

Electrochemically Induced Chain Reactions: The Electrochemical Behavior of Nitrosobenzene in the Presence of Proton Donors in Tetrahydrofuran¹

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The electrochemical reduction of nitrosobenzene in tetrahydrofuran with tetrabutylammonium hexafluorophosphate as the supporting electrolyte and in the presence of fluorene or indene at room temperature gives a mixture of an anil (1 or 3), a nitron (2 or 4), and azoxybenzene and requires only a catalytic amount of electricity. Lowering the temperature and/or increasing the proportion of proton donor favors the formation of the anil at the expense of the nitron and azoxybenzene: a 97% yield of anil 1 was obtained from an electrolysis carried out at -30 °C using 5 equiv of fluorene. The possible steps of the chain reactions involved are discussed on the basis of electrochemical and chemical data and digital simulation. With phenylacetylene as the proton donor, there is no reaction between nitrosobenzene and phenylacetylene and azoxybenzene is the main product formed.

Introduction

There are a few examples of electrochemically induced chain reactions. The S_{RN}1 aromatic substitution initiated by the electroreduction of an aryl halide has been thoroughly studied from a mechanistic point of view as well as with a variety of nucleophiles.² The oxidation of alcoholates to aldehydes and ketones by aryl halides induced by electroreduction of the halide constitutes another interesting example.³ The following reactions have also been carried out as chain processes initiated electrochemically: *cis-trans* isomerization of functionalized olefins,⁴ ligand substitution of organometallic complexes,⁵ Michael reactions,⁶ and addition of the trichloromethyl anion to aldehydes.⁷

In this paper, we report a new example of a chain process initiated by electrochemical reduction, namely the Erlich-Sachs reaction^{8,9} between a proton donor such as fluorene (FlH₂) or indene (InH₂) and nitrosobenzene (PhNO) induced by the electroreduction of the latter in THF with *n*-Bu₄NPF₆ as the supporting electrolyte.¹ We describe an investigation of the effect of temperature and of the relative proportion of proton donor and PhNO on the reaction products and on the voltammetric behavior of PhNO. We have also studied the electrochemical behavior of PhNO in the presence of phenylacetylene.

Results

Figure 1a shows the cyclic voltammogram of PhNO in THF with *n*-Bu₄NPF₆ as the supporting electrolyte on a platinum (Pt) electrode and at room temperature. Three reduction peaks A, A₁, and B are observed in the cathodic sweep (A, E_p ≈ -1.05 V; A₁, E_p ≈ -1.46 V; and B, E_p ≈ -2.10 V vs SCE). If the potential is reversed after peak B, two oxidation peaks A' and A' are found (A', E_p ≈ -1.32 V and A', E_p ≈ -0.86 V). Peak A results from the reduction of PhNO to its radical anion, peak A₁ to the reduction of azoxybenzene (AB) to its radical anion, and peak B to further reduction of these radical anions; peaks A' and A' correspond to the oxidation of the radical anions of AB and of PhNO, respectively. The dashed line of Figure 1a represents the cyclic voltammogram of AB alone. Similar voltammograms have been observed in DMF or acetonitrile.¹⁰ In the presence of 1 equiv of FlH₂ (Figure 1b), peak A decreases and has a different form (more rapid drop of current after reaching the peak potential) and a

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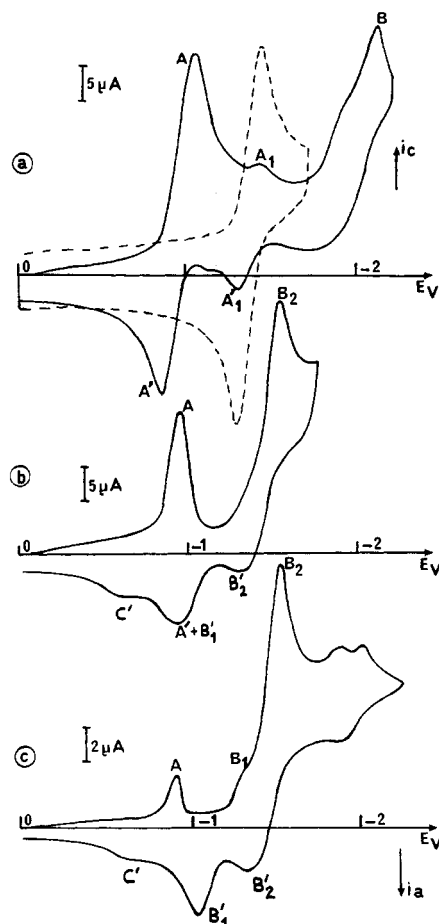


Figure 1. Cyclic voltammograms of PhNO at room temperature on a Pt electrode in *n*-Bu₄NPF₆ (0.15 M)-THF; starting potential 0 V vs SCE: (a) PhNO alone (the dashed line corresponds to the cyclic voltammogram of azoxybenzene) and (b) and (c) PhNO in the presence of 1 equiv of FIH₂; sweep rate (a and b) 0.2 V s⁻¹ and (c) 0.05 V s⁻¹.

new reduction peak, B₂ ($E_p \approx -1.56$ V), appears. Peak A decreases further on the second and subsequent scans and finally disappears. When the sweep rate is decreased, peak A becomes smaller, a new reduction peak, B₁ (shoulder at *ca.* -1.30 V), is observed (compare Figures 1b and 1c), and the oxidation peak A' disappears; there are three oxidation peaks B₂, B₁, and C' at *ca.* -1.33, -1.00, and -0.60 V, respectively (Figure 1c). Similar modifications are observed for the cyclic voltammogram of PhNO in the presence of InH₂ as shown in Figure 2 except that there are only two oxidation peaks at *ca.* -1.30 and -0.55 V.

When an electrolysis of PhNO was performed at room temperature, in the presence of an equimolar amount of FIH₂ and at the potential of the first reduction peak (peak A), the current dropped to zero after the consumption of about 0.04 electron per molecule of PhNO and the solution became green.¹¹ The cyclic voltammogram of the resulting solution (Figure 3) showed the reduction peaks B₁ and B₂ and the three oxidation peaks B'₂, B'₁, and C' that were observed in Figure 1c. In addition to fluorene, the products isolated after extraction and chromatographic separation were fluorenone anil 1, nitrone 2, and AB. Their yields are indicated in Table I, entry 1. Fluorenone was also formed in small amounts according to thin layer chromatographic (TLC) analysis.¹² Compounds 1 and 2 were

(11) There was no reaction between PhNO and FIH₂ or InH₂ in the absence of the electron source (no potential applied).

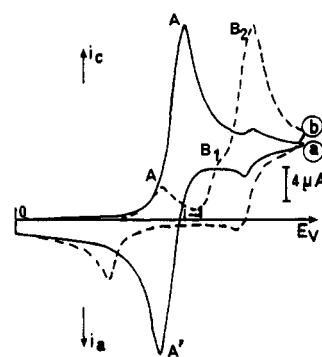


Figure 2. Cyclic voltammograms of PhNO on a Pt electrode in *n*-Bu₄NPF₆ (0.15 M)-THF; sweep rate 0.05 V s⁻¹; starting potential 0 V vs SCE: (a) PhNO alone and (b) PhNO in the presence of 1 equiv of InH₂.

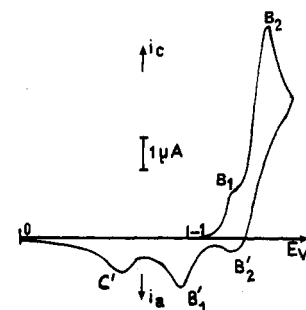


Figure 3. Cyclic voltammogram on a Pt electrode in *n*-Bu₄NPF₆ (0.15 M)-THF after electrolysis of PhNO in the presence of FIH₂ at -1 V vs SCE.

Table I. Preparative Electroreduction of PhNO in the Presence of Fluorene (FIH₂) or Indene (InH₂) as the Proton Donor (AH₂) on a Pt Electrode in THF^a

entry	AH ₂	AH ₂ /PhNO (molar ratio)	T (°C)	Q × 10 ³ (F/mol)	yield ^b (%)		
					anil (1 or 3)	nitrone (2 or 4)	AB
1	FIH ₂	1	25	37	32	36	17
2	FIH ₂	1	-30	33	37	13	24
3	FIH ₂	5	25	0.8	57	33	≤1
4	FIH ₂	5	-30	0.7	97	c	c
5	InH ₂	1	25	35	27 ^d	21	14
6	InH ₂	1	-30	38	29 ^d	13	27
7	InH ₂	5	25	1.0	38 ^d	25	4
8	InH ₂	5	-30	1.0	43 ^d	7	8

^a Electrolyses were carried out under an argon atmosphere, at -1.50 V vs SPRE, on 2 mmol of PhNO (30 mM solution), using *n*-Bu₄NPF₆ (0.15 M) as the supporting electrolyte. ^b Yield of homogeneous compounds after chromatographic separation. ^c Determined by TLC. ^d Minimum yield since indenone anil 3 is unstable and decomposes to dark products insoluble in ether which are retained on the chromatographic column.

compared to authentic samples (see the Experimental Section). The voltammograms of these two products (Figures 4 and 5, respectively) show that in Figure 3 and Figure 1c, peak B₁ is due to the reduction of nitrone 2 and peak B₂ to the reduction of anil 1. The presence of peak B₂ in the cyclic voltammogram of Figure 5 shows that nitrone 2 is reduced to anil 1. The origin of the anodic peaks B'₂ and B'₁ has not been investigated, but peak B'₂ could result from the oxidation of the radical anion (or dianion) derived from anil 1 and peak B'₁ from the oxidation of the anion resulting from reduction of the

(12) Fluorenone was formed by the reaction of unreacted fluorenone anion with oxygen upon admitting air into the cell; see: Borhani, K. J.; Hawley, M. D. *J. Electroanal. Chem.* 1979, 101, 407-417.

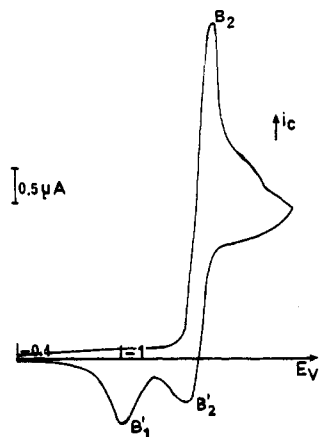


Figure 4. Cyclic voltammogram of **1** in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF on a Pt electrode; starting potential -0.4 V vs SCE; sweep rate 0.02 V s^{-1} .

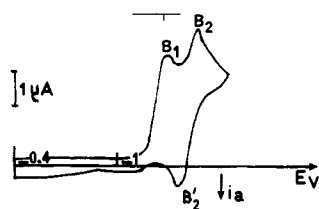
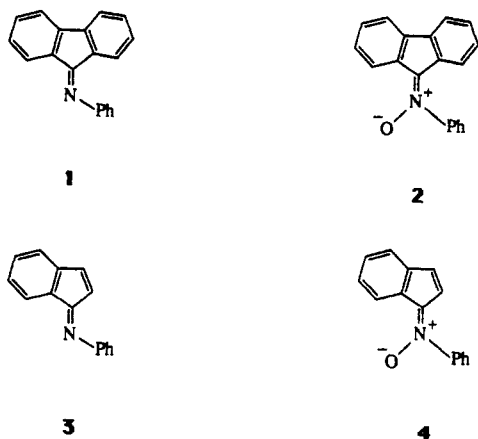


Figure 5. Cyclic voltammogram of **2** in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF on a Pt electrode; starting potential -0.4 V vs SCE; sweep rate 0.02 V s^{-1} .

protonated radical anion (or from protonation of the dianion). The anodic peak C' seen in Figures 1b, 1c, and 3, but absent in Figures 4 and 5, is due to the oxidation of the conjugate base of fluorene. Similarly, the electrolysis of PhNO at room temperature in the presence of 1 equiv of InH_2 required only about 0.04 electron and gave a mixture of indenone anil **3**, nitrone **4**,¹³ and AB in the



yields indicated in Table I, entry 5. The voltammogram of the solution at the end of the electrolysis showed the two reduction peaks B_1 and B_2 and the oxidation peak of Figure 2.

An excess of the proton donor causes a decrease in the quantity of electricity consumed (to about 10^{-3} electron

(13) Interestingly, the $\text{Cl}(\text{CH}_4)$ mass spectra of nitrones **2** and **4** show a peak corresponding to a dimeric structure at m/z 543 for **2** and m/z 442 for **4**. The EI (70 eV) mass spectra show clearly the molecular ion peak at m/z 271 and m/z 221, respectively. The CI mass spectrum of anil **1** does not show any peak corresponding to a dimeric structure; the molecular ion peak at m/z 255 is clearly seen in both the CI mass spectrum and the EI mass spectrum.

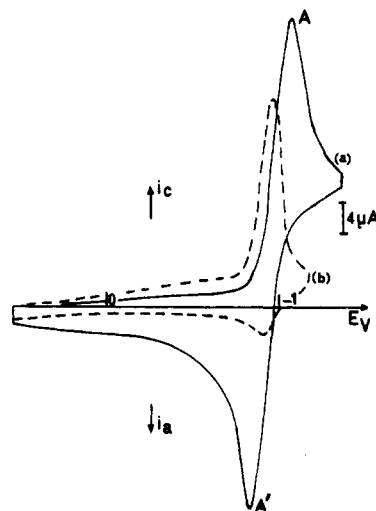


Figure 6. Cyclic voltammogram of $o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}$ in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF on a Pt electrode; sweep rate 0.2 V s^{-1} ; starting potential 0.6 V vs SCE: (a) $o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}$ alone and (b) $o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}$ in the presence of FIH_2 .

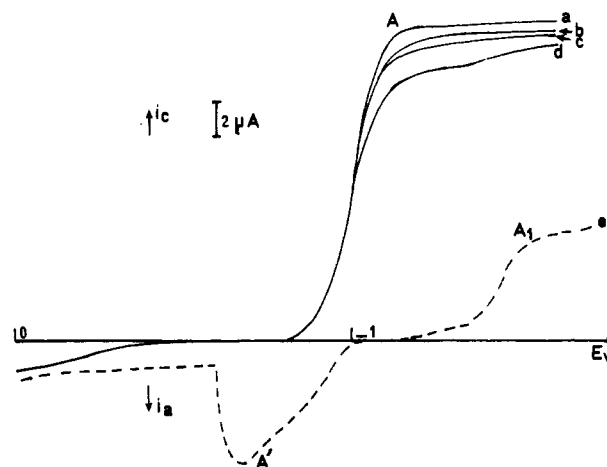


Figure 7. Polarograms (average current) of PhNO in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF ($\tau = 0.5$ s): (a) PhNO alone, (b) PhNO in the presence of 1 equiv of $\text{PhC}\equiv\text{CH}$, (c) PhNO in the presence of 2 equiv of $\text{PhC}\equiv\text{CH}$, (d) PhNO in the presence of 3 equiv of $\text{PhC}\equiv\text{CH}$, and (e) PhNO after electrolysis at -0.95 V vs SCE.

per molecule of PhNO) and favors the formation of the anil (**1** or **3**) at the expense of the nitronium (**2** or **4**) and the AB as shown in entries 3, 4, 7, and 8 of Table I. Lowering the temperature has no effect on the amount of electricity consumed but favors the formation of the anil, particularly in the case of fluorene: at -30 °C and with a 5-fold excess of fluorene, anil **1** was isolated in a 97% yield (entry 4).

The electrochemical behavior of o -nitrosotoluene in the presence of 1 equiv of FIH_2 at room temperature was similar to that of PhNO as shown by the cyclic voltammograms of Figure 6 (to be compared with Figure 1b): a decrease of peak A with a change of its morphology and a drastic decrease of peak A^1 . A microcoulometric determination at -1.0 V showed that only 0.12 electron was required for the complete consumption of o -nitrosotoluene. TLC analysis showed the presence of two major products having R_f values very similar to those of anil **1** and nitronium **2**.

As shown in Figure 7, phenylacetylene has little influence on the polarographic behavior of PhNO in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF at room temperature, even when present in excess (compare traces a, b, c, and d). The polarogram

obtained immediately after the exhaustive electrolysis at -0.95 V vs SCE (Figure 7e) shows the reduction wave of AB and an oxidation wave attributed to the phenylhydroxylamine anion. The electrolysis consumed 0.8 electron and gave AB (88% yield by VPC) after aqueous workup and extraction. Almost identical results were obtained when the electrolysis was carried out in the absence of phenylacetylene in $n\text{-Bu}_4\text{NPF}_6$ (0.15 M)-THF (n value of 0.9, 91% yield of AB) or Et_4NClO_4 (0.1 M)-DMF (n value of 0.8, 90% yield of AB). Asirvatham and Hawley¹⁰ reported n values of 0.6–0.8 and yields of AB of 76–86% for the electrolysis in Et_4NClO_4 (0.1 M)-DMF and, for the electrolysis in acetonitrile (same supporting electrolyte), a 67–75% yield of AB and an n value of 0.3. The n values smaller than unity were explained by the reaction of PhNO with the hydroxide ions produced in the formation of AB.¹⁰ Hydroxide ions do react with PhNO to form AB,^{10,14} and, in acetonitrile, the molar ratio of hydroxide ion to PhNO required for complete reaction is 0.3.¹⁰

Discussion

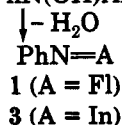
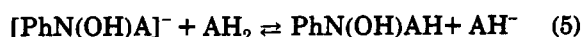
The above results and observations show that the electrochemical reduction of PhNO (and *o*-nitrosotoluene) in THF and in the presence of FlH_2 and InH_2 induces a reaction between the nitroso compound and these proton donors. Since only a small amount of electricity is consumed, chain reactions must be involved. The formation of anils 1 and 3 can be explained by the reaction mechanism described by eqs 1 and 2 as initiation steps and eqs 4 and 5 as propagation steps ($\text{AH}_2 = \text{FlH}_2$ or InH_2). The radical anion produced in reaction 1 is protonated by AH_2 forming an anion, AH^- , and a neutral radical, PhNOH^\bullet . The latter disappears in fast subsequent reactions (coupling and/or disproportionation).



Combining reactions 1 and 2, one gets



The catalytic reactions are described by eqs 4 and 5.



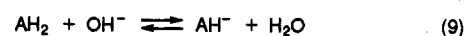
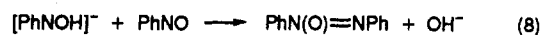
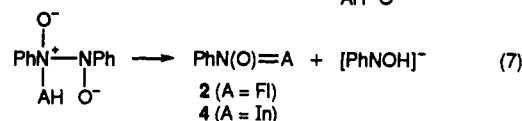
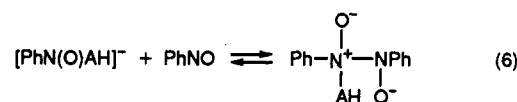
When only the anil was formed such as in the electroreduction of PhNO at -30 °C in the presence of an excess of FlH_2 (Table I, entry 4), no AB was detected. Whenever the nitrone (2 or 4) was formed, AB was formed also in an approximately equivalent amount, and this can be readily accounted for by a catalytic mechanism with eqs 1 and 2 as the initiation steps and then eqs 4 and 5 as the propagation steps. In an aprotic solvent such as

Table II. Reaction of PhNO with the Fluorene and Indene Anion in THF^a

entry	AH_2	$\text{AH}_2/\text{PhNO}/\text{NaH}$ (molar ratio)	T (°C)	yield ^b (%)		
				anil (1 or 3)	nitrone (2 or 4)	AB
1	FlH_2	1:1:1	25	9	15	19
2	FlH_2	10:5:1	25	8	16	11
3	FlH_2	5:1:1	25	11	18	10
4	FlH_2	5:1:1	-30	21	7	13
5 ^c	FlH_2	5:1:1	-30			100
6	InH_2	10:5:1	25	9 ^d	8	19
7	InH_2	5:1:1	-30	13 ^d	15	16

^a PhNO (2 mmol) was added to the yellow solution of the anion after completion of the reaction between NaH and AH_2 . The reactions were carried out under an argon atmosphere. ^b See footnote b of Table I. ^c Addition of NaH to a solution of FlH_2 and PhNO. ^d See footnote d of Table I.

DMSO, water is a weaker acid ($\text{p}K_a = 31.4$)^{15a} than FlH_2 ($\text{p}K_a = 22.6$)^{15b} and the hydroxide ion would readily abstract a proton from FlH_2 and also from InH_2 since the latter is slightly more acidic than FlH_2 ($\text{p}K_{a8}$ of 21 and 25, respectively^{15c}).



When the fluorene or indene anion was generated in THF by reaction with sodium hydride and the anion then reacted with PhNO, the anil (1 or 3), the nitrone (2 or 4), and the AB were formed. However, the yields were lower than those of the electrochemically initiated reaction as shown in Table II. The relative proportions of AH, PhNO, and NaH had little influence on the yields in the range studied. At low temperature, the yield of anil was higher (entry 4) as found in the electrochemically initiated reaction.¹⁶ This temperature effect suggests that the dependence on temperature of the rate of the two competing reactions, eq 5 leading to the anil and eq 6 leading to the nitrone, is such that the former is faster than the latter at -30 °C whereas the rates are comparable at room temperature.

The addition of sodium hydride to PhNO is much faster than the proton abstraction from fluorene at -30 °C in THF since the addition of NaH to a solution of PhNO and fluorene gave AB quantitatively (Table II, entry 5). The addition of a hydride ion to PhNO gives the conjugate base of hydroxylamine which then adds to another molecule of PhNO to give AB after elimination of a hydroxide ion (see eq 8).

The acidity of acetylene is similar to that of InH_2 (same $\text{p}K_a$)^{15c} and slightly higher than that of FlH_2 . So if the

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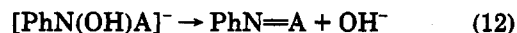
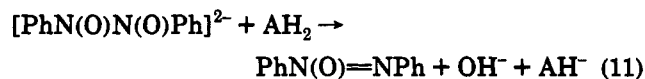
(16) Similar yields were observed when FlH^- was generated by electrochemical reduction of FlH_2 ¹² at -30 °C.

fluorene and indene anions are formed in the electrochemical reduction of PhNO in the presence of FlH_2 and InH_2 in THF, the phenylacetylde anion must be formed also when PhNO is reduced in the presence of phenylacetylene. The fact that the latter, even when present in excess, has no influence on the electrochemical behavior of PhNO suggests that the nucleophilic addition of phenylacetylde to PhNO and, most probably also, the additions of eqs 4 and 6 are reversible. When the nucleophile is generated from an active methylene compound, the second hydrogen can be involved in irreversible elimination reactions (eqs 5 and 7) driving the reaction toward the anil and/or the nitrone.

The reaction of nitroso aromatic compounds with active methylene compounds in the presence of a basic catalyst to give anils (Erlich-Sachs reaction⁸) and nitrones has been known for a long time, but most of the publications do not report yields.⁹ The reaction gives either the anil or the nitrone or a mixture of both, depending on the active methylene compound, the basic catalyst, and the reaction conditions.¹⁷ For instance, the reaction of *p*-nitrosodimethylaniline with 1 equiv of FlH_2 in boiling 95% EtOH catalyzed by sodium hydroxide was reported to give solely the nitrone (no yield mentioned).¹⁸ The adduct of eq 4 was proposed as a common intermediate for the formation of the anil (eq 5) and of the nitrone (eqs 6 and 7).^{17,19}

As pointed out in the description of the voltammograms of Figures 1 and 2, the form of the reduction peak A of PhNO is modified in the presence of FlH_2 or InH_2 : the current drops quickly after reaching the peak potential. This shows that the concentration of PhNO at the surface of the electrode falls off rapidly due to the chain reaction between PhNO and AH^- (eqs 4 and 5) outside the diffusion layer, AH^- being generated in eq 2. At first, the current is used to reduce PhNO diffusing to the electrode. As soon as the chain reaction is initiated, the anion AH^- diffuses toward the bulk of the solution; it reacts with PhNO transforming it into $\text{PhN}=\text{A}$ and thus decreasing the amount of PhNO which can reach the electrode surface. In accordance with this, the ratio of the peak current A in the presence of $\text{AH}_2(\text{Ip}')$ to the peak current in the absence of $\text{AH}_2(\text{Ip})$ decreases as the scan rate (ν) is decreased: $\text{Ip}'/\text{Ip} = 0.74, 0.62, \text{ and } 0.48$ ($\text{AH}_2 = \text{FlH}_2$) and $\text{Ip}'/\text{Ip} = 0.67, 0.50, \text{ and } 0.31$ ($\text{AH}_2 = \text{InH}_2$) for $\nu = 100, 50, \text{ and } 20 \text{ mV s}^{-1}$, respectively, using a AH_2/PhNO molar ratio of 5.²⁰ Digital simulations of the cyclic voltammograms were performed,²¹ and the shape of the reduction peak of PhNO in the presence of FlH_2 and InH_2 (rapid decrease of current after the peak, resulting in sharp and symmetric peaks) was reproduced by assuming that reaction 4 is the rate-determining step and the equilibrium of reaction 2 is shifted to the right. The second-order rate constants determined for reaction 4 are $(5.7 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of fluorene and $(8.3 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of indene. The rate of disappearance of $[\text{PhNOH}]^-$ has a small effect on the peak current. We have also considered another catalytic mechanism in which the initiation steps are the formation of radical anion

(eq 1), its dimerization (eq 10), and the protonation of the dimer by AH_2 (eq 11), reactions 4, 12, and 9 being the propagation steps. However, the obtained rate constants were sweep-rate dependent, and, therefore, this mechanism had to be rejected.



Conclusion

The Erlich-Sachs reaction^{8,9} between PhNO and fluorene and PhNO and indene initiated by electrochemical reduction of PhNO in *n*- Bu_4NPF_6 -THF constitutes a new example of an electrochemically induced chain reaction. Good yields of anils and nitrones were obtained in a short reaction time and under very mild conditions. The formation of the anil is favored over that of the nitrone by lowering the temperature and/or increasing the proportion of proton donor. A 97% yield of the *N*-phenyl imine of fluorenone (anil 1) was obtained by carrying out the electrolysis at -30°C with a five molar excess of fluorene. The chemical and electrochemical data and digital simulations support a chain mechanism in which the nucleophilic addition of the conjugate base of the proton donor to PhNO is the rate-determining step and is reversible. The adduct formed in eq 4 has been suggested before as an intermediate.¹⁸ It can either give an anil by further protonation followed by rapid and irreversible elimination of water (eq 5) or add to another molecule of PhNO (eq 6) to yield, by rapid and irreversible fragmentation (eq 7), a nitrone and the conjugate base of phenylhydroxylamine which then adds to PhNO giving azoxybenzene (eq 9). At -30°C , the protonation of the primary adduct (eq 5) is faster than its addition to another molecule of PhNO (eq 6) whereas at room temperature, the two processes appear to have similar rates.

Experimental Section

Unless stated otherwise, chemicals were purchased from commercial supplies and used without further purification. DMF was distilled under reduced pressure from calcium hydride²² and stored under argon. THF was distilled from LiAlH_4 under argon and stored in the dark under argon: it was used within three days. Tetrabutylammonium hexafluorophosphate was recrystallized three times from 95% ethanol and dried over P_2O_5 at 100°C in vacuo: mp $161.5\text{--}162.5^\circ\text{C}$. Tetraethylammonium perchlorate was prepared according to a published procedure²³ and dried in vacuo at 60°C : mp $351\text{--}352^\circ\text{C}$. Melting points were determined with a Büchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument at 250 and 62.5 MHz, respectively. Mass spectra were taken on a VG Micromass ZAB-1F spectrometer.

9-Fluorenylideneaniline (1) was prepared according to a literature procedure:²⁴ mp $84\text{--}85^\circ\text{C}$ (lit.²⁴ mp $88\text{--}89^\circ\text{C}$). HRMS: calcd for $\text{C}_{19}\text{H}_{13}\text{N}$ m/z 255.1048, found (M^+) 255.1040.

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(20) The voltammograms of PhNO alone and PhNO in the presence of FlH_2 and InH_2 at various scan rates are provided in the supplementary material.

(21) The equations and method used for the digital simulations are given in the supplementary material.

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α,α -(Biphenyl-2,2'-diyl)-*N*-phenylnitronone (**2**) was prepared according to a literature procedure:²⁶ mp 190–192 °C (lit.²⁶ 194.5–196.5 °C). IR (CHCl₃): ν_{\max} 1600, 1540, 1485, 1450, 1340, 1258, 950, 690 cm⁻¹ (no band at 1650 cm⁻¹ as reported²⁶). HRMS: calcd for C₁₉H₁₃NO m/z 271.0998, found (M^+) 271.0997.

Electrochemical Equipment and Cells. The voltammetric analyses were carried out with a Princeton Applied Research (PAR) 273 potentiostat or a Tacussel UAP4 unit in a standard three-electrode cell using a saturated calomel reference electrode (SCE) or a silver pseudoreference electrode (SPRE)²³ ($E_{\text{SPRE}} = E_{\text{SCE}} + 0.37$ V). The auxiliary electrode was a platinum wire. The dropping mercury electrode characteristics were $m = 3$ mg s⁻¹ and $\tau = 0.5$ s. The platinum working electrode (surface area 3.1 mm²) was initially polished with alumina of decreasing particle size (down to 0.05 μm) and then on a Carbinet-600 paper (Buehler) before each use. For the polarograms, a three-electrode Tacussel Tipol polarograph was used. The controlled potential electrolyses were carried out with a PAR 173 potentiostat equipped with a PAR 379 coulometer. A two-compartment cylindrical cell with a fritted glass of medium porosity separating the upper compartment (anodic) from the lower (cathodic) one²⁸ was used with a platinum gauze (surface area 3 cm²) as working electrode, a platinum plate of similar surface area as auxiliary electrode, and a SPRE as reference electrode. An opening was provided to insert a microelectrode in the cathodic compartment for voltammetric analyses during and after the electrolyses. For voltammetric analyses and electrolyses, the solutions were deoxygenated by bubbling argon or nitrogen and an inert atmosphere was maintained in the cell throughout the experiments.

Controlled Potential Electrolysis Procedure and Product Isolation. For a typical controlled potential electroreduction and product isolation (Table I, entry 3), nitrosobenzene (232 mg, 2.16 mmol) and fluorene (1660 mg, 10 mmol) were added to the cathodic compartment of the cell containing 70 mL of a 0.15 M solution of *n*-Bu₄NPF₆ in THF. The anodic compartment was filled with the *n*-Bu₄NPF₆-THF solution. The potential was set at -1.50 V. The electrolysis was stopped after the current had dropped to 0.2 mA (a few minutes). The charge passed was 0.16 C (0.8 mmol of electrons per mol of PhNO). Water was added, and the mixture was extracted with ether (4 × 35 mL). The combined extracts were washed with water and then dried over MgSO₄. The solution was filtered and the solvent evaporated in vacuo. TLC analysis of the yellow residue showed the presence of fluorene, fluorenone (trace amount), anil 1, azoxybenzene, and nitronone 2 in order of increasing polarity. Flash chromatography on silica gel with hexane-ether (95:5) as eluent gave fluorene, anil 1 (29 mg, 57%), mp 82–84 °C, azoxybenzene (~2 mg, ~1%) identified by IR and VPC, and nitronone 2 (18 mg, 33%), mp 190–192 °C. Both anil 1 and nitronone 2 proved identical (IR, ¹H NMR, ¹³C NMR, and SM) to the authentic samples prepared above.

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For the electrolyses carried out at -30 °C, the cell was placed in a cooling bath (dry ice-bromobenzene).

Electroreduction of PhNO in the Presence of Indene. The electrolysis of 2 mmol of PhNO and 10 mmol of indene was carried out exactly as above and consumed 0.19 C (1 mmol of electrons per mol of PhNO) (Table I, entry 7). The residue after workup was dark brown. The TLC analysis showed the presence of indene, anil 3, azoxybenzene, and nitronone 4 in order of increasing polarity. Flash chromatographic separation gave indene which was not recovered, a fraction that gave a dark brown residue insoluble in ether after evaporating the solvent (16 mg), azoxybenzene (8 mg, 4%), and nitronone 4 (11 mg, 25%), mp 91 °C dec. IR (CHCl₃): ν_{\max} 1508, 1450, 1335, 1260 cm⁻¹. ¹H NMR (CDCl₃): δ 8.58 (t, m, H-2'), 7.7 (m, 4H, phenyl ring), 7.37–7.25 (m, 4H, indene ring), 6.72 (d, $J = 5.8$ Hz, H-2), 6.18 (d, $J = 5.8$ Hz, H-3). ¹³C NMR (CDCl₃): δ 236 (C1), 132 (C2), 130 (C3, C1'), 129.6, 129.2 (C9, C2', C4', C6'), 129 (C3', C5'), 128 (C4), 125, 124, 122, 121 (C5, C6, C7, C8) ppm. MS m/z 221 (M^+). HRMS calcd for C₁₅H₁₁NO m/z 221.0841, found 221.0835. The compound that decomposed to a dark brown residue was assumed to be anil 3 ($\geq 38\%$ yield) since it was less polar than azoxybenzene and had an R_f similar to that of anil 1.

Reaction of PhNO with Fluorene Initiated by Sodium Hydride. For a typical procedure (see Table II, entry 2), sodium hydride (80 mg of a 60% suspension in oil, 2 mmol) was introduced into a three-necked flask dried in an oven at 120 °C and flushed with argon. The hydride was washed with hexane; then THF (50 mL) was added. The mixture was bubbled with argon for 30 min, and fluorene (1665 mg, 10 mmol) in THF (10 mL) was added. After the solution was stirred for 4 h at room temperature (6 h at -30 °C), no more sodium hydride was present and the solution was yellow. Nitrosobenzene (225 mg, 2.09 mmol) in THF (10 mL) was added at once. The reaction was over after 15 min at room temperature (by VPC). The workup and chromatographic separation were carried out as described above for the controlled potential electrolyses to give azoxybenzene (20 mg, 10%), anil 1 (59 mg, 11%), and nitronone 2 (102 mg, 18%).

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Supplementary Material Available: Cyclic voltammograms of PhNO in the presence of fluorene and indene at various scan rates and equations and method used for the digital simulations (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.