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Electrochemically Controlled Hydrogen Bonding. Redox-Dependent Formation of a 2:1 Diarylurea/Dinitrobenzene^{2-} Complex

Cindy Chan-Leonor, Stephanie L. Martin, and Diane K. Smith*

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

dsmith@sciences.sdsu.edu

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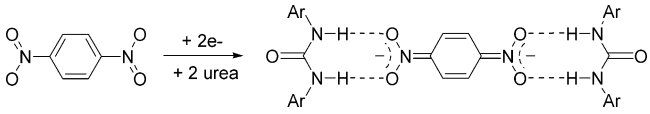
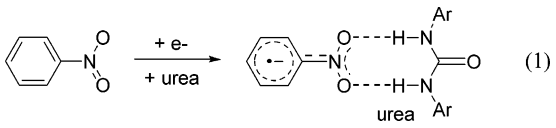


The electrochemistry of 1,2-dinitrobenzene (1,2-DNB), 1,3-dinitrobenzene (1,3-DNB), and 1,4-dinitrobenzene (1,4-DNB) is strongly affected by the presence of 1,3-diphenylurea. In DMF, the second reduction potential of all three DNBs shifts substantially positive in the presence of the urea, indicating very strong hydrogen bonding to the dianions. With 1,2- and 1,3-DNB, the hydrogen bonding leads to irreversible chemistry, likely due to proton transfer from the urea to the dianions. No such irreversible behavior is observed with 1,4-DNB. Instead, the second reduction shifts into the first reduction, producing a single, reversible, two-electron cyclic voltammetric wave at high urea concentrations. Computer simulations show that the changes in wave shape accompanying this process are well accounted for by the stepwise formation of a 1:1 and 2:1 1,3-diphenylurea/DNB^{2-} complex, with sequential binding constants of $\sim 5.5 \times 10^4$ M^{-1} and $\sim 4.0 \times 10^3$ M^{-1} in DMF.

Introduction

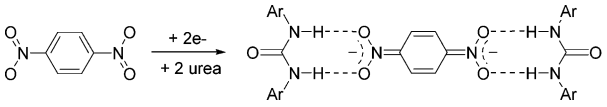
A continuing goal in supramolecular chemistry is to develop switchable systems, that is, well-defined aggregates of molecules whose structure can be controlled through an external signal. Electron transfer is particularly attractive as the signal because it provides a natural interface between the electronics of today and the molecular electronics envisioned for the future.

Recently, we described a very simple yet effective redox switch that utilizes redox-dependent H-bond formation between diarylureas and nitrobenzene derivatives in aprotic solvents.[1] This is an example of an on/off switch in that essentially no interaction is observed between the urea and the nitrobenzene in its oxidized state. However, reduction of the nitrobenzene to its radical anion leads to a strong hydrogen bond interaction ($K = 10^5$ M^{-1} in DMF) between the nitro O's and the urea N−H's, eq 1.



(1)

In this work, we extend our studies of the nitrobenzene/urea system by looking at dinitrobenzenes. These are of interest for two reasons. First, while the mononitrobenzenes only undergo one reversible reduction in aprotic solvents, all three simple dinitrobenzenes undergo two reversible reductions in aprotic media to form first the radical anion and then the dianion.[2] Second, the presence of two nitro groups leads to the possibility of forming the larger 2:1 complex, illustrated in eq 2 for the para derivative.



(2)

It is well-established that organic dianions produced by 2e- reduction are good H-bond acceptors, much stronger than the comparable radical anions. This has been particularly well studied with quinones, where addition of relatively large amounts of weaker H-donors produces little shift in the quinone$^{0/1-}$ redox potential but significant positive shifts in the quinone$^{1-/2-}$ redox potential with no loss in reversibility in aprotic media.[3] Similar effects have been observed with nitroaromatics,[4] including 1,4-dinitrobenzene.[5] In several studies, the shift

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in potential vs H-donor concentration has been used to evaluate the stoichiometry of the H-bonded complexes. With the quinone dianions, it appears that typically the stoichiometry is >2:1 H-donor/quinone^{2-}. However, in an early study along these lines, Nielsen and Parker concluded that both water and methanol only formed 1:1 and 2:1 complexes with the 1,4-dinitrobenzene dianion (1,4-DNB^{2-}) in DMF.[5] Binding constants were small: 4.7 and 4.4 M^{-1} for the 1:1 and 2:1 H_2O/1,4-DNB^{2-} complexes, respectively, and 18 and 5.9 M^{-1} for the corresponding methanol complexes. In the present work, we are using a much stronger H-donor, one that is capable of a 2-point interaction with each nitro group. Based on our previous work with 1,3-diphenylurea as a H-donor,[1,6] we expected much stronger binding, and indeed this proved to be the case.

The other point of interest in the present work is the ability to form an intrinsic 2:1 complex in a redox-dependent fashion. The vast majority of previous studies dealing with redox-dependent binding in well-defined, strongly bound complexes have involved 1:1 binding.[7] There are a few cases involving redox-dependent ion receptors where more than one of the receptor units have been covalently linked resulting in >1:1 binding.[8] There are also some examples where multiple copies of either the redox-active component or its nonredox-active binding partner have been attached to a dendrimer, presumably resulting in a more complex binding stoichiometry.[9] However, in all of the above examples, the primary interaction between receptor and substrate is still 1:1.

A recent example more directly related to the present work is a study by Hamilton, Rotello, and co-workers involving benzene diimides and triimides.[10] These compounds undergo 2 and 3 reductions, respectively, in aprotic solvents. Cyclic voltammetry studies indicated a strong, reversible interaction between the reduced imides and alkylthioureas. On the basis of the structures, the authors postulated the formation of 2:1 and 3:1 complexes. However, although this seems reasonable, the cyclic voltammetry in this case was ambiguous and studies were not done to establish the stoichiometry of the H-bond complexes.

In contrast, cyclic voltammetry studies of the dinitrobenzenes and diphenylurea are quite definitive. In the case of the ortho and meta derivatives, irreversible chemistry gets in the way of the formation of the 2:1 complex, but this is not a problem with the para derivative. Cyclic voltammetry studies provide clear evidence for the stepwise formation of a 2:1 complex between 1,3-diphenylurea and the 1,4-dinitrobenzene dianion in DMF.

Experimental Section

Reagents. All chemicals were purchased from commercial sources as reagent grade or better. 1,2-, 1,3-, and 1,4-dinitrobenzene were recrystallized from ethanol and dried overnight under vacuum at room temperature. 1,3-Diphenylurea was recrystallized from ethanol and dried overnight in a vacuum oven at 100 °C. Tetrabutylammonium hexafluorophosphate was recrystallized three times from 95% ethanol and dried overnight in a vacuum oven at 100 °C.

General Voltammetry Procedures. Cyclic voltammetry (CV) experiments were performed with a PAR model 263 digital potentiostat using the model 270 electrochemistry software package. The acquisition mode was set to "ramp" in order to simulate an analogue experiment. All measurements were conducted under N_2 in a jacketed, one-compartment cell with a Au disk working electrode (~2 mm diameter), a Pt wire counter electrode, and a Ag wire pseudoreference electrode. The solvent, anhydrous grade *N*,*N*-dimethylformamide (DMF), was passed through a column of activated alumina directly into the cell. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the electrolyte. In most experiments, ferrocene (Fc) was also added (~1 mM) as an internal potential reference. For the CVs used for computer simulation, ferrocene was not added. Instead, the Ag wire reference was placed in a separate compartment so the reference potential would not change when substrate was added. O_2 was removed from the electrolyte solution by bubbling N_2 through the solvent for several minutes prior to making a measurement. Temperature was controlled by using a circulating water bath to run 25 °C water through the outer cell jacket.

Voltammetric Titrations. To determine the equilibrium and rate constants associated with the redox-dependent binding, titration experiments were run in 0.1 M NBu_4PF_6/DMF with 1,4-DNB and 1,3-diphenylurea. For these experiments, background CVs in the absence of 1,4-DNB and urea were recorded at 200, 500, and 1000 mV/s. 1,4-DNB was then added to give a concentration of 1 mM, and a new set of CVs were run at the same scan rates. Next, the urea was added in increments to give 0.5, 1, 2, 5, 10, 20, and 50 mM solutions. CVs at the different scan rates were run after each addition.

CV Simulation. The background-subtracted CV's from the titration experiments were fit to the mechanism shown in Scheme 1 using the DigiSim program (v 3.03, BioAnalytical Systems). The formal redox potentials of 1,4-DNB, E_1 and E_2, the diffusion coefficient, D, and the uncompensated resistance in the cell, R_u, were determined first by fitting the CVs with no added urea using Butler–Volmer kinetics and assuming that at these scan rates the voltammetry of the first 1,4-DNB reduction should be completely reversible. The peak-to-peak separation was then fit by adjusting the R_u value. This resulted in an R_u value of 750 Ω.

The E_1, E_2, D, and R_u values determined in the above manner were then used to fit the complete set of titration CVs (all scan rates and urea concentrations). All species were assumed to have the same D. Initial simulations indicated that reasonable starting values for the adjustable parameters were as follows (see Scheme 1 for definitions): $K_1 = 10\ M^{-1}$, $K_2 = 10\ M^{-1}$, $K_3 = 1 \times 10^5\ M^{-1}$, $K_4 = 1 \times 10^4\ M^{-1}$, all kf's $= 1 \times 10^5\ M^{-1}\ s^{-1}$ and all k_s's = 1 cm/s. Starting values 10 times larger and smaller were also used with similar final results. Best fits were obtained both by allowing the program to adjust all of the above parameters simultaneously and by using an iterative procedure in which first the Ks were adjusted, then the k_f's, and finally the k_s's. The cycle was then repeated subject to the following rules: if a k_f became greater than $1 \times 10^{10}\ M^{-1}\ s^{-1}$ the value was set to $1 \times 10^{10}\ M^{-1}\ s^{-1}$ with no further adjustment allowed, if a k_s became greater than 10 the value was set to 10 with no further adjustment, and if any parameter

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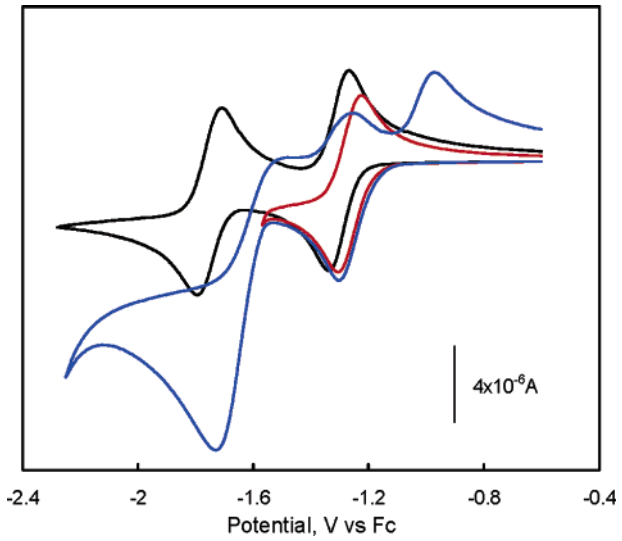


FIGURE 1. Cyclic voltammograms of 1 mM 1,3-DNB in 0.1 M NBu_4PF_6/DMF by itself (black) and in the presence of 10 mM 1,3-diphenylurea (red and blue). Scan rate = 100 mV/s.

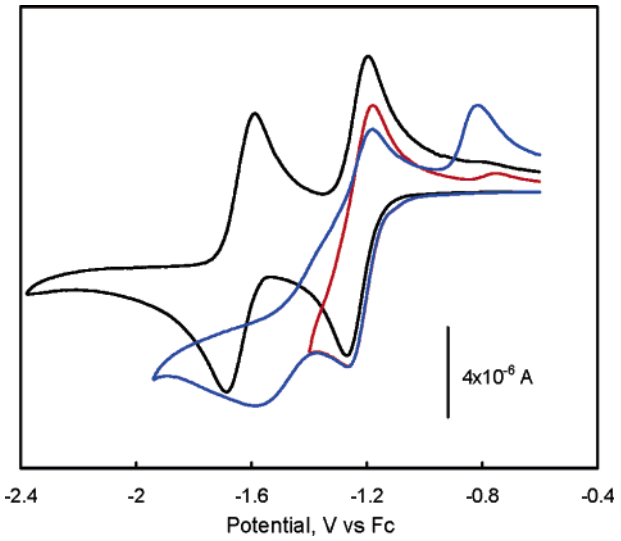


FIGURE 2. Cyclic voltammograms of 1 mM 1,2-DNB in 0.1 M NBu_4PF_6/DMF by itself (black) and in the presence of 10 mM 1,3-diphenylurea (red and blue scans). Scan rate = 100 mV/s.

changed <5% from the previous cycle the value was set with no further adjustment allowed. Iterations were repeated until no significant improvement in the fit was observed between cycles. Best fits obtained both by the direct and iterative procedures resulted in very similar looking CV's and comparable values for K_3 and K_4. However, we felt that the very best results were obtained using the iterative procedure, and this is what is shown in Figure 4.

Results and Discussion

Redox-dependent binding is most conveniently detected by looking at the voltammetry of the redox-active component (receptor) with and without its binding partner (substrate) present. Simply speaking, if the substrate binds more strongly to the oxidized form of the receptor, it makes it more difficult to reduce the receptor and the half-wave potential, $E_{1/2}$, of the receptor shifts toward more negative potentials in the presence of the substrate. On the other hand, if the substrate binds more strongly to the reduced form of the receptor, it will be easier to reduce the receptor in the presence of the substrate and the $E_{1/2}$ shifts toward more positive potentials.

Voltammetry of Dinitrobenzenes in the Presence of 1,3-Diphenylurea. As shown in Figures 1−3, all three simple dinitrobenzene derivatives exhibit two reversible, one-electron reductions in aprotic media. The first cyclic voltammetric (CV) wave (more positive potential) corresponds to reduction of the dinitrobenzene, DNB, to the radical anion, DNB^-. The second CV wave (more negative potential) corresponds to reduction of the radical anion to the dianion, DNB^{2-}. Addition of 1,3-diphenylurea to all the DNB derivatives has a marked effect on the voltammetry, but, interestingly, the effect varies considerably depending on the substitution pattern.

The meta derivative, 1,3-DNB, shows behavior most similar to the previously studied mononitrobenzenes.[1] This is illustrated in Figure 1, which shows CVs of 1 mM 1,3-DNB by itself (black scan) and in the presence of 10 mM 1,3-diphenylurea (blue and red scans). As was observed with nitrobenzene, addition of the urea causes the first reduction to shift toward more positive potentials with no significant change in wave height. This indicates a strong reversible interaction between the urea and the radical anion that from structural considerations we presume to be H-bonding between the urea N−H's and the nitro O's. If the potential is switched immediately after the first reduction (red scan), the height of the return peak in the presence of 1,3-diphenylurea remains the same as the forward peak, indicating that the radical anion is stable under these conditions. On the other hand, if the potential is scanned more negative (blue scan), an even larger positive shift in potential is observed for the second reduction. This is accompanied by a large increase in reduction current. The lack of a return peak for the second reduction, as well as the appearance of a new oxidation peak on the return scan, indicates irreversible chemistry has occurred, likely initiated by proton transfer from the urea to the more basic dianion. This type of behavior was also observed with the mononitrobenzenes when the potential was scanned significantly negative of the nitrobenzene$^{0/-1}$ CV wave.[1]

The corresponding CVs for the ortho derivative, 1,2-DNB, are shown in Figure 2. Unlike 1,3-DNB or the mononitrobenzenes, the addition of 1,3-diphenylurea produces no potential shift in the first reduction wave. This indicates no significant interaction between the radical anion and the urea. However, scanning beyond the first reduction shows that like 1,3-DNB, the second reduction shifts significantly positive. Unlike the 1,3 derivative there is no large increase in current, but the broadness of the second reduction peak clearly indicates kinetic effects, and, once again, the lack of a return peak as well as the appearance of a new oxidation peak indicates irreversible chemistry likely initiated by proton transfer to the dianion.

While the irreversible chemistry observed with 1,3-DNB and 1,2-DNB in the presence of the diphenylurea is interesting, it also makes studying redox-dependent hydrogen bonding more difficult. From this standpoint, it is the para derivative, 1,4-DNB, that shows the most promising behavior. As shown in Figure 3, no evidence

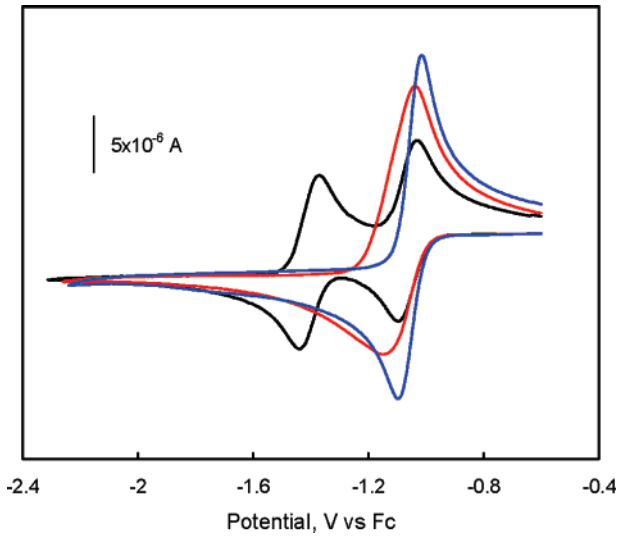


FIGURE 3. Cyclic voltammograms of 1 mM 1,4-DNB in 0.1 M NBu_4PF_6/DMF by itself (black) and in the presence of 10 mM (red) and 50 mM (blue) 1,3-diphenylurea. Scan rate = 100 mV/s.

for irreversible chemistry between 1,4-DNB and the urea is observed. Like 1,2-DNB, addition of 10 mM diphenylurea to a 1 mM solution of 1,4-DNB (red scan) produces no significant potential shift in the first reduction. However, once again the second reduction shifts considerably, so much so that it appears essentially on top of the first reduction, producing a single broad peak. Unlike the 1,2 and 1,3 derivatives, this peak is chemically reversible in that the return peak is of equal area as the forward peak, and no new oxidation peaks appear. Further addition of urea to 50 mM (blue scan) causes the single CV wave to sharpen until it appears close to an ideal, reversible two-electron wave. (Note that the oxidation peak at 50 mM urea is actually larger than it should be. This could be explained by some adsorption of the reduced species on the electrode surface.)

Qualitatively, the differences in behavior between the three DNBs can be rationalized by simple structural arguments. In the case of 1,3-DNB, the meta arrangement precludes a direct resonance connection between the two nitro groups, resulting in the negative charge on the radical anion residing primarily on one of the nitro groups, as it would in the mononitrobenzenes. This results in relatively strong binding to the radical anion and a potential shift in the first reduction, albeit a smaller one than observed with nitrobenzene itself. In contrast, with the 1,2 and 1,4 derivatives the nitro groups are connected by resonance so the negative charge in the radical anion should be fully spread over both nitro groups. This means there will be a smaller negative charge on each nitro group in the radical anion and much weaker H-bonding to the radical anion. The result is no shift in the first reduction. On the other hand, addition of the second electron produces close to a full negative charge on both nitro groups resulting in strong binding to the dianion and the observed large positive shift in the second reduction wave.

As mentioned previously, the irreversible chemistry observed for both the 1,2 and 1,3 derivatives in the presence of the urea is likely due to the greater basicity of

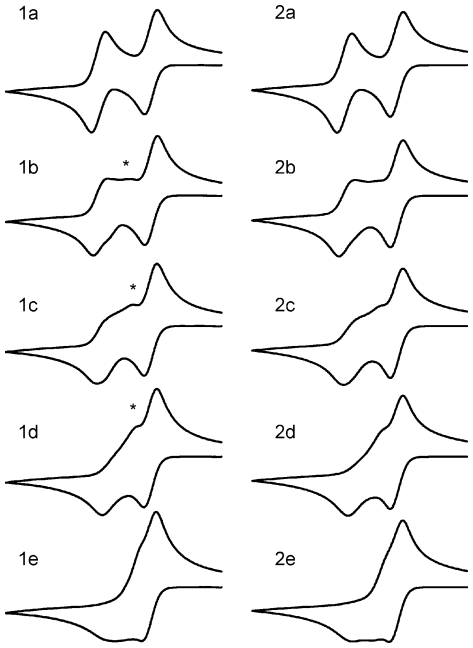
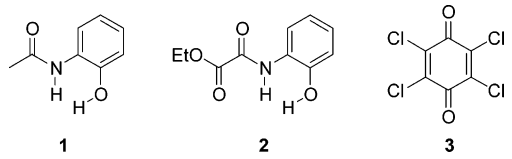


FIGURE 4. (1) Experimental and (2) simulated[13] CV's of 1 mM 1,4-DNB in 0.1 M NBu_4PF_6/DMF in the presence of increasing amounts of 1,3-diphenylurea: (a) 0 mM urea, (b) 0.5 mM urea, (c) 1 mM urea, (d) 2 mM urea, (e) 5 mM urea. Scan rate = 1 V/s.

their dianions. This is undoubtably related to the observation that the reduction potentials for these isomers are considerably more negative than that of 1,4-DNB, indicating that the radical anion and dianion of the 1,2 and 1,3 isomers are more energetic than that of the 1,4. For 1,3-DNB, this can once again be explained by the lack of resonance connection between the two nitro groups resulting in less delocalization of the negative charge. In the case of 1,2-DNB, less delocalization of the −2 charge would also be expected because steric interference between the two nitro groups will force them to be rotated out of the benzene plane, hampering the resonance effect.

Experimental and Simulated Voltammetry of 1,4-Dinitrobenzene in the Presence of 1,3-Diphenylurea. A clearer understanding of what happens when 1,3-diphenylurea is added to 1,4-DNB can be obtained by observing the effect of smaller additions of urea on the voltammetry. This is shown in Figure 4. The voltammograms on the left are the experimental CVs and those on the right are simulated CVs. The top left voltammogram (1a) is once again 1,4-DNB by itself in DMF. (See black CV in Figure 3 for the potential scale.) Addition of 0.5 equiv of urea (1b) has very little effect on the $DNB^{0/1-}$ wave but causes both the cathodic and anodic peaks of the $DNB^{1-/2-}$ wave to decrease and a small wave to appear between the two main waves. This new wave is seen as a shoulder on the positive side of the $DNB^{1-/2-}$ cathodic peak and as a small anodic peak (marked with an asterisk) located between the original $DNB^{1-/2-}$ and $DNB^{0/1-}$ anodic peaks. Addition of another 0.5 equiv of urea to give a total of 1 equiv (1c) causes the original $DNB^{1-/2-}$ anodic peak to decrease to approximately half its original size and the anodic peak of the new wave to increase so that it is about the same height, taking into consideration that it is on top of the increasing anodic current for the $DNB^{0/1-}$ wave. Further increase to 2 equiv

urea leads to the complete disappearance of the original $DNB^{1-/2-}$ anodic peak and the new anodic peak (now appearing as a broad shoulder on the negative side of the $DNB^{0/1-}$ anodic peak) to grow to about the same height as the original $DNB^{1-/2-}$ anodic peak before the urea was added. Additional increases in urea cause this new peak to continue to move positive eventually completely overlapping the first wave to give a single 2-electron wave at the potential of the original $DNB^{0/1-}$ wave.



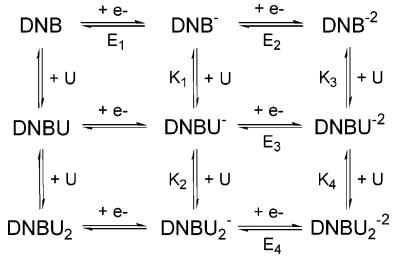
1 **2** **3**

The fact that the original $DNB^{1-/2-}$ wave disappears and the "new" wave is fully formed at a 2:1 ratio of urea to DNB is good evidence that a 2:1 urea/DNB complex is being formed. Similar behavior was observed previously by Gonzalez and co-workers when they added amides **1** and **2** to a DMSO solution of chloranil, **3**.[11] These workers also found that the second CV wave corresponding to the $quinone^{1-/2-}$ redox couple split into two overlapping waves at less than 2 equiv of added guest and then merged back into one wave at more positive potentials with greater than 2 equiv of guest. Unlike the 1,4-DNB/urea system, the two one-electron quinone CV waves do not merge into a single wave, but this is simply due to the greater potential separation between the CV waves to begin with. (It is interesting to note the structural similarities between the amide guests used by Gonzalez and co-workers and 1,3-diphenylurea. Both contain two good H-donor groups, two aromatic amide N−H's in the case of the urea and an aromatic amide and phenolic OH in the case of amides 1 and 2. In both cases, the H-donor groups can orientate so that they can simultaneously interact with a H-acceptor.)

Gonzalez and co-workers also explained the observed CV behavior in their system due to the stepwise formation of a 2:1 complex between the amides and the chloranil dianion. This conclusion was supported by computer simulation of the experimental voltammograms based on this mechanism. We have employed the same strategy for the 1,4-DNB/diphenylurea system. This technique also provides the best means to determine binding constants from CV data in systems such as this where there is not strong binding to all oxidation states.[12]

Assuming only electron transfer and hydrogen bonding equilibria, the complete mechanism for stepwise formation of a 2:1 complex between dianion and guest is described by the 9-membered square scheme shown in Scheme 1. In the 1,4-DNB/urea case, some simplification can be achieved by noting that no significant hydrogen bonding to the 0 oxidation state is expected. This eliminates two H-bonding and two electron transfer reactions from the mechanism. Also, since the thermodynamic parameters are not completely independent of one another, thermodynamic parameters for two of the eight remaining reactions are defined by the other six. Definitive thermodynamic values for two of the reactions, E_1 and E_2, can be obtained by fitting the CVs without adding urea. However, this still leaves four thermodynamic parameters (which we chose to be the four equilibrium constants K_1, K_2, K_3, and K_4) as well as eight sets of kinetic parameters to be determined by fitting the experimental CVs. Needless to say, with this many adjustable parameters even results that produce good fits to the data should be greeted with a healthy dose of skepticism. That being said, this effort is not completely in vain since some predictions about what constitute reasonable results can be made and these can be used to both guide the fitting process by providing reasonable starting values for the different parameters and to evaluate the reasonableness of the results.

SCHEME 1. H-Bonding and E-Transfer Equilibria Involved in the Stepwise Formation of a 2:1 Complex between 1,3-Diphenylurea (U) and 1,4-DNB^{2-}



One thing that is clear from a qualitative evaluation of the CVs is that K_1 and K_2 have to be relatively small; otherwise, there would be a significant shift in the first reduction upon addition of excess urea to 1,4-DNB. On the other hand, K_3 and K_4 must be large in order to produce the observed large positive shift in potential of the second reduction. Preliminary simulations confirmed the above predictions and indicated that K_1 and K_2 could not be larger than $\sim 10\ M^{-1}$ or a shift in the first reduction would be observed. It was also found that K_3 and K_4 had to be $\sim 10^5\ M^{-1}$ in order for the second peak to split into two peaks at less than 2 equiv of urea. (At lower values the second peak merely shifts.) Another reasonable assumption is that H-bonding of the second urea should be weaker than H-bonding of the first, since H-bonding of the first urea would tend to remove electron density making the dianion a poorer H-donor. This means that K_4 would be expected to be less than K_3 (and K_2 less than K_1). As to the rates of H-bonding, given the lack of steric hindrance and the relative rigidity of both 1,4-DNB and the urea, it is reasonable to expect very rapid values for the kf's of the H-bonding reactions. Indeed, in previous simulation work with nitroaniline and 1,3-diphenylurea, we found that extremely rapid rates of H-bonding, $10^8-10^9\ M^{-1}\ s^{-1}$, best fit the data. In this case, we found that

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(13) Parameters used for the simulated voltammograms are as follows: $E_1 = -0.660$ V; $E_2 = -0.996$ V; $E_3 = -0.775$ V; $E_4 = -0.519$ V; $k_{s,1} = 10$ cm/s; $k_{s,2} = 0.0311$ cm/s; $k_{s,3} = 0.230$ cm/s; $k_{s,4} = 10$ cm/s; all α's = 0.5; $K_1 = 11.08\ M^{-1}$; $K_2 = 0.175\ M^{-1}$; $K_3 = 6.17 \times 10^4\ M^{-1}$; $K_4 = 3.70 \times 10^3\ M^{-1}$; $k_{f,1} = 2.18 \times 10^4\ M^{-1}\ s^{-1}$; $k_{f,2} = 8.01 \times 10^4\ M^{-1}\ s^{-1}$; $k_{f,3} = 8.34 \times 10^7\ M^{-1}\ s^{-1}$; $k_{f,4} = 1 \times 10^{10}\ M^{-1}\ s^{-1}$; all D's $= 7.71 \times 10^{-6}$ cm^2/s; $R_u = 750\omega$; $A = 0.0302\ cm^2$. Note that the E's used for the simulations are relative to an Ag wire reference, so they differ in an absolute sense from those seen in Figure 4 where the voltage is relative to the ferrocene/ferrocenium redox potential.

the best results were obtained by starting with smaller, although still quite rapid, k_f values of 10^5-10^6 M^{-1} s^{-1}.

With the above considerations, we were able to achieve quite good fits to the experimental data as shown by the voltammograms on the right side of Figure 4. In particular, the changes in peak potentials and wave shape in the simulated CVs match those in the experimental CVs nicely. The most significant difference between the two sets is that the anodic peak of the $DNB^{0/1-}$ wave in the presence of urea is consistently larger in the experimental voltammograms than in the simulations. As mentioned previously this could be reasonably accounted for by some absorption of the $DNB(urea)_2^{2-}$ complex on the electrode.

As expected, we were not able to determine a unique set of parameters that clearly represented the one best fit to the experimental voltammograms, rather the CVs shown in Figure 4 are representative of what we believe to be the *best* family of best fits. Characteristics of this family are $K_3 \sim 5.5 \times 10^4$ M^{-1}, $K_4 \sim 4.0 \times 10^3$ M^{-1}, and $K_1 < \sim 10$ M^{-1}. Values of K_2 varied over a much larger range indicating that the data is not very sensitive to this parameter. Forward rate constants for H-bonding to DNB^- were generally smaller (10^4-10^5 M^{-1} s^{-1}) than those for binding to DNB^{2-} ($>10^8$ M^{-1} s^{-1}). The latter are comparable to those we determined previously for nitroaniline radical anion.[1]

The fact that we are able to obtain such good fits to the experimental voltammograms with reasonable values for the thermodynamic and kinetic parameters provides strong support for the mechanism proposed in Scheme 1 and the formation of a 2:1 complex between diphenylurea and 1,4-DNB^{2-}. Based on the average K_3 and K_4 values determined from the simulations, the amounts of 1:1 and 2:1 complexes present at different amounts of urea can be calculated. These results are shown graphically in Figure 5 for a 1 mM 1,4-DNB solution. As expected, at a 1:1 ratio of urea to DNB^{2-}, most of the DNB^{2-} exists as the 1:1 complex, but significant amounts of the 2:1 and uncomplexed DNB^{2-} are also present. The exact ratios are 65% 1:1, 15% 2:1, and 20% uncomplexed. At a 2:1 ratio, the 2:1 complex becomes the major component at 61%, with the 1:1 complex dropping to 37% and only 2% remaining uncomplexed. As the amount of urea is increased, the percentage of 2:1 complex continues to grow. With 10 equiv of urea, 97% of the DNB^{2-} exists as the 2:1 complex.

Conclusions

CVs of all three simple dinitrobenzene derivatives are strongly affected by the presence of 1,3-diphenylurea in DMF. These effects are readily explained by a combination of H-bonding and proton transfer from the urea to the reduced forms of the dinitrobenzenes. 1,3-DNB is the only one of the three where reasonably strong H-bonding to the radical anion is observed. However, the dianions

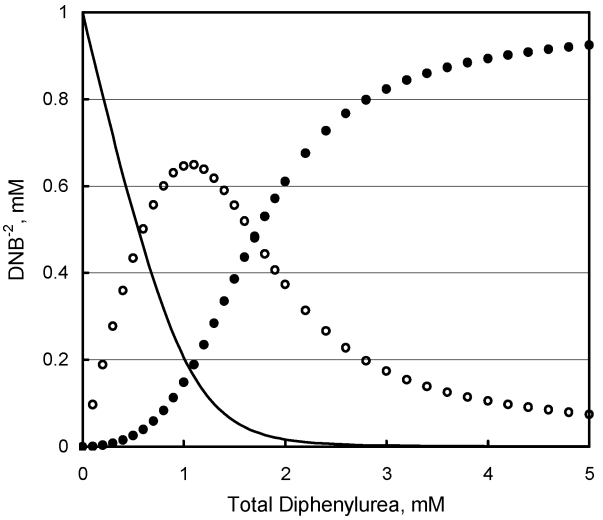

FIGURE 5. Equilibrium concentrations of 1,4-DNB^{2-}-containing species as a function of total 1,3-diphenylurea concentration assuming $K_3 = 5.5 \times 10^4$ M^{-1} and $K_4 = 4.0 \times 10^3$ M^{-1}: 1,4-DNB^{2-} (solid line), 1,4-$DNBU^{2-}$ (open circles), 1,4-$DNBU_2^{2-}$ (filled circles).

of all three of the dinitrobenzenes appear to strongly H-bond to the urea. In the case of 1,3- and 1,2-DNB, the resulting positive shift in potential of the second reduction is accompanied with irreversible behavior that is likely due to proton transfer from the urea to the basic dianions. No such irreversible behavior is observed with the 1,4 derivative. Instead, the second reduction shifts into the first reduction, producing a single, reversible, two-electron CV wave at high urea concentrations. CV simulations show that the changes in wave shape accompanying this process are well accounted for by the stepwise formation of a 1:1 and 2:1 urea/DNB^{2-} complex.

As mentioned previously, redox-dependent formation of intrinsic 2:1 complexes such as that observed here have not been studied to a significant extent. One of the interesting things this opens up is the possibility of forming even larger aggregates in a redox-dependent fashion. For example, by combining 1,4-DNB with another component that contains two or more urea functional groups it may be possible to create redox-dependent supramolecular polymers. Further studies along this line are planned and will be reported in due course.

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