

dimethyl-3,4-dihydrophenanthrene, 97277-98-0; 1-keto-3-methyl-THP, 4655-56-5; 1,3-dimethyl-1-hydroxy-THP, 97278-00-7; 1,3-dimethyl-3,4-dihydrophenanthrene, 97278-26-7; 4-keto-1-methyl-THP, 97278-01-8; *cis*-1,4-dimethyl-4-hydroxy-THP, 97278-02-9; *trans*-1,4-dimethyl-4-hydroxy-THP, 97278-03-0; 1-methyl-4-methylene-THP, 97278-04-1; 1,4-dimethyl-1,2-dihydrophenanthrene, 97278-05-2; 1-(1-naphthyl)-2-propanone, 33744-50-2; ethyl 2,3-dimethyl-3-hydroxy-4-(1-naphthyl)butanoate, 97278-06-3; ethyl 2,3-dimethyl-4-(1-naphthyl)crotonate, 97278-27-8; 2,3-dimethyl-4-(1-naphthyl)butanoic acid, 7476-04-2; 2,3-dimethyl-4-(1-naphthyl)butanoyl chloride, 97278-07-4; 2,3-dimethyl-1-keto-THP, 97278-08-5; 2,3-dimethyl-1-hydroxy-THP, 97278-09-6; 2,3-dimethyl-3,4-dihydrophenanthrene, 97278-10-9; 4-keto-2-methyl-THP, 97278-11-0; 2,4-dimethyl-4-hydroxy-THP, 97278-28-9; 2,4-dimethyl-1,2-dihydrophenanthrene, 97278-12-1; 1-keto-THP, 573-22-8; 2,2-dimethyl-1-keto-THP, 97278-13-2; 4-keto-THP, 778-48-3; 3,3-dimethyl-4-keto-THP, 97278-14-3; 3,3-dimethyl-4-hydroxy-THP, 97278-15-4; diethyl [2-(1-

naphthyl)-2-propyl]malonate, 97278-29-0; [2-(1-naphthyl)-2-propyl]malonic acid, 97278-16-5; 3-methyl-3-(1-naphthyl)butanoic acid, 63253-34-9; 4-methyl-4-(1-naphthyl)butanoic acid, 63253-37-2; 4-methyl-4-(1-naphthyl)butanoyl chloride, 97278-17-6; 4,4-dimethyl-1-keto-THP, 97278-18-7; 4,4-dimethyl-1-hydroxy-THP, 97278-30-3; 4,4-dimethyl-3,4-dihydrophenanthrene, 97278-19-8; 2-bromo-2'-acetonephthone, 613-54-7; 2-methyl-2-(2-naphthoyl-methyl)malonic acid, 97278-20-1; 2-methyl-3-(2-naphthoyl)propanoic acid, 16206-42-1; 2-methyl-4-(2-naphthyl)butanoic acid, 97278-21-2; 2-methyl-4-(2-naphthyl)butanoyl chloride, 97278-22-3; 3-methyl-4-keto-THP, 40154-19-6; 3,4-dimethyl-4-hydroxy-THP, 97278-23-4; 3,4-dimethyl-1,2-dihydrophenanthrene, 97278-24-5; 2,2'-diacetyl biphenyl, 24017-95-6; (*R**,*R**)-2,2'-bis(1-hydroxyethyl)biphenyl, 18152-34-6; (*R**,*R**)-2,2'-bis(1-hydroxyethyl)biphenyl, 18152-33-5; 2,2'-bis(1-bromoethyl)biphenyl, 97278-25-6; 10,10-dimethyl-9-keto-DHP, 6948-59-0; 9,10,10-trimethyl-9-hydroxy-DHP, 97278-31-4; 2,3-dimethyl-THP picrate, 97278-34-7; 2,4-dimethyl-THP picrate, 97278-36-9.

Electrogenerated Bases: The Role of Weak Electroinactive Proton Donors and the Effect of Electrocatalysis on the Redox Behavior of Azobenzene

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The stepwise electrochemical reduction of PhN=NPh in DMF-0.1 M (CH₃)₄NPF₆ can give, depending upon proton availability, three anionic reduction products. The basicities of these electrogenerated bases increase in the order PhN=NPh⁻ < PhNHN⁻Ph < PhN⁻N⁻Ph. Water (pK_a^{Me₂SO} = 31.6), which is capable only of protonating PhN⁻N⁻Ph, causes the reversible PhN=NPh⁻/PhN⁻N⁻Ph redox couple to shift to more positive potential. From the magnitude of the potential shift and the reported value of pK_a^{DMF}(H₂O) = 34.7, pK_a^{DMF}(PhNHN⁻Ph) is estimated to be 38.1. Ph₂C=NNH₂ and PhNHNHPh both protonate PhN⁻N⁻Ph irreversibly. The PhNHN⁻Ph that is produced in this reaction is subsequently consumed in an electrocatalytic cycle which involves PhN=NPh as the oxidant, the less easily oxidized PhNHN⁻Ph as the reductant, and proton transfer from PhNHN⁻Ph to the conjugate base of the added proton donor as the rapid, irreversible follow-up reaction. The anodic peak for the irreversible oxidation of PhNHN⁻Ph is discernible only at scan rates in excess of about 1 V/s at -51 °C. Protonation of PhNHN⁻Ph by both diethyl malonate (pK_a^{Me₂SO} = 16.4) and fluorene (pK_a^{Me₂SO} = 22.6) and of PhN=NPh⁻ by diethyl malonate is irreversible and affords PhNHNHPh and the conjugate base of the added proton donor as the principal electroactive products.

The electrochemical reduction of azobenzene (PhN=NPh) in aprotic media is reported to occur in two successive one-electron steps.¹⁻⁶ Although PhN=NPh⁻ is quite stable in the absence of added proton donors and can be reoxidized quantitatively on the cyclic voltammetric time scale, the lifetime of the corresponding dianion is sufficiently short in most solvent-electrolyte systems so as to preclude a cyclic voltammetric anodic peak for its re-oxidation. Rapid reaction of the dianion involves its protonation by acidic impurities such as water and is generally believed to afford hydrazobenzene (PhNHNHPh) or its conjugate base as the principal product.⁴

Because of the basicity of PhN⁻N⁻Ph and the ease with which it can be prepared in known amount, electrogenerated PhN⁻N⁻Ph has been used widely as a strong base in electroorganic synthesis⁷⁻¹⁰ and diagnostic electrochem-

ical studies.^{11,12} Our current interest in PhN⁻N⁻Ph as an electrogenerated base was created by our need to prepare certain carbanions and nitranions in *N,N*-dimethylformamide (DMF) in order to measure their oxidation potentials and to determine their reactivities with selected substrates. Although evidence indicated that electrogenerated PhN⁻N⁻Ph reacted rapidly with the added proton donor, a cyclic voltammetric anodic wave for the oxidation of the conjugate base of the proton donor frequently could not be found on the reverse, positive-going sweep. The studies that are described here examine the chemical and electrochemical reactions that cause this behavior.

Results and Discussion

The basicity of the electrogenerated bases in the azobenzene series increases in the order PhN=NPh⁻ <

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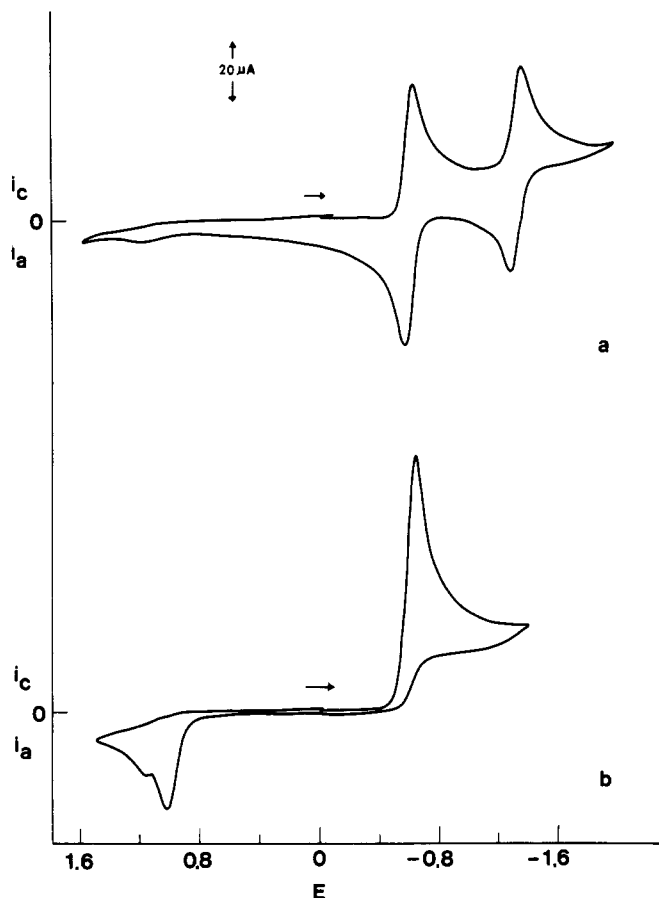


Figure 1. (a) Cyclic voltammogram for the reduction of 5.5 mM PhN=NPh at a planar platinum electrode in DMF-0.1 M (C₂H₅)₄NPF₆ at 22 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s. (b) Same as (a) except 11 mM diethyl malonate is present.

PhNHN-Ph < PhN⁻-Ph. In order to illustrate the effects of varying acid strength on the redox behavior of PhN=NPh, proton donors that are electroinactive in the potential range of interest have been selected which cause protonation of (a) all electrogenerated anions and anion radicals, (b) PhNHN-Ph and PhN⁻-Ph, but not PhN=NPh⁻, (c) PhN⁻-Ph only, with proton transfer irreversible on the cyclic voltammetric time scale, or (d) PhN⁻-Ph only, but with proton transfer reversible. The order of presentation is in ascending value of the p*K*_a of the electroinactive proton donor.

Protonation of All Electrogenerated Anion Radicals and Anions. The cyclic voltammetric reduction of azobenzene in DMF-0.1 M (CH₃)₄NPF₆ is seen in Figure 1a to occur in two successive one-electron steps to give, first, the anion radical at *E*_{p,c,1} = -0.64 V and then the dianion at *E*_{p,c,2} = -1.39 V. Both processes are chemically reversible at either platinum or glassy carbon working electrodes as long as care is taken to exclude large amounts of water, other acidic impurities, and supporting electrolytes which function as proton donors (e.g., (*n*-Bu)₄N⁺). When a relatively strong, electroinactive proton donor is added, such as (EtO₂C)₂CH₂ (p*K*_a^{Me₂SO} = 16.4,¹³ the expected behavior that is associated with protonation of the electrogenerated PhN=NPh⁻ occurs: the cathodic peak for the initial reduction of PhN=NPh shifts slightly in the anodic direction and doubles in magnitude, while the peaks that are associated with both the reduction (*E*_{p,c} = -1.39 V) and the oxidation (*E*_{p,a} = -0.58 V) of PhN=NPh⁻

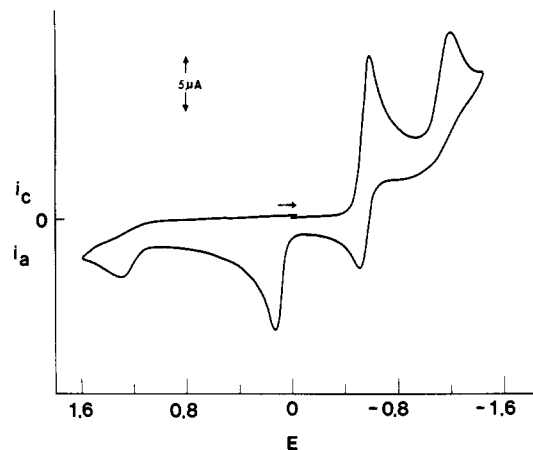
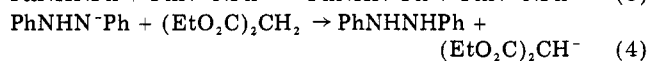
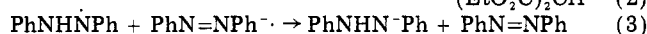
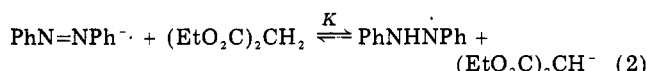
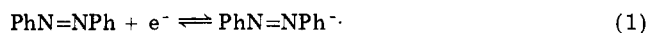
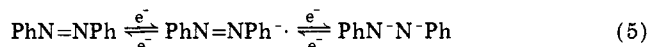


Figure 2. Cyclic voltammogram for the reduction of 5.2 mM PhN=NPh at a planar platinum electrode in the presence of 11.3 mM fluorene in DMF-0.1 M (CH₃)₄NPF₆ at 22 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s.

Scheme I



Scheme II^a



^a FlH₂ = fluorene.

disappear (Figure 1b). Concomitantly, two new anodic peaks appear on the reverse, positive-going scan for the irreversible oxidation of (EtO₂C)₂CH⁻ (*E*_{p,a} = 1.09 V) and PhNHNHPh (*E*_{p,a} = 1.28 V).¹⁴ This behavior, which is well understood, is consistent with the reactions that are described by eq 1-4 in Scheme I.

Protonation of PhN⁻-Ph and PhNHN-Ph but Not PhN=NPh⁻. Fluorene (p*K*_a^{Me₂SO} = 22.6)¹⁵ does not protonate PhN=NPh⁻ at a significant rate, as evidenced by the presence of cathodic (*E*_{p,c,2} = -1.21 V)^{16,17} and anodic (*E*_{p,a,1} = -0.58 V) peaks for the reduction and oxidation, respectively, of PhN=NPh⁻ (Figure 2). Protonation of both PhN⁻-Ph and PhNHN-Ph is indicated by the disappearance for the anodic peak for the reoxidation of PhN⁻-Ph near -1.2 V and the appearances of two new anodic peaks for the irreversible oxidations of 9-fluorenyl anion¹⁸ at *E*_{p,a} = 0.12 V and of PhNHNHPh at *E*_{p,a} = 1.28 V. A scheme that is consistent with this behavior is described by eq 5 and 6 in Scheme II.

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(16) The protonation of PhN⁻-Ph (eq 6) enhances the rate of PhN=NPh⁻ reduction, causing *E*_{p,c} for the PhN=NPh⁻/PhN⁻-Ph redox couple to shift positively. The magnitude of the shift is a function of both the proton donor and its concentration.¹⁷

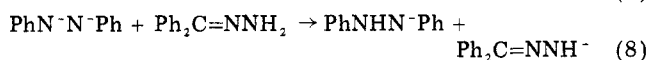
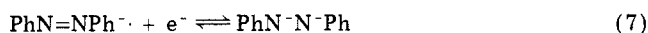
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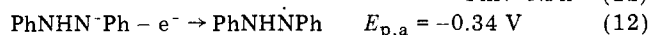
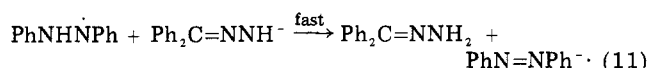
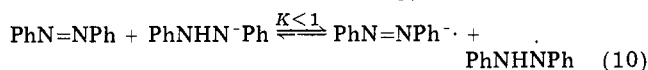
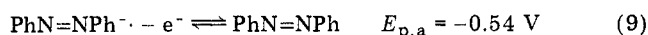
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Scheme III

negative-going scan



positive-going scan



Irreversible Protonation of PhN⁻N⁻Ph. As demonstrated above, a necessary condition for the appearances of anodic peaks for the oxidations of PhNHNPh and the conjugate base of the proton donor is protonation of either PhN⁻NPh⁻ or PhNHN⁻Ph. However, when the p*K*_a of the proton donor is raised sufficiently such that PhN⁻NPh is the only species protonated, relatively unusual electrochemical behavior results. As seen in Figure 3a, benzophenone hydrazone (Ph₂C=NNH₂), a proton donor that creates this behavior, is reduced near -1.76 V when no azobenzene is present. Although Ph₂C=NNH₂⁻ is too short-lived to give a corresponding anodic peak for its reoxidation on the reverse, positive-going sweep, an anodic peak is seen near 0.15 V for the irreversible oxidation of Ph₂C=NNH⁻. Ph₂C=NNH⁻ presumably is formed when anionic products of the Ph₂C=NNH₂⁻ decomposition reaction abstract a proton from unreacted Ph₂C=NNH₂.¹⁹

When an equimolar amount of the more readily reduced PhN=NPh is added to the solution of Ph₂C=NNH₂, the cathodic peak for Ph₂C=NNH₂ at -1.76 V disappears while cathodic peaks due to the stepwise reduction of PhN=NPh to its dianion (*E*_{p,c,1} = -0.64 and *E*_{p,c,2} = -1.28 V) arise on the negative-going scan (Figure 3b). After the direction of the potential scan is reversed at -2.0 V, a single anodic peak (*E*_{p,a} = -0.58 V) arises at the same potential as that for the reversible oxidation of PhN=NPh⁻ to PhN=NPh. Interestingly, while the disappearance of the Ph₂C=NNH₂ cathodic peak at -1.76 V clearly indicates that Ph₂C=NNH₂ has been consumed by electrogenerated PhN⁻NPh, neither an anodic peak for the oxidation of Ph₂C=NNH⁻ near 0.15 V nor an anodic peak for either PhNHN⁻Ph or PhNHNPh (*E*_{p,a} = 1.28 V) is evident in Figure 3b. The explanation for the absence of anodic peaks for Ph₂C=NNH₂ and Ph₂C=NNH⁻ becomes apparent when more rapid scan rates are employed. At 5 V/s and *T* = -51 °C, a second anodic peak is seen (*E*_{p,a} = -0.34 V) on the positive-going sweep at a potential which is slightly more positive than the peak that is due to the oxidation of PhN=NPh⁻ (*E*_{p,a} = -0.54 V at -51 °C) (Figure 3c). The relative magnitude of the more positive of these anodic processes increases at the expense of the more negative anodic peak for PhN=NPh⁻ with increasing scan rate. We assign the more positive anodic peak to the irreversible oxidation of PhNHN⁻Ph and the cause of this relatively unusual electrochemical behavior to the electrocatalytic oxidation of PhNHN⁻Ph by PhN=NPh. A reaction scheme that is consistent with these results is described by eq 7–12 in Scheme III.

Several aspects of the cyclic voltammograms in Figure 3 require comment. First, the absence of an anodic peak

for the reoxidation of PhN⁻N⁻Ph near -1.2 V in the presence of added Ph₂C=NNH₂ demonstrates that the transfer of a proton from Ph₂C=NNH₂ to PhN⁻N⁻Ph (eq 8) is irreversible on the time scale of this experiment. Second, significant cathodic current is normally expected in the potential range from -0.7 to -1.1 V (Figures 3b and 3c) on the reverse, positive-going sweep because of the continual diffusion of PhN=NPh from bulk solution to the electrode surface. Thus, the absence of any current in this potential span means that all PhN=NPh that diffuses from bulk solution is consumed before it reaches the electrode surface by some nonelectrochemical reaction. The reactions (eq 10 and 11) that are responsible for the disappearance of PhN=NPh are the same reactions that cause the anodic peak for PhNHN⁻Ph to disappear at slower scan rates. On the basis of the difference ($\Delta E = 200 \text{ mV}$ at -51 °C) in the anodic peak potentials for the reversible oxidation of PhN=NPh⁻ and the irreversible oxidation of PhNHN⁻Ph, an upper limit of 10^{-4.5} can be calculated from the expression $\Delta E = (RT/nF) \ln K$ for the equilibrium constant in eq 10. We emphasize that this is an upper limit for *K* because the follow-up reaction (eq 11) involving the removal of a proton from PhNHNPh by Ph₂C=NNH⁻ will facilitate the oxidation of PhNHN⁻Ph, thereby causing the anodic peak for PhNHN⁻Ph to shift to more negative potential.¹⁷ Even though the actual value of the equilibrium constant may be considerably smaller than the upper limit given here, reaction 10 can proceed rapidly because the equilibrium concentration of PhNHNPh is rendered small by proton-transfer reaction 11. The occurrence of reaction 11 also explains why an anodic peak is not observed for the oxidation of Ph₂C=NNH⁻ near 0.15 V on the reverse, positive-going sweep. Whether or not an anodic peak is observed for the oxidation of unreacted PhNHN⁻Ph depends on the cyclic voltammetric scan rate and the overall rate of reactions 9–11. At the relatively rapid scan rate that was employed in Figure 3c, the sequence of chemical reactions that causes all PhNHN⁻Ph to be oxidized by electrogenerated PhN=NPh was "outrun" by the cyclic voltammetric experiment.

The occurrences of reactions 10 and 11 have practical importance in the synthetic preparation of the conjugate bases of weak proton donors via electrogenerated PhN⁻N⁻Ph. In the presence of the stronger proton donors that were used to effect the reactions described in Schemes I and II, a pathway involving oxidation of PhNHN⁻Ph by unreacted PhN=NPh would be precluded by the competing pathway involving the rapid protonation of PhNHN⁻Ph. In Schemes I and II the number of equivalents of conjugate base of the proton donor that are generated during the electroreduction of PhN=NPh equals the number of equivalents of PhN=NPh that are reduced (*E* < -0.6 V for Scheme I and *E* < -1.2 V for Scheme II). In contrast, if the proton donor cannot protonate PhNHN⁻Ph and, instead, PhNHN⁻Ph is oxidized by unreacted PhN=NPh (Scheme III), no accumulation of the conjugate base of the proton donor will be possible until all PhN=NPh has been reduced to its anion radical. Thereafter, the rate of accumulation of the conjugate base of the added proton donor will equal the rate of the electrochemical reduction of PhN=NPh⁻ to PhN⁻N⁻Ph.

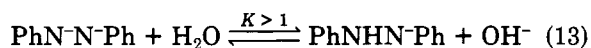
Electrocatalysis, as used in this context, involves the indirect electrochemical oxidation of a more difficultly oxidized substrate (PhNHN⁻Ph) by a more readily prepared electrogenerated oxidant (PhN=NPh). Although this redox reaction (eq 10) is thermodynamically unfavorable, the reaction proceeds rapidly because one product,

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PhN=NPh⁻, is oxidized (eq 9) at the applied potential while the second product, PhNHNPh, is rapidly deprotonated by the conjugate base of the added proton donor (eq 11). The feature that distinguishes this example from most other electrocatalytic reactions²⁰⁻²³ (e.g., the chemical reduction of the more difficultly reduced bromobenzene by electrogenerated benzonitrile anion radical²³) is that the follow-up deprotonation reaction (eq 11) also generates the reduced form of the reagent that participates in the electrocatalytic reactions. Other examples in which follow-up chemical reactions generate additional reagent for the electrocatalytic cycle include the oxidation of 9-amino-fluorenyl anion by electrogenerated fluorenone imine,¹¹ the oxidation of the conjugate bases of certain hydroquinones by electrogenerated quinones,²⁴ and the base-induced decomposition of 1,2-diphenylethanol by electrogenerated benzophenone anion radical.²⁵

Reversible Protonation of PhN⁻N-Ph. As in the cases of Ph₂C=NNH₂ and fluorene, the addition of water ($pK_a^{Me_2SO} = 31.4$)²⁶ as a weak, electroinactive proton donor has no effect on either the cyclic voltammetric peak height or the peak potential location for the reversible reduction of PhN=NPh to PhN=NPh⁻. However, unlike the proton donors above, water causes a new reversible cyclic voltammetric peak to appear at a potential that is approximately 200 mV more positive than the original peak for the reversible reduction of PhN=NPh⁻ to PhN⁻N-Ph (Figure 4). This new reversible peak grows at the expense of the original peak for the reduction of PhN=NPh⁻ to PhN⁻N-Ph with increasing water concentration. The original peak disappears entirely when the ratio of water to azobenzene exceeds one.

The appearance of a reversible process at a more positive potential when water is added as a proton donor is consistent with a proton transfer from water to PhN⁻N-Ph (eq 13) that is reversible on the time-scale of this exper-



iment.²⁷ From the difference in the peak potential for the reduction of PhN=NPh⁻ to PhN⁻N-Ph in the presence ($E_{p,c,2} = -1.19$ V) and absence ($E_{p,c,2} = -1.39$ V) of water, we calculate a value of approximately $10^{3.4}$ for the equilibrium constant for this reaction at room temperature. This result now allows us to estimate the pK_a of PhNHN-Ph in DMF. From the relationship $pK_a(\text{PhNHN-Ph}) = pK_a(\text{H}_2\text{O}) + \log K$ and the pK_a of 34.7 that has been reported by Sawyer and co-workers²⁸ for H₂O in DMF, $pK_a(\text{PhNHN-Ph})$ is estimated to be 38.1. Although presumably more accurate static measurements of $pK_a^{DMF}(\text{H}_2\text{O})$ may cause $pK_a^{DMF}(\text{H}_2\text{O})$ and, hence, $pK_a^{DMF}(\text{PhNHN-Ph})$ to be revised downward by as much as 3 or 4 pK_a units, the results still clearly indicate that PhN⁻N-Ph is an extremely strong base with considerable synthetic utility.

PhNHNPh as an Added Proton Donor. If PhNHNPh were to protonate PhN⁻N-Ph reversibly, as in the case of H₂O, the displacement in the reversible reduction potential for the PhN=NPh⁻/PhN⁻N-Ph redox couple upon addition of PhNHNPh would permit calculation of $pK_a^{DMF}(\text{PhNHNPh})$ relative to $pK_a^{DMF}(\text{PhNHN-Ph})$. Unfortunately, the effect of PhNHNPh is similar to that for Ph₂C=NNH₂ (vide ante); that is, while the peak for the reduction of PhN=NPh⁻ is shifted in the positive direction by the addition of PhNHNPh, there is no corresponding peak for the reoxidation of PhN⁻N-Ph. Although this result means that proton transfer is irreversible on the time scale of this experiment, the rate constant for proton transfer from PhNHNPh to PhN⁻N-Ph can be calculated from the magnitude of the shift of the cathodic peak potential.¹⁷ In the present case, the shift of 180 mV at a scan rate of 0.2 V/s affords a value of approximately 10^5 s⁻¹ for the pseudo-first-order rate constant, from which a value of 4×10^6 M⁻¹ s⁻¹ is calculated for the second-order rate constant.

Comparison of the Acidities of PhNHNPh and PhNHNPh. Although the methods that were employed here cannot be used to measure $pK_a^{DMF}(\text{PhNHNPh})$, its value is not expected to be too different from that for PhNH₂ ($pK_a^{Me_2SO} = 30.7$).²⁹ In the case of PhNHNPh, the fact that fluorene ($pK_a^{Me_2SO} = 22.6$)¹⁵ is unable to protonate PhN=NPh⁻ at a significant rate under the conditions of our cyclic voltammetric experiments suggests that $pK_a^{DMF}(\text{PhNHNPh}) \ll pK_a^{DMF}(\text{fluorene})$. The actual measurement of $pK_a^{DMF}(\text{PhNHNPh})$ is precluded in the condensed phase because of the ready reduction of PhNHNPh by PhN=NPh⁻ when the reduction product, PhNHN-Ph, is subsequently protonated.

Even though the pK_a 's of PhNHNPh and PhNHNPh are not attainable from our results, our data require PhNHNPh to be a significantly stronger proton donor than PhNHNPh. The lower basicity of PhN=NPh⁻ than PhNHN-Ph is consistent with the greater delocalization of charge in the anion radical. The fact that PhN=NPh⁻ and many other relatively stable anion radicals serve effectively as electrogenerated bases is due either to the rapid reduction of the conjugate acid by unreacted anion radical, which renders proton transfer to the anion radical irreversible, or to the disproportionation of the anion radical to give the more strongly basic dianion.

Experimental Section

Instrumental. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.^{30,31} Control of the potentiostat and the acquisition and processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 2000, LSI 11/2).

Cell, Electrodes, and General Procedures. All electrochemical experiments were performed on an all-glass vacuum line. Approximately 30 mL of the solvent, DMF, was transferred by trap-to-trap distillation into an uncompartmentalized electrochemical cell that had been loaded previously with the supporting electrolyte. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. Traces of oxygen, if present either before or after the addition of the electroactive species, were removed by several freeze-

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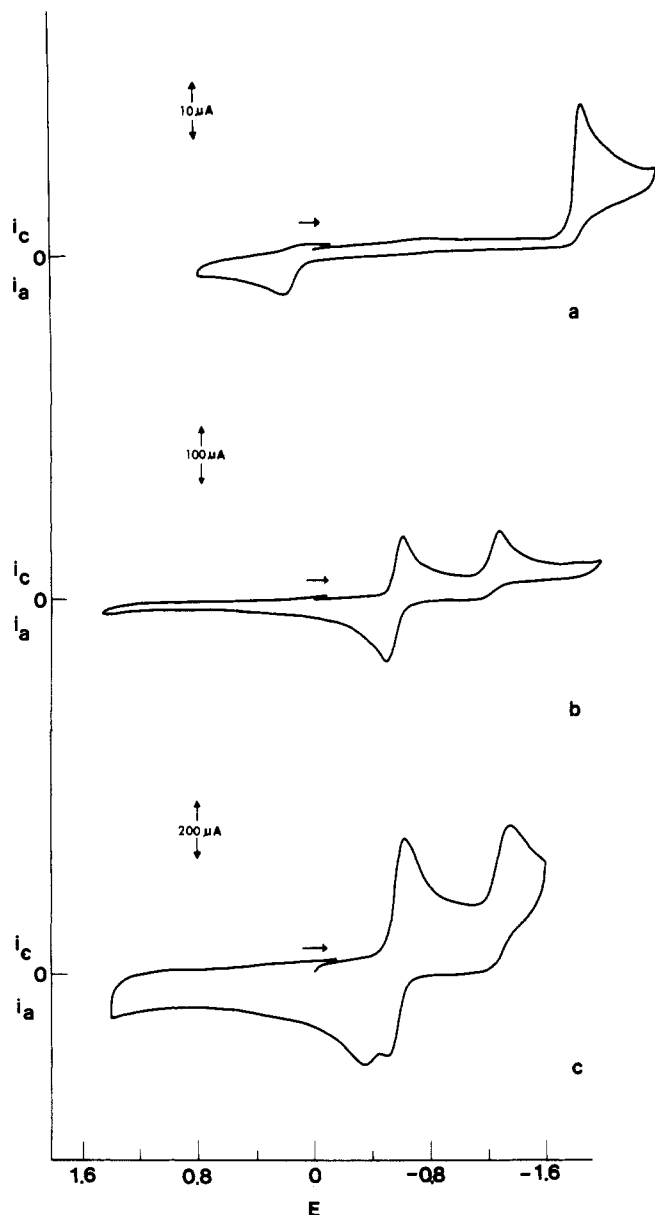


Figure 3. (a) Cyclic voltammogram for the reduction of 4 mM $\text{Ph}_2\text{C}=\text{NNH}_2$ at a spherical platinum electrode in DMF-0.1 M $(\text{CH}_3)_4\text{NPF}_6$ at -51°C . The scan rate is 1 V/s. (b) Cyclic voltammogram for the reduction of 2.4 mM $\text{PhN}=\text{NPh}$ at a planar glassy carbon electrode in the presence of 2.5 mM $\text{Ph}_2\text{C}=\text{NNH}_2$ in DMF-0.1 M $(\text{CH}_3)_4\text{NPF}_6$ at -51°C . The scan rate is 0.2 V/s. (c) Same as (b) except that the scan rate is 5 V/s.

pump-thaw cycles. Helium was used to bring the cell up to atmospheric pressure. Slush baths, which were prepared from liquid nitrogen and the appropriate liquid,³² were used to maintain the cell at constant, subambient temperature.

Planar platinum ($A = 0.03\text{ cm}^2$) and vitreous carbon ($A = 0.20\text{ cm}^2$) working electrodes were used for most of the cyclic voltammetric experiments. The auxiliary electrode was a piece of platinum foil (ca. 1 cm^2) that was parallel to and approximately 1 cm away from the working electrode. All potentials listed were measured with respect to a cadmium amalgam which is in contact with a DMF solution that is saturated with both sodium chloride and cadmium chloride (Type A-III).³³ The potential of this electrode is -0.75 V vs. SCE. Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.³⁴

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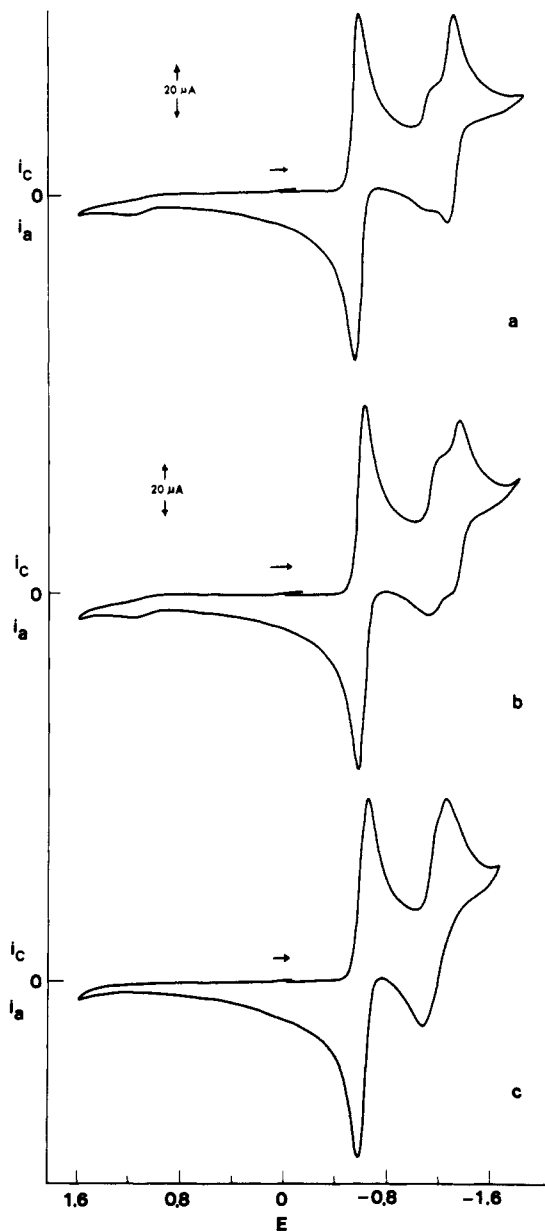


Figure 4. Cyclic voltammograms for the reduction of 9.0 mM $\text{PhN}=\text{NPh}$ at a planar platinum electrode in DMF-0.1 M $(\text{CH}_3)_4\text{NPF}_6$ at 23°C . The scan rate is 0.2 V/s. The mole ratio of water to $\text{PhN}=\text{NPh}$ is (a) 30%, (b) 59%, and (c) 100%.

The second reference electrode, which was a platinum wire in series with a $0.1\text{ }\mu\text{F}$ capacitor, was placed in parallel with the cadmium amalgam electrode.

Chemicals. One-liter aliquots of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500 g, 80-200 mesh, Brockman activity 1, activated at 600°C overnight) and was collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Benzophenone hydrazone, synthesized according to a reported procedure, had mp $97-98^\circ\text{C}$ (lit. mp $97-98^\circ\text{C}$).³⁵ All other compounds were commercially available. Purities and identities of all compounds were verified electrochemically, chromatographically (GC and/or HPLC), and spectroscopically.

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