while they may adequately fit the kinetic behavior they are not consistent with EPR studies^{3,6,20} and spectroelectrochemical studies⁵ which indicate that the radical cation is the major product after the first voltammetric wave. In addition, the H⁺ transfer step, eq 4, will likely be quite unfavorable based on the reported aqueous pK_a of the p-phenylenediamine radical cation of 12.0.¹⁸ Assuming the relative pK_a's are similar in acetonitrile, this reaction would have a K ~ 10⁻⁶.

Based on the above, our original thought was that the first voltammetric wave for H₂PD must correspond to production of the radical cation, H₂PD⁺, and that the too small second CV wave was most likely a result of proton transfer between outgoing H₂PD²⁺ being produced at the electrode at the potential of the second CV wave and incoming H₂PD from the bulk, reaction 8. Based on the pK_a's shown in Scheme 1, H₂PD²⁺ is 10 orders of magnitude more acidic than H₂PD⁺, so, in contrast to eq 4, eq 8 should be quite favorable with a K ~ 10⁴. If this reaction is fast enough, it could, in conjunction with other possible proton and electron transfer steps, decrease the flux of H₂PD to the electrode at the potentials where H₂PD²⁺ is being formed, resulting in a smaller than expected second CV wave. A related mechanism involving reversible dimerization of the completely reduced and completely oxidized forms has been suggested to explain the too small second reduction wave for quinones.¹³ More recently, Macias-Ruvalcaba et al. have suggested another mechanism, involving reversible dimerization of the quinone radical anions, followed by 1 e⁻ reduction of the dimer at close to the same potential as the monomer -1/-2 potential.²¹ Such a mechanism could be possible for phenylenediamines as well, since their radical cations are also known to dimerize.²²

In order to test whether either of the above reactions, or some other solution-phase bimolecular reaction, could explain the too small second CV wave for H₂PD, we have investigated the cyclic voltammetry of H₂PD in acetonitrile over a very large concentration range from 5 μM to 5 mM. Since the rates of bimolecular reactions will be strongly concentration dependent, the expectation was that the second wave would get relatively larger as the concentration is decreased and the rates of the bi-molecular reactions slowed relative to the unimolecular heterogeneous e⁻ transfers. In fact, the exact opposite concentration dependence is observed, with the second wave disappearing completely at the

lowest concentrations. Interpretation of this data leads us to concede that the dissolved radical cation, H_2PD^+ , is not the initial product of the electrode reaction at the first CV wave. However, our data do indicate that it is the thermodynamic product, and that the second CV wave is in fact due to oxidation of the radical cation to the quinonediimine. To account for these results we propose a new mechanism for oxidation of NH phenylenediamines in aprotic solvents in which oxidation at the first voltammetric wave initially produces a kinetic product, X, that corresponds to 1 e⁻ per H_2PD and cannot be further oxidized. In solution, bimolecular reactions with H_2PD convert X to the radical cation, H_2PD^+ , which is then oxidized to H_2PD^{2+} in the second voltammetric wave.

Experimental

Reagents

2,3,5,6-tetramethyl-1,4-phenylenediamine (H_2PD) and N,N,N',N'-tetramethylphenylenediamine (Me_2PD) were purchased from commercial sources as reagent grade. H_2PD was dried under vacuum overnight and Me_2PD was further purified by sublimation under vacuum. Acetonitrile was distilled from CaH_2 . The electrolyte, tetrabutylammonium hexafluorophosphate, was recrystallized three times from 95% ethanol and vacuumed dried overnight at 100°C.

General voltammetry procedures

All experiments were conducted in 0.10 M NBu_4PF_6 /acetonitrile under Ar or N_2 gas in a jacketed one-compartment cell with either a Pt, Au or glassy C disk working electrode, a Pt wire counter electrode and Ag wire pseudo-reference electrode in a separate compartment. The working electrode was polished immediately prior to use with 1/4 μm diamond polishing paste (Buehler), washed thoroughly with water, then polished with 0.05 μm alumina paste (Buehler) and washed with water and acetone. Anhydrous acetonitrile was passed through a column of activated alumina directly into the cell. O_2 was removed from the electrolyte solution by bubbling Ar or N_2 through the solvent for several minutes before measurements were made. Temperature was controlled by using a circulating water bath to flow 25 °C water through the outer jacket of the cell.

Cyclic voltammetry studies of H_2PD and Me_2PD at different concentrations

Cyclic voltammetry (CV) experiments were performed with a CH Instruments model 600c digital potentiostat using their standard software package. All CV's for the concentration dependence studies were run with a Pt disk working electrode (area = 0.0362 cm^2). In order to get stable backgrounds for reliable subtraction at the lowest concentrations it was necessary to cycle the electrode through the desired potential range a number of times in the blank electrolyte solution until the currents stabilized. Typically this involved 3 sets of 10 cycles at 1 V/s. After the background had stabilized, CV's for the background subtraction were recorded at 0.10, 0.20, 0.50, 1.0 and 2.0 V/s. The appropriate amount of H_2PD or Me_2PD was then added to the cell by making additions from a concentrated stock solution using 10 to 100 μL gas-tight syringes. The total volume of all the additions was significantly smaller than the electrolyte solution volume (5 mL) to ensure the volume in the cell did not change significantly over the course of an experiment. For concentrations ranging from

0.005 to 0.2 mM a stock solution of ~0.010 M was used; for concentrations ranging from 0.5 to 5 mM a ~0.10 M stock solution was used. The stock solutions were generally prepared immediately before the experimental run by difference weighing into a 1 mL volumetric flask and dilution with the CaH₂-dried acetonitrile. The flask was then capped with a rubber septum to minimize moisture addition. After each addition, CV's were recorded at 0.10, 0.20, 0.50, 1.0 and 2.0 V/s.

CV simulation

The background-subtracted CV's for H₂PD and Me₂PD from the higher concentration experiments were fit to the mechanism shown in equation 2 using the Digisim CV simulation software (v 3.03, BioAnalytical Systems). CV's at 3 different scan rates (0.5, 1.0 and 2 V/s) at 4 different concentrations (0.5, 1, 2 and 5 mM) were used for the fittings (a total of 12 CV's for each). The simulations assumed an uncompensated solution resistance, R_u , of 250 Ω . This value was determined by adjusting R_u so as to best fit the peak potentials for CV's of the first wave of Me₂PD. Since the kinetics of this reaction are expected to be very fast, any deviation from reversibility at the scan rates used is assumed to be due to R_u . For Me₂PD, the diffusion coefficient D (assumed to be the same for all intermediates) and the E° 's were then optimized to fit the CV's of both waves, followed by the k_s 's (alpha set to 0.5). The best fit results were $D = 2.33 \times 10^{-5} \text{ cm}^2/\text{s}$; Me₂PD^{0/+}: $E^\circ = -0.286 \text{ V vs Fc}^{0/+}$ and $k_s = 0.27 \text{ cm/s}$; Me₂PD⁺²⁺: $E^\circ = 0.309 \text{ V vs Fc}^{0/+}$ and $k_s = 0.13 \text{ cm/s}$. For H₂PD, the D was fit using CV's covering only the first oxidation peak. This value was then used to fit the CV's of both waves. The best fit results (which do not provide a satisfactory fit for the second wave as discussed in the Results and Discussion section) are $D = 2.12 \times 10^{-5} \text{ cm}^2/\text{s}$; H₂PD^{0/+}: $E^\circ = -0.258 \text{ V vs Fc}^{0/+}$ and $k_s = 0.011 \text{ cm/s}$; H₂PD⁺²⁺: $E^\circ = 0.260 \text{ V vs Fc}^{0/+}$ and $k_s = 0.016 \text{ cm/s}$.

Differential Pulse Voltammetry Studies of H₂PD at Different Concentrations

Differential pulse voltammetry (DPV) was used to explore the effect of the electrode surface on the concentration dependence of H₂PD voltammetry. It was not possible to do this with CV because background subtraction is needed at the very low concentrations with this technique and only Pt gave stable enough backgrounds over the necessary voltage range. In contrast, DPV is much more sensitive at low concentrations and does not require explicit background subtraction. DPV experiments were performed using a PAR Model 263 potentiostat with the model 270 software and the following parameters: pulse height = 25 mV, pulse width = 50 ms, step time = 0.1 s and scan increment = 2 mV. The cell setup and addition procedures were similar to the CV experiments, except at each addition DPV's were recorded with a Pt disk working electrode (area = 0.0362 cm²), a Au disk working electrode (0.02324 cm²) and a glassy C disk working electrode (0.0707 cm²). The peak currents were recorded as the difference between the peak height and a baseline drawn through the current on either side of the peak. The values for the first and second peaks were normalized by dividing by electrode area and H₂PD concentration. The resulting values are reported in Figure 7 as the average of three independent experiments with 90% confidence limits.

Spectroelectrochemical studies

UV/Vis spectroelectrochemical experiments were performed in order to confirm that the main products of the successive electron transfer reactions for Me₂PD and H₂PD are indeed the radical cation followed by the quinonediimine, reaction 2. All experiments were conducted under Ar gas in a non-jacketed quartz cell which had two flat, round optical-grade quartz windows (~1 in diameter) welded on opposite sides of the cell. (For additional clarity, a diagram of the complete spectroelectrochemical cell is provided in the Supporting Information) The working electrode was constructed out of electroformed Au grid (500 wires/in with 60% transmission purchased from Buckbee Mears, St Paul, MN) placed inside a thin 0.1 mM path length quartz UV/Vis cell with a removable face plate (purchased from NSG Precision Cells). The bottom part of the UV/Vis cell was cut off to enable solution to enter by capillary action. The top part of the face plate was also cut off to allow for electrical contact to the gold grid. This was made by placing a flattened Cu coil on the grid and tightly wrapping it in place with teflon tape. Teflon tape was also used to bind the face plate to the body of the quartz UV/Vis cell. The working electrode assembly was then placed in the electrochemical cell and electrolyte solution containing 0.5 mM H₂PD or Me₂PD added just past the open bottom edge of the assembly. Capillary action drew the electrolyte solution up into the thin layer and across the Au grid. The whole electrochemical cell was then placed into the spectrophotometer cavity and positioned so the spectrophotometer beam went through the quartz window on the side of the cell, above the electrolyte solution and through the center of the Au grid. The counter electrode (Pt wire) and reference electrode (Ag wire in separate compartment) were placed in the electrolyte solution out of the beam path. CV's were recorded at a slow scan rate (10 mV/s) using a Pine Instruments model AFRDE4 bipotentiostat with a PAR model 175 potential programmer and a Kipp-Zonen XY chart recorder. The scan was stopped at different points in the voltammogram and held for a few seconds before recording spectra using a Cary model 50 Bio UV-Vis spectrophotometer.

CV studies of H₂PD in the presence of HClO₄

CV studies of H₂PD in the presence of the strong acid HClO₄ were conducted in order to determine the voltammetry properties of the mono and di-protonated forms, H₃PD⁺ and H₄PD²⁺. The voltammetry setup was the same as for the concentration studies except a glassy C electrode was used as the working electrode because it was found that Pt readily reduced the H⁺'s in H₃PD⁺ and H₄PD²⁺ at the initial voltage, resulting in smaller H⁺ concentrations than expected. After background scans were recorded, enough solid H₂PD was added to the cell to make a 1.0 mM solution. CV's were then recorded at different scan rates for this solution and after 1.0 and 2.0 equivalents of HClO₄ were added. This was done via addition of an appropriate amount of an ~ 0.2 M stock solution. The stock solution was prepared by weighing an appropriate amount of nominally pure HClO₄ acid (purchased from Aldrich and listed as 99.999% pure) into a 5 mL volumetric and diluting with CaH₂-dried acetonitrile. 1.0 mL of the stock solution was removed with a pipet and titrated with 0.10 M NBu₄OH solution (in methanol/toluene, purchased from Acros) using phenolphthalein as the indicator. The concentration was determined from the average of 3 separate titrations.

CV studies of H₂PD in the presence of pyridine

CV studies of H₂PD in the presence of pyridine were done in order to determine the effect of a weak base (one with a strength comparable to that of H₂PD and Me₂PD) on the voltammetry. The voltammetry setup was the same as that of the concentration dependent studies. Solid H₂PD was added to give a 1 mM solution. Pure pyridine was added in aliquots using a microliter syringe.

Computational studies on a PD-H₄PD²⁺ dimer

Based on the above results we believe the most likely initial product of one electron oxidation of H₂PD is a pi-dimer between PD and H₄PD²⁺. The viability of such a structure was checked by performing B3LYP density functional calculations using the cc-pVDZ basis set.²³ The optimized geometry, shown in Figure 9, shows the monomers bound by two hydrogen bonds that separate the N atoms of the distinct monomers by roughly 2.7 Å. The gas-phase ΔG° for dimerization of the two monomers was estimated from the calculated energy of the dimer minus that of the monomers. The energies were corrected for vibrational contributions at 298 K. A counterpoise correction²⁴ for basis set superposition error was also done. The resulting value, -100 kJ/mol, is consistent with two strong ionic H-bonds.

Results and Discussion

Cyclic voltammetry of H₂PD and Me₂PD in acetonitrile

Figure 1 shows cyclic voltammograms (CV's) of 0.5 mM Me₂PD at a Pt electrode in 0.1 M NBu₄PF₆/CH₃CN. Scan (a) is the experimental CV. Scan (b) is the simulated CV for the same conditions. The simulation assumes a simple two-step mechanism involving sequential one electron transfers, reaction 2. The parameters used are the best fit values obtained from fitting CV's of Me₂PD at 0.5, 1.0 and 2.0 V/s with Me₂PD concentrations equal to 0.5, 1, 2 and 5 mM. The good quality of the fit clearly indicates that this simple mechanism nicely describes the voltammetry of Me₂PD under these experimental conditions.

In contrast, it is not possible to adequately fit the CV's of H₂PD using the same mechanism, as shown in Figure 2. This Figure shows (a) experimental and (b) simulated CV's of H₂PD under the same experimental conditions as shown for Me₂PD in Figure 1. The simulation also assumes the same two step mechanism. In this case the parameters for the first electron transfer were obtained by first fitting CV's of wave 1 only, at 0.5, 1.0 and 2.0 V/s with H₂PD concentrations equal to 0.5, 1, 2 and 5 mM. These parameters were then used to fit CV's of both waves under the same experimental conditions. In the latter case, the simulation program was only allowed to vary the parameters for the second electron transfer in order to find the best fit to the data. The result, shown in red in Figure 2 is clearly not a very good fit at all. The real wave 2 is quite obviously much smaller than it should be based on the simple two step mechanism.

UV/Vis spectroelectrochemistry

UV-Vis spectroelectrochemical experiments were run in order to confirm that, despite the non-ideal CV of H₂PD, the first CV wave does correspond to conversion of H₂PD to the radical cation, H₂PD^{•+}, and the second CV wave corresponds to conversion of H₂PD^{•+} to the

quinonediimine, H_2PD^{2+} . Figure 3 shows the resulting UV-Vis spectra, taken with 0.5 mM H_2PD in a 0.1 mm pathlength quartz cell using a Au mesh working electrode. Spectrum (a) is the initial spectrum, which shows characteristic absorptions at 243 and 310 nm for H_2PD . Spectrum (b) was taken near the top of the first CV wave. The absorption at 243 nm for H_2PD has decreased in intensity and new absorptions at 325 nm in the UV and 450 and 478 nm in the visible are seen. The new absorption peaks are very similar to those reported for the radical cation of 1,4-phenylenediamine generated chemically.^{22,25} In particular, the broad, double hump wave in the visible is quite characteristic of these radicals. The Me_2PD radical also shows a similarly shaped visible absorption, but at longer wavelengths. If the electrode potential is now held between the two CV waves, spectrum (c) results. As would be expected for conversion of H_2PD to H_2PD^+ , the original absorptions of H_2PD at 243 nm appears to be gone and the peaks associated with the radical at 325, 450 and 478 nm are at full height. Moving the electrode potential into the second CV wave produces spectrum (d). As expected for conversion of H_2PD^+ to H_2PD^{2+} , the radical absorptions decrease and a new absorption peak starts to grow in at 295 nm. If the electrode potential is now held past the second CV wave, spectrum (e) results. The radical absorptions are now mostly gone and the peak at 295 nm has reached full height. The resulting spectrum is very similar to that observed for Me_2PD at the same point in the voltammogram, and to the UV/Vis spectra of other quinonediimines generated chemically,²⁶ supporting the conclusion that the second CV wave does indeed correspond to conversion of H_2PD^+ to H_2PD^{2+} .

Another important point gleaned from the UV/Vis data is that there is no evidence for the formation of a pi dimer between the radical cations of either H_2PD or Me_2PD under the experimental conditions used. This type of dimer, where the radicals spin pair to form a diamagnetic pi-stacked complex is well-known for aromatic radicals in general,²⁷ and for phenylenediamine radical cations in particular, but is typically observed in more polar solvents at lower temperatures. The dimers are characterized by broad visible absorptions both at shorter and longer wavelengths than the monomers.²²

Concentration Dependence

As discussed in the Introduction, there are several possible bi-molecular reactions between H_2PD intermediates in solution that may explain the too small second CV wave. A simple way to test this hypothesis is to look at the concentration dependence of the voltammetry. At lower concentrations, the rate of a solution bimolecular reaction between H_2PD intermediates will decrease relative to the unimolecular heterogeneous electron transfer reactions. Therefore, if a bimolecular reaction in solution is responsible for the too small second CV wave, the relative height of this wave will most likely increase as the concentration is lowered.

Typical results for the concentration study are shown in Figure 4. The CV's, all at 200 mV/s, have been background subtracted and the currents normalized by dividing by concentration. Since currents should be directly proportional to concentration, if the behavior was ideal, all the CV's would exactly overlay each other after this treatment. Interestingly, both waves show deviations from the ideal, but in opposite directions. Wave 1 is relatively the largest at the lowest concentrations, decreasing 10 to 25% in relative terms as the concentration

increases from 5 μM to 200 μM . The exact amount of this decrease varies from experiment to experiment, but above about 200 μM the normalized current settles down to a constant value that is reproducible between experiments, within the limits of our concentration accuracy.

The second H_2PD CV wave, on the other hand, gradually increases as the concentration is increased. In fact, at the lowest concentration, 5 μM , wave 2 is not seen at all, Figure 4, scan (a). As the concentration of H_2PD is increased to 10 μM and 20 μM a new small wave appears, wave 3, about 0.15 V positive of wave 2, Fig. 4, scans (b) and (c). It is not until 50 μM that wave 2 clearly appears, Figure 4, scan (d). As the concentration is increased, this wave continues to increase relative to the first up to the highest concentration examined, 5 mM (not shown in Figure 4).

The scan rate dependence of both CV waves also varies with concentration. With wave 1, the anodic (forward) peak current is directly proportional to the square-root of the scan rate at all concentrations as expected for fast, diffusion-controlled electron transfer. In addition, the ratio of the forward to reverse peak currents is close to 1 at the higher concentrations. However, at the lower concentrations, where only wave 1 is observed, the peak current ratio decreases from unity as the scan rate increases. The amount of the decrease appears quite sensitive to experimental conditions. In some cases, obvious irreversibility is observed at 0.5 V/s; in other cases the wave appears completely reversible up to 2 V/s. (Some representative data showing the scan rate dependence of wave 1 at 10 μM H_2PD is given in the Supporting Information.)

An even stronger scan rate dependence is observed with the second CV wave as shown in Figure 5. In this Figure, CV's at different scan rates with 50 μM H_2PD (data from same experiment as Fig. 4) are overlaid on top of each other. The currents are now normalized by dividing by the square root of the scan rate. For a diffusion-controlled reaction, with no kinetic issues, the CV waves should again directly overlay each other. Under these conditions, wave 1 comes very close to showing this ideal behavior, but wave 2 does not. At the fastest scan rate, corresponding to the shortest measurement time, only wave 3 is evident past the first CV wave, but as the scan rate is slowed, this wave decreases and wave 2, corresponding to the "normal" second oxidation, grows in.

Similar concentration dependent studies were also done with Me_2PD . Representative results are shown in Figure 6. Since Me_2PD gives close to ideal behavior in the mM concentration range, one might expect to see continued ideal behavior down to the lower concentrations. But, as with H_2PD , in the μM regime we generally observe a relative decrease in the height of wave 1 as the concentration increases, although the amount varies from experiment to experiment. However, unlike H_2PD , wave 2 is clearly present at all concentrations, and, in fact, is relatively the largest on the forward scan at the lowest concentrations. In contrast, the return peak is the smallest at the lowest concentrations, indicating some irreversibility to the second oxidation. As the concentration is increased, the forward scan decreases and the return scan increases so by about 50 μM both CV waves of Me_2PD show the ideal CV behavior observed at mM concentrations.

The above concentration experiments were all done with a Pt electrode because of the need to do background subtractions and the fact that of the electrode materials examined, Pt, Au and glassy C, Pt gave the most stable backgrounds over the necessary voltage range. However, qualitatively similar CV behavior is observed at the other electrodes as well. The second CV wave also decreases with concentration at Au and glassy C, appearing to disappear entirely at the lowest concentrations. This behavior can also be seen in differential pulse voltammograms (DPV's) of H₂PD. The results are summarized in Figure 7 which gives the normalized DPV peak currents (current/concentration/electrode area), at Pt, Au and glassy C electrodes with 20, 50 and 100 μ M H₂PD. The results are the average of three independent measurements, with error bars corresponding to the 90% confidence limits. The normalized DPV peak currents of the first oxidation (black bars) are independent of both electrode material and concentration. The normalized peak currents for the second oxidation (red bars) are also independent of electrode material, but are dependent on concentration. Consistent with the CV results, the peaks for the second oxidation are significantly smaller than the first at all three concentrations, but the difference decreases as the concentration increases.

A new hypothesis

The above concentration data appear to rule out our original hypothesis that the too small second CV wave for H₂PD is due to some type of bimolecular reaction between H₂PD and/or H₂PD-based reaction intermediates in solution. Such a mechanism would generally be expected to result in the second CV wave getting larger as the concentration decreases and the rates of the bimolecular reactions slow.²⁸ But, in fact, the exact opposite concentration dependence is observed. This means bi-molecular reactions are important, but not in the way originally envisioned.

Based on the evolution of features in the CV's of H₂PD as the concentration and scan rate change, a rather surprising time line emerges. At the lowest concentrations, corresponding to the slowest bi-molecular reactions in solution, oxidation at wave 1 produces an initial product at the electrode that is not the dissolved radical cation. We know this because the UV/Vis spectroelectrochemical experiments clearly indicate that the "normal" second CV wave corresponds to oxidation of the radical cation and this CV wave is not present at the lowest concentrations, Figure 4, scan (a). The radical cation is certainly the most thermodynamically stable product in solution at potentials between the two CV waves, but it evidently is not the most rapidly formed. This kinetic product is something that can not be further oxidized (no additional oxidation peak is observed out to the solvent limit), but whose formation appears to involve more than just electron transfer. This can be deduced from the fact that the current does not decline in a simple diffusion-controlled fashion after the peak.

As the concentration of H₂PD increases, the first clear new feature that appears in the CV's is wave 3, Figure 4, scans (b) and (c). Finally, at higher concentrations and longer times (slower scan rates), wave 2, corresponding to the radical cation oxidation/reduction starts to appear, Figure 4, scans (d), (e), and (f). It is notable that when this wave first appears the current does not decline in a diffusion-controlled fashion after the peak, but continues to

show enhanced oxidation current Fig 4, scan (d). On the return scan, the reduction peak appears substantially larger than the initial oxidation peak. This wave shape is characteristic of a "CE" mechanism (chemical step, followed by electrode step)²⁹ where the chemical step forms the electroactive species, H_2PD^+ in this case, which subsequently undergoes oxidation at the electrode. With further increases in H_2PD concentration, the normal second CV wave continues to grow in relative height, and differences in size between the oxidation and reduction peaks become less obvious.

One possible explanation for the "normal" second CV wave growing in relative height as the concentration of H_2PD increases is that the presence of additional H_2PD increases the rate of conversion of the initial kinetic product to H_2PD^+ . In particular, the concentration dependence could be qualitatively explained if a bimolecular reaction or reactions between the initial product and H_2PD leads to conversion of the initial product to H_2PD^+ . Wave 3 could then be due to an intermediate formed in the process of converting the kinetic product to the radical cation. This mechanism is outlined by reactions (9) to (12), where X represents the kinetic product and I1, I2 and I3 different intermediates.

Role of H_3PD^+

As noted above, the first electroactive product formed after initial oxidation of H_2PD in wave 1, is oxidized slightly negative of H_2PD^+ in wave 3. This could be H_3PD^+ , the mono-protonated form of H_2PD . In order to test whether this is reasonable, CV's of H_2PD were run in the presence of 1 and 2 equivalents of HClO_4 . For these studies, it was necessary to use a C electrode, since Pt readily reduces H^+ at the starting potential. The results are shown in Fig. 8. Scan (a) is 1 mM H_2PD by itself at a glassy C electrode, scan (b) is in the presence of 1 mM HClO_4 , and scan (c) is in the presence of 2 mM HClO_4 . In the latter case the primary bulk species should be H_4PD^{2+} , which is expected to be electroinactive, Scheme 1. This is confirmed by the complete loss of both CV waves upon addition of the two equivalents of HClO_4 .

With only one equivalent of HClO_4 , Figure 8 scan (b), the main species in solution should be H_3PD^+ . Accordingly, wave 1 disappears and several new features appear. One of these is a shoulder, labeled wave 3, on the negative side of what still appears to be wave 2 (oxidation of H_2PD^+). The position of this shoulder is close to where wave 3 appears in Figure 5. If this shoulder is indeed due to oxidation of H_3PD^+ , then analysis of the thermodynamics as

shown in Scheme 1, indicates that H_3PD^{2+} is very acidic, and likely readily loses a H^+ to H_3PD^+ , reaction 13. H_2PD^+ once formed would then be oxidized at wave 2.

In addition to the above features, there is another feature in Figure 8 scan (b) requiring explanation: a broad oxidation shoulder starting at around 0.4 V, labeled wave 4, which appears to have a corresponding reduction peak at 0.35 V on the return scan. If wave 3 is indeed due to oxidation of H_3PD^+ , then wave 4 is due to something that is easier to oxidize. One possibility is that it is due to oxidation of a H-bonded form of H_3PD^+ . Another simpler explanation is that it is due to oxidation of H_2PD formed by dissociation of H_3PD^+ , reaction 14. Even though H_3PD^+ should be the principle species in the bulk solution in the presence of 1 equivalent of HClO_4 , the rate of the reverse reaction could be sufficiently fast to allow for a small amount of H_2PD to be formed and subsequently oxidized prior to the H_3PD^+ oxidation. This would be a CE_{rev} reaction. The observed wave shape, with a smaller forward peak and a larger return peak, is consistent with such a mechanism.

Possible kinetic products "X"

The above data are consistent with I1 in the preliminary mechanism (reactions 9 – 12) being H_3PD^+ . The next and more significant question is, what is the identity of our mystery product "X", formed prior to H_3PD^+ ? Perhaps the simplest possibility is that it is just very strongly adsorbed radical cation, H_2PD^+ , which for some reason can be reversibly reduced, but can not be further oxidized. Of course, it is not clear why that would be the case. This hypothesis also appears to be ruled out by the data with Me_2PD , which does show evidence for adsorption of the radical cation, but also shows a definite second oxidation peak at all concentrations, Figure 6. This suggests that if X could simply be described as adsorbed radical cation then there should be a second oxidation peak for H_2PD as well at all concentrations, and clearly there is not.

As noted previously, X has to be something, formed in the first CV wave, that cannot be further oxidized and whose formation involves more than just simple e^- transfer. It is also something whose formation corresponds to 1 e^- per H_2PD based on our data showing that the first wave is comparable in height to that of Me_2PD (whose first wave definitely corresponds to a 1 e^- oxidation to Me_2PD^+). This also agrees with the coulometry studies by several others that show the first voltammetric wave for NH phenylenediamines in aprotic solvents corresponds to 1 e^- per phenylenediamine.^{4,7,20}

Having ruled out strongly adsorbed, oxidatively inactive radical cation as a possibility, all of the above considerations seem to point back to the original hypothesis of Solis et al⁷ that the first oxidation corresponds to formation of one fully oxidized and one fully reduced, protonated phenylenediamine, reaction 6. The only change would be to amend the proposal to reaction 15 to account for the fact that X is formed prior to H_3PD^+ . Since H_4PD^{2+} is electroinactive, its presence would not be detected.

As noted previously there are mechanistic issues with the above reaction, but ignoring these for the moment, a good first question to ask would be, is this thermodynamically reasonable? A convenient way to assess this is to consider the equilibrium constant (or G°) of the disproportionation/proton transfer reaction, reaction 16.^{30,31} For reaction 15 to occur in a single voltammetric wave, then reaction 16 must be thermodynamically favorable. To determine this we can break the reaction into the three component reactions, a disproportionation, reaction 17, and two proton transfers, reactions 18 and 19. The K for the disproportionation reaction can be determined from the difference in $E_{1/2}$ between the two CV waves.³¹ This analysis gives $K = 10^{-8.77}$ and $G^0 = +50$ kJ/mol. From the estimated aqueous pK_a of H_2PD^{2+} (1.5)¹⁹ and the known value of H_3PD^+ (6.1),¹⁷ K of reaction 18 is $10^{4.6}$ and $G^0 = -26$ kJ/mol. Finally, from the pK_a of HPD^+ (5.8)¹⁹ and the pK_a of H_3PD^+ (3.3)¹⁷, K of reaction 19 is $10^{-2.5}$ and $G^0 = 14$ kJ/mol. Summing the G^0 values gives an overall G^0 for reaction 16 of 38 kJ/mol, so, as is, the reaction does not appear to be favorable. However, it also seems reasonable to propose that the products, H_4PD^{2+} and PD , could further interact with each other through a combination of H-bonding and pi-stacking to form a dimer, reaction 20. This dimer would be an analogue of the well-known quinhydrone complex,³² the pi-stacked dimer formed between benzoquinone and benzohydroquinone. If G^0 for its formation was < -38 kJ/mol, then reaction 21 would be favorable, and reaction 22 could occur in a single voltammetric wave.

DFT calculations were performed in order to probe whether the proposed dimer, $\text{PD} - \text{H}_4\text{PD}^{2+}$, is at all reasonable and to determine if its formation in acetonitrile would likely be favorable enough to make reaction 22 possible. The answer to both questions appears to be yes. The resulting structure is shown in Figure 9. PD is on top and H_4PD^{2+} is on the bottom

in both views. View (a) shows the side view with the Me's in front. From this angle it is apparent that the PD is bent into a boat shape^{9, 33} and the C-N bonds in the H_4PD^{2+} are bent out of the aromatic plane in order to form two strong H bonds. The H-bonds are even more apparent with the N's in front, view (b). This orientation clearly shows that one of the N-H bonds in each NH_3^+ unit of H_4PD^{2+} is pointed straight towards the N in the PD half. The N-N distance is 2.7 Å. This view also shows that the two monomers are offset slightly, with the PD at an angle, presumably to minimize the steric repulsion between the Me groups.

From the DFT calculations, the gas-phase ΔG° for dimerization of the two monomers, reaction 20, is estimated to be -100 kJ/mol , consistent with the formation of two, relatively strong, ionic H-bonds. A solvent correction was attempted using the COSMO-RS method,³⁴ but the complicated surface of the dimer appeared to introduce substantial error. This error, coupled with the fact that the magnitude of the solvent interaction with the dication is many times greater than the monomer-monomer interaction energy, obscured the relatively delicate H-bonding interactions. Nonetheless, the gas-phase energy suggests that the H-bonding should be strong enough to make the 2 e⁻ oxidation, reaction 22, thermodynamically possible in a weakly competitive solvent such as acetonitrile.

The role of adsorbed intermediates

Even if $\text{PD-H}_4\text{PD}^{2+}$ is the identity of X, there is still the issue of the feasibility of its formation at very low concentrations in a single CV wave. The problem is illustrated by the data in Figure 10 that show CV's of H_2PD in the presence of pyridine. Pyridine has a similar base strength (pK_a of pyridinium = 5.1) as H_2PD (pK_a of H_3PD^+ = 6.1). It also should be a strong enough base to deprotonate the quinonediimine H_2PD^{2+} , but not the radical cation H_2PD^+ . A similar thermodynamic analysis as was done with H_2PD as the base shows that pyridine could result in a single 2 e⁻ wave by a combination of H^+ transfer and H-bonding between pyridinium and HPD^+ or PD. However, as the data in Figure 10 clearly show, if you just add 1 equivalent of pyridine, you do not get a single 2 e⁻ wave. Eventually you do get a single wave, but, in order to get this CV, 100 equivalents of pyridine needed to be added. So how can you get a single wave with H_2PD at orders of magnitude lower concentrations with essentially 1 equivalent of the base (another H_2PD)? The answer is that the formation of a dimer such as $\text{PD-H}_4\text{PD}^{2+}$ would have to be occurring in an adsorbed monolayer on the electrode surface. The effective concentration of a monolayer can be $>1\text{M}$, which could very well be large enough to make dimer formation possible in a single voltammetric wave.

There are several pieces of evidence that support the above hypothesis. First, the concentration dependent data for both Me_2PD , Figure 6, and H_2PD , Figure 4, show that the normalized current for the first wave generally decreases as the concentration increases. This behavior is consistent with some adsorption of Me_2PD and H_2PD on the electrode surface. The enhanced current that results will be most significant at the lowest concentrations, where current from Me_2PD and H_2PD in solution will be the smallest. The fact that the amount of this enhancement varies from experiment to experiment is also consistent with adsorption since the condition of the electrode surface will also inevitably vary from experiment to experiment. Second, despite variations in the current enhancement between

experiments, the current enhancement at low Me₂PD concentrations is always observed to be larger for the second oxidation peak than the first, suggesting that the radical cations have an even greater tendency to adsorb than the reduced forms.

Another intriguing piece of data that supports the formation of PD-H₄PD²⁺ in an adsorbed monolayer is that integration of the CV wave that is observed at the low concentrations and fast scan rates, before the H₃PD⁺ and H₂PD⁺ waves start to appear, corresponds to a surface coverage of 7 to 8×10⁻¹¹ mol/cm². This is a reasonable coverage for a monolayer. Only when the amount of charge passed in the first CV wave starts to exceed that of a monolayer do the waves corresponding to H₃PD⁺ and H₂PD⁺ in solution start to appear.

The next question is whether this is a strongly chemisorbed monolayer or a more weakly bound physisorbed layer. All evidence points to the latter. In one experiment, the electrode was held positive of the first wave of H₂PD, then removed from the electrolyte solution, dipped in pure acetonitrile to remove residual solution, and put in fresh electrolyte solution with no H₂PD. Reversal of the voltage produced no current corresponding to reduction of an adsorbed layer. The voltammetric behavior was also examined under steady state conditions with a 25 μm diameter microelectrode. If the radical cation or dimer strongly adsorbed, a stripping peak should have been seen on the return scan. In a couple of cases, there might have been a very small peak, but the results were not reproducible.

The lack of evidence for a strongly chemisorbed layer is consistent with the DPV data, Figure 7, that shows no significant difference between the behavior of H₂PD at Pt, Au and C electrodes. If a strongly chemisorbed layer was involved then we would expect a significant electrode effect.

A possible mechanism

Based on all of the above lines of evidence the following mechanism, outlined in Scheme 2, can be proposed. First, oxidation of H₂PD produces the adsorbed radical cation H₂PD⁺. Another H₂PD coming in from the bulk preferentially interacts with the already adsorbed H₂PD⁺ forming a type of pi dimer on the surface. These type of dimers have been observed for Me₂PD and Me₂PD⁺ in methylene chloride.³⁴ Next, a series of fast reactions needs to occur to convert the adsorbed H₂PD⁺-H₂PD dimer into the adsorbed PD-H₄PD²⁺ dimer. These, not necessarily in order, are removal of 1 more e⁻, transfer of 2 H⁺'s, and formation of 2 H-bonds. Overall these steps correspond to reaction 9 of our preliminary mechanism, with X being the adsorbed PD-H₄PD²⁺ dimer.

Note that just removal of one more electron to form the well-known homo-valent pi dimer²² between two radical cations is not sufficient to explain the electrochemistry. Recently Macias-Ruvalcaba and Evans have shown that formation of the pi-dimer with the closely related benzidines does affect the voltammetry³⁶ and they have also evoked formation of a pi-dimer as an explanation for the too small second CV wave often observed for quinones in aprotic media.²¹ However, in both these cases the second CV wave is still present, either because break up of the homo-valent dimer is very fast³⁶ or because the dimer itself can undergo a second electron transfer.²¹ The additional e⁻ transfer, H⁺ transfer and H-bonding

steps proposed in this case would be expected to give greater kinetic stability to the dimer, which would not be expected to undergo a second oxidation.

The single CV wave observed for H_2PD at the lowest concentrations appears quite reversible at 200 mV/s as shown in Figure 4. However, as mentioned earlier, at faster scan rates the current in the return peak does decrease compared to the forward peak. This can be explained by an equilibrium between two forms of the dimer, with the more stable form being not reducible and the less stable form being reducible at close to the same potential as $\text{H}_2\text{PD}/\text{H}_2\text{PD}^+$.³⁷ At fast scan rates the equilibration to the reducible form is slow on the timescale of the experiment, resulting in a diminished return peak. However, at slower scan rates the equilibrium is fast enough to allow one electron reduction of the dimer, which then falls apart in a rapid chemical step to give H_2PD and H_2PD^+ . Reduction of the H_2PD^+ completes the cycle.

Based on available thermodynamic information and DFT calculations, an overall small, favorable K for formation of $\text{PD-H}_4\text{PD}^{2+}$ seems reasonable. If this is the case, then the dimer could be the majority species at equilibrium in a monolayer on the electrode surface where the effective concentration will be $>1\text{M}$. However, our lack of evidence for a strongly adsorbed layer means that the dimer must not be that strongly adsorbed on the surface and may be easily displaced by incoming H_2PD from the bulk. Once the dimer desorbs into solution, where its concentration is now many orders of magnitude smaller, the equilibrium position will strongly favor the monomers over the dimer. Still, break up of the dimer may be somewhat slow because of the two strong H-bonds. It is reasonable, however, that equilibration is sped up by transfer of a H^+ from $\text{PD-H}_4\text{PD}^{2+}$ to H_2PD to form H_3PD^+ and $\text{PD-H}_3\text{PD}^+$ (reaction 10 in the preliminary mechanism with $\text{I1} = \text{H}_3\text{PD}^+$ and $\text{I2} = \text{PD-H}_3\text{PD}^+$). This is consistent with the appearance of H_3PD^+ in the CV's before the appearance of H_2PD^+ . As the H-bonds break and the dimer falls apart, reverse e- transfer and H^+ transfer become favorable, and the radical cation H_2PD^+ starts to appear. H_2PD would also be re-generated from H_3PD^+ in the process. Overall, the series of reactions would correspond to reaction 11 in the preliminary mechanism with $\text{I3} = \text{H}_2\text{PD}$. In effect, the proposal is that H_2PD acts as a catalyst, speeding up the decomposition of the dimer to 2 H_2PD^+ in solution. This results in the second CV wave growing in faster at higher H_2PD concentrations.

There are of course other mechanistic pathways that could lead to a similar result. One possibility which seems quite plausible with a Pt electrode is that a H^+ is transferred from the adsorbed radical to the electrode first and then to another H_2PD . However, if the electrode surface was this intimately involved with the reaction then we would expect a strong dependence on electrode material, and the DPV data in Figure 7 show no such dependence.

Another possibility is that there are two parallel mechanisms taking place, with formation of the dimer on the surface dominating at low concentrations and direct oxidation of H_2PD to dissolved H_2PD^+ and H_2PD^{2+} becoming more important at higher concentrations. As noted earlier, the second CV wave first appears after about a monolayer worth of H_2PD has been oxidized. In Scheme 2 we hypothesize that the appearance of wave 2 is due to the breakup

of the dimer to give H_2PD^+ in solution after its desorption from the electrode. An alternative explanation is that the appearance of wave 2 is simply due to oxidation of solution-phase H_2PD coming in from the bulk. In this explanation, the initial current that flows in wave 1 goes towards making a monolayer of dimer, but, once the monolayer is formed, any additional current would simply go towards oxidizing H_2PD in solution. However, if this was the case, then a normal wave shape would be expected for wave 2 rather than the distorted shape, characteristic of a CE mechanism, that is observed at the concentrations and scan rates where wave 2 first appears. Furthermore if the monolayer remained constant (no exchange with H_2PD in solution), then, by the time the solution concentration reached mM values, the CV would be completely dominated by the current from the solution process and we would expect to see two waves of equal height, as we see with Me_2PD at these concentrations. Nonetheless, it is certainly possible that some direct oxidation of H_2PD (without going through a dimer intermediate) could be occurring at higher concentrations. Indeed this might offer a simpler explanation than that shown in Scheme 2 as to why wave 2 gets relatively larger as the H_2PD concentration increases.

Conclusion

Thorough concentration-dependent studies of H_2PD voltammetry have led us to the entirely unexpected conclusion that the radical cation H_2PD^+ is not the initial solution product of the first oxidation of H_2PD in acetonitrile. Perhaps the single most telling evidence of this is the scan rate data in Figure 5 which shows only wave 3, due to H_3PD^+ oxidation, at 2 V/s, but, as the scan rate is slowed, wave 2, due to H_2PD^+ oxidation, starts to appear. At 0.2 V/s the H_3PD^+ peak is gone and only the oxidation wave for H_2PD^+ is present. This is very clear evidence that there is a time lag in the appearance of H_2PD^+ in solution after the first oxidation.

The question is then, what is the initial product? A number of lines of evidence suggest one reasonable possibility is that it is a mixed valent dimer, $\text{PD-H}_4\text{PD}^{2+}$, formed on the electrode through proton transfer and H-bonding between adsorbed radical cations. This dimer is stable enough to be the major species at the effective high concentrations present in the monolayer, but once it desorbs into solution the monomers become favored. The gradual break up of the dimer in solution leads to dissolved H_2PD^+ and the appearance of wave 2 in the CV.

In future work we plan to look for spectroscopic evidence for the proposed dimer. UV/Vis should be particularly informative in this regard. By constructing a long path length spectroelectrochemical cell it may be possible to measure absorptions at the very low concentrations where the dimer appears to have some kinetic stability in solution. We also plan to explore the use of reflectance IR and UV/Vis as a means to determine the identity of adsorbed species. However, irrespective of the outcome of future studies, it is clear in the work presented here that the ability of NH phenylenediamines to undergo proton transfer and H-bonding between themselves gives rise to an unexpectedly complex mechanism for what is nominally a simple, reversible 1 e⁻ transfer.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research. Support for S.M.M. and K.K. by the SDSU MBRS/IMSD Program (2R25GM058906-09A2) is also gratefully acknowledged.

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28. It is not possible to say definitively that there is no mechanism involving only solution-phase chemical steps that will give the observed concentration dependence. Indeed, a reviewer suggested one mechanism involving three e- transfer steps (H_2PD/H_2PD^+ , H_2PD^+/H_2PD^{2+} and HPD/HPD^+) and three solution-phase chemical steps that does give a smaller second CV wave at lower concentrations. The chemical steps are reaction 8, followed by reaction of the products, H_3PD^+ and HPD^+ , to form a dimer ($K = 1 \times 10^5$), which can break apart in solution to form two H_2PD^+ ($K = 0.6$). The rates of the forward reactions can be set so that reaction 8 occurs to make H_3PD^+ and HPD^+ even at very low concentrations, but the reverse reaction or the forward reaction to form the dimer is too slow. Since the electron transfer reaction involving oxidation of H_3PD^+ to H_3PD^{2+} (Scheme 1) is not included, the H_2PD gets trapped in the form of H_3PD^+ and HPD^+ at the lower concentrations. In contrast at higher concentrations the rates onward to form the dimer are fast enough to get out of the H_3PD^+/HPD^+ trap and the simulated CV shows two reversible waves almost undistorted by the chemical reactions. The problem with this mechanism is that H_3PD^+ is oxidizable (see Figure 8) and inclusion of this reaction along with a favorable H^+ transfer between H_3PD^{2+} and HPD^+ ($K = 160$ from pK_a 's in Scheme 1) removes the “trap” at the low concentrations, resulting in a simulated CV similar to that seen at higher concentrations. We have extensively explored other possible mechanisms involving only solution-phase chemical steps, but have not been able to come up with one that includes all likely reactions and gives, even qualitatively, the observed concentration dependence.
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33. A similar geometry has been reported before for the doubly oxidized form of the completely methylated analogue, N,N,N',N'-2,3,5,6-octamethylphenylenediamine. In this case, steric hindrance between the C-Me H's and the N-Me H's in the quinoidal state forces the bending. It is also interesting to note that the oxidation of this compound is one of the rare examples of a single 2 e- process in non-aqueous solutions. This is because the intermediate radical state is destabilized more by the steric effects than the fully reduced or fully oxidized forms Gruhn NE, Macias-Ruvalcaba NA, Evans DH. *J. Phys. Chem. A.* 2006; 110:5650–5655. [PubMed: 16640359]
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37. That a form of the dimer is reducible at close to the same potential as $H_2PD^{0/+}$ is in accord with the hypothesis that the overall K for dimer formation from H_2PD^+ , reaction 21, is fairly small. Indeed, if $K = 1$ for the dimerization, then E° of $2 H_2PD/PD-H_4PD^{2+} = E^\circ$ of H_2PD/H_2PD^+ .

Figure 1.
CV of 0.5 mM Me₂PD in 0.1 M NBu₄PF₆/CH₃CN at 1 V/s: (a) experimental; (b) simulated.
See Experimental section for simulation parameters.

Figure 2.
CV of 0.5 mM H₂PD in 0.1 M NBu₄PF₆/CH₃CN at 1 V/s: (a) experimental; (b) simulated.
See Experimental section for simulation parameters.

Figure 3.

UV/Vis spectra of 0.5 mM H₂PD in 0.1 M NBu₄PF₆/CH₃CN taken at different points in the CV of H₂PD: (a) initial; (b) top of the first CV wave; (c) between the two CV waves; (d) beginning of the second CV wave; (e) after the second CV wave.

Figure 4.

Representative CV's of H₂PD in 0.1 M NBu₄PF₆/CH₃CN at different concentrations with a Pt electrode at 200 mV/s. The CV's have been background subtracted and the currents normalized by dividing by concentration. (a) 0.005 mM; (b) 0.010 mM; (c) 0.020 mM; (d) 0.050 mM; (e) 0.10 mM; (f) 0.20 mM.

Figure 5.

CV's of 0.050 mM H₂PD in 0.1 M NBu₄PF₆/CH₃CN with a Pt electrode at different scan rates. The CV's have been background subtracted and the currents normalized by dividing by the square root of the scan rate. (a) 0.10 V/s; (b) 0.20 V/s; (c) 0.50 V/s; (d) 1.0 V/s; (e) 2.0 V/s.

Figure 6.

CV's of Me_2PD in $0.1 \text{ M NBu}_4\text{PF}_6/\text{CH}_3\text{CN}$ with a Pt electrode at 200 mV/s at different concentrations. The CV's have been background subtracted and the currents normalized by dividing by concentration. (a) 0.005 mM; (b) 0.010 mM; (c) 0.020 mM; (d) 0.050 mM; (e) 0.10 mM; (f) 0.20 mM.

Figure 7.

Normalized peak currents (current/electrode area/H₂PD concentration) for DPV's of different concentrations of H₂PD in 0.1 M NBu₄PF₆/CH₃CN at platinum, glassy carbon and gold electrodes. Gray bars = normalized current for 1st peak (H₂PD^{0/+}); Red bars = normalized current for 2nd peak (H₂PD^{+/2+}). Each value is the average of 3 independent measurements. Error bars are the 90% confidence limits.

Figure 8.

CV's of 1.0 mM H₂PD in 0.10 M NBu₄PF₆/CH₃CN with a C electrode at 100 mV/s in the presence of increasing concentrations of HClO₄: (a) 0 mM HClO₄; (b) 1 mM HClO₄ and (c) 2 mM HClO₄.

Figure 9.

DFT(B3LYP) optimized structure for PD- H_4PD^{2+} . PD is on top and H_4PD^{2+} is on bottom in both views. (a) side view with Me's forward; (b) side view with N's forward.

Figure 10.

CV's of 1.0 mM H₂PD in 0.10 M NBu₄PF₆/CH₃CN at 100 mV/s in the presence of increasing concentrations of pyridine: (a) 0 mM; (b) 1 mM; (c) 10 mM; (d) 25 mM; (e) 50 mM; (f) 100 mM.

Scheme 1.
Possible protonation/oxidation states of H_2PD

Scheme 2.
Proposed Mechanism for 1 e⁻ Oxidation of H₂PD