Electrochemical Determination of Rate Constants and Product Yields for the Spontaneous Dediazoniation of *p*-Nitrobenzenediazonium Tetrafluoroborate in Acidic Aqueous Solution

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ABSTRACT: We have examined the kinetics and mechanisms of the dediazoniation of *p*-nitrobenzenediazonium tetrafluoroborate in acidic aqueous solutions by employing differential pulse polarography (DPP) and differential pulse voltammetry (DPV) on a glassy carbon electrode combined with the use of a coupling reaction to quench unreacted *p*-nitrobenzenediazonium ion. These electrochemical techniques show an effective sensitivity and selectivity for detecting arenediazonium ions and arenedediazoniation products under the appropriate experimental conditions (pH, solvent, electrolyte), which allows simultaneous monitoring of the rates of arenediazonium ion loss and product formation and determination of product yields. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 419–430, 2000

INTRODUCTION

Arenediazonium salts have been shown to be very important for both the dyestuff industry [1] and synthetic chemistry [2] and a substantial body of knowledge about their industrial aspects [3] and about their use in preparative chemistry is available [4]. The mechanism of arenediazonium reactions continue to be controversial because they vary dramatically with experimental conditions [5-8], which change the reaction pathway and the amounts of dediazoniation products.

Arenediazonium reactions are normally divided [6,9] into two groups (see Scheme I), those that occur

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Scheme I Possible classification of arenediazonium salts reactions, dediazoniations (1A) and addition (1B) and heterolytic (1C) and homolytic (1D) dediazoniation mechanisms.

at the arene ring (dediazoniation reactions, 1A) and those that occur at the terminal nitrogen of the diazonium group (nucleophilic addition, 1B). Addition reactions are the classical route to obtain azo dyes and pigments [1,5]. Dediazoniation reactions, 1A, occur with a wide variety of nucleophiles and they are believed to take place through two main mechanisms [6], heterolytic (1C), and homolytic (1D). Competition between or coexistence of the pathways may occur depending on the substituents of the aromatic ring [10,11] and experimental conditions such as pH [6], solvent [5,6], or even atmosphere [11] (O₂ or N₂). The homolytic mechanism shows [6,12] a wider variety of pathways compared to the heterolytic one and many of them are still not completely understood [6,12].

A large number of reducing agents can be used to

generate aryl radicals [5,6], but probably the most convenient source of free aryl radicals is the electrochemical reduction of arenediazonium salts [6,13-15] because they have been shown to be easily reducible species. Electrochemical reduction with metal electrodes such as Cu, Fe, Hg, and Ti has been used [14,15] to generate any radicals that act as initiators of polymerization [16]. When a arenediazonium ion acquires an electron [12,14,15], it forms a diazenyl radical that yields an aryl radical and N₂, as shown in Scheme II. Polarographic half-wave reduction potentials, $E_{1/2}$, for a number of arenediazonium salts have been measured in a variety of solvents [17-19]. $E_{1/2}$ for benzenediazonium tetrafluoroborate in sulfolane is +0.295 V vs SCE (saturated calomel electrode), increasing to +0.450 V with a *p*-NO₂ substituent or de-





creasing to +0.140 V measured for the *p*-methoxy benzenediazonium salt.

The reduction of a number of 4-substituted benzenediazonium tetrafluoroborates has also been studied in aqueous solution [15] by employing a dropping mercury electrode (DME). The results have some confusing features. Two polarographic waves are observed in potential regions of +0.05V to -0.02 V (vs Ag/AgCl), a potential where few organic compounds are electroactive [20], and around -0.97 V to -1.03V. Microcoulometry [14] at the DME shows that the two waves correspond to the uptake of one electron, vielding a diazenyl radical and four (overall) electrons, respectively, yielding phenylhydrazine [13], as shown in Scheme IIIA. At a specific pH [21,22], the diffusion currents are proportional to the arenediazonium salt concentration. Therefore, a DME electrode can be used to determine arenediazonium salts [17] both qualitatively and quantitatively by comparing the measured diffusion current with a calibration curve obtained from diffusion current-salt concentration profile.

As previously noted, the classical route to obtain azo dyes are addition reactions. Azo dyes have been well studied by modern electrochemical techniques [23-25], which can be employed to determine their contents in industrial products, such as food additives, or to monitor trace concentrations of them in the environment around industrial areas. Their reduction mechanisms have been described in detail [25] (Scheme IIIB).

A number of methods have been developed to monitor dediazoniations [26-28]; however, little attention has been paid to the use of electrochemical methods [6,14,15,17,32]. Here we examined the dediazoniation of *p*-nitrobenzenediazonium tetrafluoroborate, pNBD, in aqueous solution by employing differential pulse polarography (DPP) at a DME and differential pulse voltammetry (DPV) on glassy carbon electrode (GCE) combined with a recently reported method [28] for using coupling reagents to quench the dediazoniation process at convenient times (Scheme IV). The azo dye formed in the quenching step, which is proportional to the amount of unreacted arenediazonium salt, contains electroactive groups (-N=N- and $-NO_2$), and both homolytic and heterolytic pNBD dediazoniation products, that is, p-nitrophenol or p-nitrobenzene, are also electroactive. The net reduction reactions of these electroactive groups are showed in Scheme IIIB and IIIC. Thus, dediazoniation rate constants can be obtained electrochemically by monitoring directly arenediazonium ion loss, by monitoring dediazoniation product formation, and by monitoring azo dye formation.



Scheme III Electrochemical reduction processes: A) arenediazonium salts in acidic aqueous solution, B) azo group, and C) nitro group (the second step proceeds with aromatic compounds only in acidic solution).



pNBD

2N6S

6S2NpN

Scheme IV Representation of the coupling reaction that was employed to quench the *p*NBD dediazoniation between *p*NBD and 2N6S to give the azo dye 6S2N*p*N.

EXPERIMENTAL

Instrumentation

Differential pulse polarographic (DPP) and differential pulse voltammetric (DPV) measurements were obtained with a Metrohm E506 Polarecord, in conjunction with the cell systems described below. For DPP experiments, a 663 VA-Stand (Metrohm) equipped with a water-jacketed voltammetric cell was used. The multimode working electrode was used in the DME mode. The three-electrode system was attached to a glassy carbon rod (2 \times 65 mm) auxiliary electrode and a Ag/AgCl (3M KCl) reference electrode. For DPV experiments, a 10 mL cell [Model VC-2 glass vial, Bioanalytical Systems (BAS)] with a fitted top was used. The three-electrode system was: a glassy carbon disk (GCE) (Model MF-2012, BAS) as the working electrode, an Ag/AgCl (Model RE-5, BAS) as the reference electrode, and a platinum wire (Model MW-1032) as the auxiliary electrode. GCE electrodes were polished with a 0.4 μ m alumina slurry (Aldrich) and washed thoroughly and dried before use. A scan rate of 7.5 mVs⁻¹ was used for both DPP at the DME (drop time 0.4 s and pulse amplitude -80 mV) and DPV (pulse amplitude +80 mV) on GCE. Solutions used in polarographic measurements were bubbled with N₂ gas (99.999%) for at least 10 min and kept under a nitrogen atmosphere during the electrochemical runs. pH was measured using a previously calibrated Metrohm model 744 pH-meter.

All potentials given hereafter will be relative to the just-mentioned Ag/AgCl electrodes.

Materials

p-Nitrobenzenediazonium tetrafluoroborate, *p*NBD, was purchased from Aldrich (97%), and recrystallized twice with cold ether. To minimize possible decomposition of *p*NBD via the Schieman [9] reaction and by reactions with water vapor, it was stored in the dark in a dessicator at low temperature and recrystallized periodically. Other reagents were of the maximum purity available and were used without further purification. *p*-Nitrophenol (*p*NB-OH), nitrobenzene (*p*NB-H), and *p*-nitrochlorobenzene (*p*NB-Cl) were purchased from Aldrich; 2-naphthol-6-sulfonic acid, so-dium salt (2N6S), was from Pfaltz & Baüer. Other materials employed were prepared by using Milli-Q grade water ($\kappa = 1.2 \ \mu S \ cm^{-1}$).

The azo dye 6-sulfonate-2-naphthol-1-azo-*p*-nitrobenzene, 6S2N*p*N, was prepared *in situ* following a published procedure [28] by coupling *p*NBD with 2N6S in solution containing TRIS buffer to give, after mixing, final 2N6S concentrations of about 7-fold excess over that of *p*NBD and a pH about 9.3. A linear correlation (cc > 0.995) not shown, between the amount of azo dye formed and the amount of *p*NBD employed was obtained.

Methods

Kinetic data were obtained by employing both DPP and DPV techniques. Observed rate constants were calculated by fitting the peak current, ip, to the integrated first-order equation 1 using a nonlinear leastsquares method provided by a commercial computer program, where M is the peak current of the solution component that is monitored.

$$Ln \, \frac{(M_{\infty} - M_t)}{(M_{\infty} - M_0)} = -k_{\rm obs} t \tag{1}$$

Dediazoniation experiments were carried out at 60°C at two HCl concentrations, 0.01 M and 1.0 M, with pNBD as limiting reagent. Following a published procedure [28], the aliquots of dediazoniation reaction were quenched periodically at convenient times with a stock quenching solution, which was prepared by dissolving 2N6S in a solution containing TRIS buffer ([TRIS] = 0.05 M) to give final 2N6S concentrations about 7-fold excess over that of arenediazonium salt and a pH of about 9.3. This pH was chosen to maximize the rate of 6S2NpN azo dye formation [6,29,30] because naphthoxide ions couple much more rapidly than their protonated forms [8,31]. We have found that the methodology still works at pH = 12.2, thus the competing diazotate formation with OH⁻ is still insignificant [32]. The selected pH and buffer provide the appropriate experimental conditions to achieve a high selectivity (different peak potentials for each dediazoniation product) and satisfactory sensitivity (favorable signal/noise ratio to achieve the lowest limit of detection) from the polarograms of all products formed during dediazoniation.

Product yields, *Y*, were estimated from the ratio of the final product concentration, *P*, and the initial arenediazonium salt concentration, $(\%)Y = 100 \ [P]/[pNBD]$. Final product concentrations were obtained from the peak current values at infinite time (22 h), that is, when dediazonation is essentially over (98%), employing the appropriate calibration curve (*vide in-fra*).

Preliminary DPP and DPV Experiments

Residual currents in both DPP and DPV experiments were obtained by using acidic (HCl) TRIS-2N6S solutions.

Polarograms of the 6S2NpN azo dye in a TRIS/ 2N6S buffer solution show two well-defined peaks (Fig. 1, peaks I and II) which are attributed to the reduction of the azo group to the hydrazo intermediate and to the resulting anilines (Scheme IIIB), peak I at -0.415 V, in agreement with published results for other azo dyes [25], and to the reduction of the NO₂ group to hydroxyaniline intermediate, peak II at -0.542 V (first step in Scheme IIIC). Linear calibra-



Figure 1 DP polarograms of *p*NB-OH (2.86×10^{-5} M) (dashed line) and 6S2NpN azo dye (2.71×10^{-5} M) (full line) in TRIS/2N6S buffer (pH = 9.3). Inset: Cathodic peak currents vs concentration plots for *p*NB-OH (\blacktriangle) and for

6S2NpN azo dye, peak I (\bigcirc) and peak II (\bigcirc).

tion curves (cc > 0.999) for converting peak heights into concentrations were obtained by employing solutions of increasing 6S2NpN concentration up to $[6S2NpN] = 80\mu$ M (inset in Fig. 1). The equations obtained were: ip(μ A) = (-0.040 ± 0.006) + (9.8 ± 0.1) × 10^{-3} [6S2NpN] (μ M) (azo group reduction, peak I) and ip(μ A) = (-0.023 ± 0.006) + (1.02 ± 0.01) × 10^{-2} [6S2NpN] (μ M) (nitro group reduction, peak II).

Polarograms of *p*NBD in aqueous acid (HCl 0.01 M) (not shown) contain three well-defined peaks and one shoulder. Two peaks that appear at -0.012 V (slightly overlapped with the peak of nitro reduction) and -0.474 V are attributed to the reduction of the arenediazonium ion to phenylhydrazine, Ar—NH— NH₂ (Scheme IIIA) in agreement with reported results for other arenediazonium salts [12,14,15,32]. The first peak of the diazo reduction is independent of pH up to pH = 5 and, at higher pH, a peak potential shift of

38.4 mV per pH unit is observed up to pH 8 (this change in the peak potential/pH slope is probably related to the behavior of pNBD as a Lewis acid [6]). The peak at -0.089 V and the shoulder at -0.262 V in the polarogram are attributed to the reduction of -NO₂ group to corresponding aniline group [23], Ar-NH₂. A peak potential shift of 58.6 mV per unit pH is observed up to pH 10. This value is in agreement with the classical irreversible reduction of the nitro group following a four-electron/four-proton process [23,24] (Scheme IIIC-first step). A linear relationship between ip at -0.089 V (pH = 2.0) and concentration for $[pNBD] = 3.04 \times 10^{-4}$ M with the equation: $ip(\mu A) = (0.080 \pm 0.009) + (5.45 \pm 0.01) \times 10^{-3}$ [pNBD] (μM) (nitro and diazonio groups reduction) was found.

DP polarograms for a number of possible dediazoniation products, *p*NB-OH, *p*NB-Cl, and *p*NB-H, were also obtained (Figs. 1 and 2). Figure 1 (peak III at -0.720 V) shows the *p*-nitrophenol DP polarogram in TRIS/2N6S buffer solution. Its cathodic peak current increases linearly (cc > 0.999) with [*p*NB-OH] up to [*p*NB-OH] = 1.2×10^{-4} M (inset in Fig. 1), and the equation obtained for converting peak heights into concentrations was ip(μ A) = (0.274 ± 0.003) + (1.55 ± 0.00) $\times 10^{-2}$ [*p*NB-OH] (μ M) (nitro group reduction).

Preliminary DPP experiments indicate that the presence of any one of the dediazoniation products, pNB-OH, pNB-Cl, and pNB-H, leads to detectable shifts in the peak potential values of the cathodic peaks of the other ones. Figure 2 (full line-peak "a") shows the cathodic reduction peak obtained for p-nitrophenol dissolved in a TRIS buffer solution. Upon addition of an aliquot of a *p*-NBCl solution, three reduction peaks are obtained (Fig. 2, dotted line); the peak labeled "a", attributed to pNB-OH, was shifted to -0.772 V and peaks " b_1 " -0.544 V) and the shoulder " b_2 " -1.060 V) are associated with the reduction of pNB-Cl. When pNB-H is added to the latter solution, that is, when the three dediazoniation products investigated are present simultaneously in solution, an additional cathodic peak due to the reduction of the nitro group of pNB-H (peak "c" at -0.642 V) is observed in the polarogram (Fig. 2, dashed line), and again shifts in the peak potentials of the other products are observed. Therefore, the peak potential values can provide us with selective information about the nature of the dediazoniation products present in solution.

Because both 6S2NpN and pNB-OH contain electro-oxidable groups -OH), DPV voltammograms were obtained for these products. Figure 3 shows the anodic peak at +1.130 V due to the oxidation of the

hydroxy group of *p*NB-OH to give *p*-nitrobenzoquinone. The anodic peak of the 6S2N*p*N azo dye appears at a peak potential value lower than 0.800 V (Fig. 3). Linear (cc > 0.999) calibration curves for converting peak heights into concentrations up to [*p*NB-OH] = 1.2×10^{-4} were obtained (inset in Fig. 3), yielding ip(μ A) = (0.323 ± 0.108) + (6.93 ± 0.15) × 10⁻² [*p*NB-OH] (μ M). The significant deviation from linearity at higher *p*NB-OH concentrations is attributed to electrode fouling by oxidation products and in some cases to polymerization/adsorption phenomena on the electrode surface [20,32,33].

RESULTS

Polargraphic Kinetic Data

DPP observed rate constants, k_{obs} , for disappearance of the arenediazonium ion and formation of dediazon-



Figure 2 DP polarograms of solutions of *p*NB-OH (full line), *p*NB-OH + *p*NB-Cl (dotted line) and *p*NB-OH + *p*NB-Cl + *p*NB-H (dashed line) in TRIS buffer (pH = 9.3). [*p*NB-OH] = 1.2×10^{-5} M, [*p*NB-Cl] = 5.4×10^{-5} M and [*p*NB-H] = 8.2×10^{-5} M. See text for full description of polarograms.



Figure 3 Anodic peak current vs. concentration plot for pNB-OH at GCE in TRIS/2N6S buffer (pH = 9.3) and the corresponding DP voltammograms.

iation products in 0.01 M HCl aqueous solutions were obtained from polarograms of quenched solutions. Figure 4 shows representative polarograms obtained at different times. Three peaks are observed with an excellent resolution. Heights of peaks I (at -0.415 V) and II (at -0.542 V), which are associated with the reduction of the azo and nitro groups of the 6S2N*p*N azo dye, respectively, decrease with time while the growth of peak III (at -0.744 V) is due to reduction of the nitro group of *p*NB-OH. No peaks attributable to *p*NB-Cl or *p*NB-H were detected.

Figure 5, chosen as representative, shows the variation of the peak current, ip, of peaks I (5A) and II (5B) with time and their corresponding first-order plots. The rate constants for dediazoniation, $k_{\rm obs} = 3.39 \times 10^{-5} \, {\rm s}^{-1}$ (peak I) and $k_{\rm obs} = 3.39 \times 10^{-5} \, {\rm s}^{-1}$ (peak I) and $k_{\rm obs} = 3.39 \times 10^{-5} \, {\rm s}^{-1}$ (peak II) in 0.01 M HCl at 60°C, are in excellent agreement with literature values obtained employing other techniques (Table I). $k_{\rm obs}$ values for formation of *p*NB-

OH were also obtained from the variation of peak current due to the reduction of its nitro group (peak III at -0.744 V, Fig. 6). A k_{obs} value 3.18×10^{-5} s⁻¹ was obtained, which is equal, within experimental error, to those obtained following azo dye disappearance (Table I).

Figure 7 shows the polarograms of quenched solutions obtained at different times when dediazoniation is carried out in 1 M HCl. Peaks I and III are associated with the reduction of the azo group of the 6S2NpN azo dye and the reduction of the NO₂ group of the pNB-OH. Peak II, associated with the reduction of the NO₂ group of the 6S2NpN azo dye, overlaps with that of *p*NB-Cl; therefore, peak II is not as suitable as the others to obtain k_{obs} values. Consequently, k_{obs} values were obtained employing only data from peaks I and III (Fig. 8). Average k_{obs} values, $3.49 \times 10^{-5} \text{ s}^{-1}$ (peak I) and $3.03 \times 10^{-5} \text{ s}^{-1}$ (peak III) were obtained, which are equal, within experimental error, to those obtained at 0.01 M HCl (Table I).



Figure 4 DP polarograms in TRIS/2N6S buffer (pH = 9.3) as a function of time for disappearance of 6S2N*p*N (peaks I and II) and for formation of *p*NB-OH (peak III). [*p*NBD] = 1.81×10^{-4} M, [HCl] = 0.01 M, *T* = 60°C.



Figure 5 Variation of 6S2N*p*N peak currents with time (\bigcirc) and ln plot (\bullet). (A) peak I and (B) peak II in Figure 4. [*p*NBD] = 1.81 × 10⁻⁴ M, [HCl] = 0.01 M, *T* = 60°C.

Voltammetric Kinetic Data

DPV kinetic data were obtained by monitoring pNB-OH formation following the oxidation of its hydroxy group. Figure 9, chosen as representative, shows the

Methods	HCl = 1.0 M			HCl = 0.01 M	
	$10^5 k_{\rm obs} ({\rm s}^{-1})$	Y_{pNB-OH}	$\mathbf{Y}_{p\mathrm{NB-Cl}}$	$10^5 k_{\rm obs} ({\rm s}^{-1})$	Y_{pNB-OH}
DPP (peak I) ^a	3.49			3.39	
DPP (peak II) ^a				3.39	
DPP (peak III) ^b	3.03	82	10	3.18	92
DPV ^b				3.18	93
UV-VIS ^{a,c}	3.47			3.37	
UV-VIS ^{b,c}	3.67			3.68	
HPLC ^c	3.34	83	12.5	3.42	94
N ₂ Evolution ^d				3.30	
Pressure changes ^c	3.22				

Table I

variation in peak heights, ip (μ A), for the anodic peak of *p*-nitrophenol with time and the corresponding ln plot. From the slope of the ln plots, an average k_{obs} value of 3.18×10^{-5} s⁻¹ was obtained, which is equal, within the experimental error, with those obtained by DPP (Table I).

Estimation of Product Yields

DPP and DPV experiments show that the major dediazoniation product is *p*NB-OH. Yields of *p*NB-OH can be estimated from the corresponding peak current values at infinite time, that is, when dediazoniation is essentially over (98%). In 0.01 M HCl, conversion to products is almost quantitative, with *p*NB-OH (Y =93), as major product. Upon increasing Cl⁻ concentration, *p*NB-OH yield decreases with a concomitant increase in *p*NB-Cl; *Y*(*p*NB-OH) = 82 and *Y*(*p*NB-Cl) = 10 at 1.0 M HCl. These results agree with those reported for *p*NBD [34] determined by HPLC (Table I).

DISCUSSION

The stability of arenediazonium ions depends strongly on both the position and nature of the substituents on the aromatic ring [6,35]. Most meta- and para-substituents, including electron-withdrawing (like p-NO₂) and electron-donating groups (like —CH₃) show a marked stabilizing effect. Consequently, all dediazoniation experiments were carried out at $T = 60^{\circ}$ C to speed the reaction [34]. Direct DPP monitoring of *p*NBD loss by using any of its reduction peaks was not possible. At the temperature employed, large variations in the dropping time were observed, probably

^a Azo dye formation

 $^{\rm b}$ pNB-OH formation

^c Values from ref. 34 and references therein

^d Value from ref. 36



Figure 6 Variation of peak current with time for *p*NB-OH formation (\bigcirc) and ln plot (\bigcirc). [*p*NBD] = 1.81 × 10⁻⁴ M, [HCl] = 0.01 M, *T* = 60°C.

due to high Hg volatility and convection currents in the electrode. Lower temperatures allow direct monitoring of arenediazonium ion loss by DPP [32], but slow *p*NBD dediazoniation significantly [36] ($E_A = 124 \text{ kJ mol}^{-1}$).

DPP experiments show that only two dediazoniation products are formed, pNB-OH and pNB-Cl. No extraneous peaks with significant heights that might be associated with reduction products like p-nitrobenzene were detected, consistent with the heterolytic mechanism [6]. Kinetic DPP and DPV data indicate that the rate of formation of pNB-OH is the same as that of loss of the arenediazonium ion, and that both observed rate constants are virtually unaffected by changes in the acidity or in Cl⁻ concentration. These results are consistent with the $D_N + A_N$ mechanism, that is, formation of a highly reactive aryl cation that shows a very low selectivity toward nucleophiles like Cl⁻ compared with water and are in agreement with published results [34,36] for pNBD dediazoniation obtained employing other techniques (Table I).

The selectivity of the arenediazonium ion toward Cl^{-} and H_2O is defined by equation 2:

$$S_{\rm W}^{\rm Cl} = \frac{(\% Y_{\rm ArCl})[{\rm H_2O}]}{(\% Y_{\rm ArOH})[{\rm Cl^-}]}$$
(2)

As noted before, product yields can be estimated from the peak current values at infinite time, i.e., when dediazoniation is essentially over (98%) and a selec-



Figure 7 DP polarograms in TRIS/2N6S buffer (pH = 9.3), for disappearance of 6S2NpN (peaks I and II) and formation of *p*NB-OH (peak III) at increasingly longer intervals of time.



Figure 8 (A) Variation of peak current (\bigcirc) of 6S2N*p*N (peak I in Fig. 7) with time and ln plot (\bigcirc). (B) Variation of peak current (\bigcirc) for formation of *p*NB-OH (peak III in Fig. 7) with time and ln plot (\bigcirc). Experimental conditions: [*p*NBD] = 1.81×10^{-4} M, [HCl] = 1.0 M, $T = 60^{\circ}$ C.

tivity value of $S_{\rm w}^{\rm Cl} = 6.6$ ([H₂O] = 54.5 M in 1.0 M NaCl [37]) is obtained. This low value is comparable with those reported for other arenediazonium ions [27,28,35], which range from 2 to 10 and are ionic strength dependent, and with that obtained by HPLC under similar experimental conditions [34], $S_{\rm w}^{\rm Cl} = 5.4$. The difference in the selectivity values obtained probably stems from the slight variations in the experimental conditions and from variations in the selectivity with ionic strength [27].

Our results show that dediazoniations can be monitored by electrochemical methods. Differential pulse techniques provide an effective sensitivity useful for trace measurements of electroactive species, at lower concentrations of products or derivative products, improving detection limits when compared with those employing UV-VIS detection. Furthermore, electrochemical measurements are very selective because a substantial number of both cathodic and anodic peaks can be used to obtain dediazoniation rate constants and to get estimates of product yields. Peak potential values also provide information about the nature of the dediazoniation products present in solution, providing information similar to that obtained by chromatographic techniques with UV-VIS detection [34,35,38]. As a result, three possible dediazoniation products and the azo dye formed can be measured simultaneously at concentrations levels down to 5×10^{-7} – $1 \times$ 10^{-8} M, using relatively inexpensive instrumentation. Application of all these techniques to dediazoniations in other solvents, where both heterolytic and homo-



Figure 9 Typical plot for the formation of *p*NB-OH obtained by measuring the variation of its anodic peak current with time (\triangle) and ln plot (\triangle). [*p*NBD] = 1.81 × 10⁻⁴ M, [HCl] = 0.01 M, *T* = 60°C.

lytic mechanisms can coexist, and metal catalyzed dediazoniations is in progress in our lab.

CONCLUSIONS

We have shown that electrochemical methods can be employed to monitor dediazoniation reactions, including simultaneous estimations of dediazoniation product yields and the rate constants for product formation and arenediazonium ion loss. Our results are consistent with the $D_N + A_N$ heterolytic mechanism, that is, ratedetermining formation of an aryl cation that reacts immediately with available nucleophiles, because of the absence of products associated with the radical pathway and because the rate of product formation is the same as that for pNBD loss and both are independent of nucleophile concentration. The low selectivity of the reaction toward Cl- vs H₂O is also consistent with the formation of a highly reactive aryl cation. The measured rate constants and product yields are in agreement with those obtained by other methods.

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