JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 130–140 (1999)

Rates and pH-dependent product distributions of the $CuCl_2$-catalyzed dediazoniation of *p*-nitrobenzenediazonium tetrafluoroborate in aqueous acid

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Received 11 March 1998; revised 14 May 1998; accepted 19 May 1998

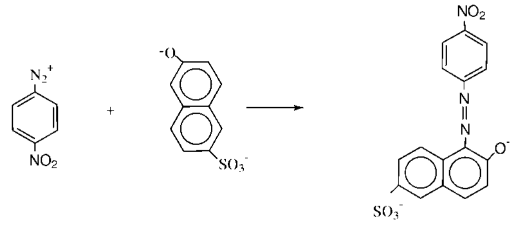
ABSTRACT: The rates of formation and yields of products from the dediazoniation of *p*-nitrobenzenediazonium tetrafluoroborate (PNBD) in aqueous solutions over a range of HCl, NaCl and $CuCl_2$ concentrations at 60 °C were examined. Two main products were observed: *p*-nitrophenol (ArOH) and *p*-nitrochlorobenzene (ArCl). Trace amounts of nitrobenzene (ArH) and *p*-nitrofluorobenzene (ArF) were detected. Added $CuCl_2$ speeds the reaction and both the rate of dediazoniation and ArOH yield (unlike ArCl) are very sensitive to pH. The results are completely consistent with the heterolytic dediazoniation mechanism, i.e. rate-determining formation of a highly reactive aryl cation followed by competitive formation of dediazoniation products. PNBD kinetics are first order (with respect to PNBD) in the absence of and presence of $CuCl_2$, except at low acidity and in the presence of low to moderate $CuCl_2$ concentrations. The non-first-order kinetics are attributed to a competing reaction between PNBD and the ArOH product. The results suggest a simple method for preparing halobenzenes in high yield. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: *p*-nitrobenzenediazonium tetrafluoroborate; catalytic dediazoniation; reaction rate; product distribution

INTRODUCTION

Aromatic diazonium compounds became industrially important[1] after Griess discovered the azo-coupling reaction, i.e. replacement of an electrofugic atom or group at a nucleophilic carbon atom by an arenediazonium ion. Scheme 1 shows the coupling reaction between *p*-nitrobenzenediazonium ion (PNBD) and 2-naphthol-6-sulfonic acid (sodium salt),[1] which was used to trap unreacted PNBD in the experiments described here. Aromatic diazonium salts are also as important in preparative and synthetic chemistry.[2–4]

Dediazoniations occur with a wide variety of nucleophiles[3] via both spontaneous, e.g. Griess (Nu = Cl^-, Br^-, I^-) and Schiemann (Nu = F^-) reactions, and by catalyzed reactions, e.g. the Sandmeyer reaction (Nu = Cl^-, Br^-, CN^-, etc.). In all these reactions aryl cation or radical intermediates may be involved, depending on the structure of the arenediazonium ion and experimental conditions such as solvent and nucleophiles [Scheme 2A and B]. In aqueous acid, in the dark, dediazoniation is believed to proceed via rate-determining loss of nitrogen to generate a highly reactive aryl cation that reacts with low selectivity with available nucleophiles [Scheme 2A]. Evidence for aryl cation intermediates in dediazoniations have been reported by numerous workers.[5–12] Swain *et al.*[9,10] suggested that the aryl cation is formed reversibly and a molecular orbital study of the benzenediazonium cation in water is consistent with the formation of stable



PNBD 2N6S AZO DYE

Scheme 1. Coupling reaction between *p*-nitrobenzenediazonium ion (PNBD) and 2-naphthol-6-sulfonic acid (sodium salt)

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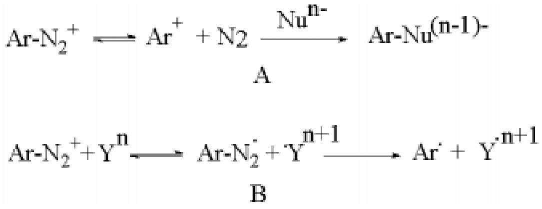
Contract/grant sponsor: Spanish Ministry of Education (DGICYT); *Contract/grant number:* PB94-0741.
Contract/grant sponsor: Xunta de Galicia; *Contract/grant number:* XUGA 38305A94.
Contract/grant sponsor: University of Vigo.

CCC 0894–3230/99/020130–11 $17.50

molecule–ion pairs.[11] Bergstrom *et al.*[12] concluded that molecular nitrogen reacts reversibly with aryl cation intermediate.

Arenediazonium salts are believed to undergo homolytic clevage to produce aryl radicals in the presence of certain electron donors, e.g. Cu(I).[13] In non-aqueous solvents,[3,4] products associated with free radicals are also observed, especially when electron-withdrawing groups are attached to the arenediazonium ion [Scheme 2B]. Evidence for the involvement of free radicals in dediazoniations has been obtained primarily by product analyses (primarily by gas chromatography–mass spectrometry) and from EPR measurements.[13–15]



Scheme 2. Dediazoniation mechanisms: (A) heterolytic mechanism; (B) homolytic mechanism

Sandmeyer[16] first reported enhanced yields of haloarenes on addition of Cu(I) salts. Since then, catalysis by copper metal, Cu(II) and other metal salts has been reported.[13] Galli[17] pointed out that good yields of chlorobenzene are obtained by adding Cu(II) (as nitrate) in the presence of NaCl and stimulants such as $SnCl_2$, but that Cu(II) is ineffective by itself. Later investigations by Galli[13] and Hanson *et al.*[14] suggested that the copper salt in the Sandmeyer reaction has a dual role, first as an electron transfer reagent and second as a ligand transfer oxidant. However, initiators such as ascorbic acid[13,] *p*-benzohydroquinone[18] or metal halides[17] with suitable half-wave reduction potentials [e.g. Sn(II), Cu(I) or Fe(II)] must be present to generate aryl radicals. Reductive fragmentation of arenediazonium salts has also been shown to occur in the presence of catechol with intentionally added metal ions such as Cu^{2+}.[14] The primary function of catechol is to reduce the metal ion, which then reacts with the ArN_2^+, but the possibility that catechol can directly reduce the ArN_2^+ was not considered, as already pointed out by Reszka and Chignell.[19]

Few studies involving arenediazonium salts and $CuCl_2$ alone (i.e. without initiators or ligand transfer agents) in water have been reported. Zollinger[3] did not mention the use of $CuCl_2$, without reductants or without ligand transfer agents, to obtain halo-dediazoniation or hydro-dediazoniation products. There is also some controversy about the kinetic behavior of *p*-nitrobenzenediazonium ion (PNBD). Lewis and Hinds[20] detected non-first-order kinetics in water, which they ascribed to a second-order reaction with a nucleophilic solute (Br). Maskill and McCrudden[21] found in some experiments that the rate and mechanism of solvolysis of PNBD in TFE–H_2O mixtures is not cleanly first order. However, in earlier reports, the observation of non-first-order kinetics was not mentioned.[22–24]

To clarify this problem, we investigated the kinetics and mechanism of the PNBD dediazoniation reaction in aqueous acidic solution in the presence and absence of $CuCl_2$ but without added reductant or ligand transfer agent. Kinetics were studied both spectrophotometrically (UV–visible) and by quenching the dediazoniation reaction with a suitable coupling agent at periodic time intervals and measuring the product yields.[25] The quenching method allows the simultaneous determination of the yields of all dediazoniation products, the rate constants for their formation and, indirectly, the rate constant of the disappearance of arenediazonium ion.

EXPERIMENTAL

Instrumentation. Absorption spectra were measured and some kinetic experiments were performed using Beckman DU-640 and Perkin-Elmer 559A spectrophotometers equipped with thermostated cell carriers attached to computers for data storage. Product analyses were carried out on a Waters high-performance liquid chromatographic (HPLC) system, which included a model 560 pump, a Model 717 automatic injector, a Model 486 UV–visible detector and a computer for data storage, and on a Perkin-Elmer HPLC system, which included a Model 410 quaternary pump, a Model ISS 200 LC autosampler, a Model LC-235 diode-array detector and a computer for data storage. Products were separated by using a Microsorb-MV C-18 (Rainin) reversed-phase column (25 cm × 4.6 mm i.d., particle size 5 μm) with a mobile phase of MeOH–H_2O (65:35, v/v) containing 10^{-4} M HCl. The injection volume was 25 μl in all runs and the UV detector was set at 220 or 250 nm. pH was measured by using previously calibrated Metrohm Model 713 and Corning Model 130 pH-meters. ^1H NMR spectra were obtained on a Varian VXR 200 spectrometer.

Materials. Reagents were of the maximum purity available and were used without further purification. *p*-Nitrophenol (ArOH), *p*-nitrochlorobenzene (ArCl), *p*-nitrofluorobenzene (ArF), *p*-nitrobenzene (ArH), copper(II) chloride (99.999%) and the reagents used in the preparation of PNBD (see below) were purchased from Aldrich. 2-Naphthol-6-sulfonic acid, sodium salt (2N6S) was purchased from Pfaltz & Bauer. Other materials employed were obtained from Fisher or Riedel-de Haën. All solutions were prepared by using Milli-Q grade water (millipore).

PNBD was prepared as its tetrafluoroborate salt under non-aqueous conditions[26] and stored in the dark at low temperature to minimize its decomposition. The UV–visible spectrum of 1.0×10^{-4} M PNBD in 3.0×10^{-3} M

Table 1. Values of slopes, intercepts, correlation coefficients (r) and typical retention times (t_R) for converting peak areas into concentrations obtained by linear least-squares fits[a]

ArX	10^{-9} slope	10^{-4} intercept	r	t_R (min)
ArOH	5.00 ± 0.02^b	2.0 ± 3.0^b	0.999_6	5.3
	11.97 ± 0.03^c	9.2 ± 9.4^c	0.999_4	
ArF	3.20 ± 0.01^b	-4.0 ± 3.0^b	0.999_7	7.7
ArH	2.60 ± 0.01^b	0.1 ± 4.0^b	0.999_9	8.6
	7.18 ± 0.06^c	5.0 ± 3.7^c	0.999_1	
ArCl	5.70 ± 0.02^b	-2.0 ± 3.0^b	0.999_7	11.3
	11.70 ± 0.01^c	4.8 ± 2.2^c	0.998_9	

[a] Products were dissolved in 50% (v/v) MeOH–H_2O containing 1.0 M NaCl and 0.01 M HCl. The highest concentrations were about 1×10^{-4} M or sufficient to ensure that the peak areas were converted to concentrations by interpolation.
[b] $\lambda = 220$ nm.
[c] $\lambda = 250$ nm.

HCl solution shows two broad bands, the main one centered at 258 nm and a shoulder at 310 nm, consistent with literature results.[20] The Beer's law plot up to 9.3×10^{-4} M PNBD in 3.36×10^{-4} M HCl is linear (correlation coefficient = 0.999) yielding $\varepsilon_{258} = 16400$ M^{-1} cm^{-1}, in agreement with the literature value.[20] The ^{1}H NMR spectrum of PNBD in CD_3CN at 25 °C is a pair of doublets of equal area centered at δ 8.72 ppm ($j = 5$ Hz) and δ 8.86 ppm ($j = 5$ Hz).

Methods. As noted above, kinetic data were obtained both spectrophotometrically and chromatographically. Observed rate constants were obtained by fitting absorbance–time or concentration–time data to the integrated first–order equation

$$\ln(M_t - M_\infty) = \ln(M_0 - M_\infty) - k_0 t \qquad (1)$$

using a commercial non-linear least-squares method, where M is the measured magnitude of the absorbance or HPLC peak area. All measurements were made at 60 ± 0.1 °C with PNBD as the limiting reagent.

Spectrophotometric kinetic data were obtained by following ArOH formation at 350 nm to minimize interferences primarily from chlorocuprate(II) complexes. Stock standard solutions were prepared by dissolving the appropriate amount of PNBD in aqueous HCl (to minimize diazotate formation) to give final concentrations of about 1×10^{-4} M and [HCl] = 3.6×10^{-3} M. The stock standard solutions were generally used immediately or stored in an ice-bath to minimize decomposition until needed, but for not more than 10 h.

Calibration graphs for converting HPLC peak areas into concentrations were obtained simultaneously for all dediazoniation products, ArOH, ArCl, ArH and ArF, by using commercial samples dissolved in solutions of similar composition to those used in the HPLC analysis of dediazoniation products (see below). Table 1 lists the slopes and intercepts obtained by linear least-squares fits for each product and their typical retention times under the chromatographic conditions used.

Percentage yields of each dediazoniation product were obtained from the dediazoniation product concentration, [analyte], and the initial PNBD (by weight), using the equation

$$Y = 100[\text{analyte}]/[\text{PNBD}] \qquad (2)$$

(Note that hereafter percentage yield will be shortened to 'yield' and represented by Y in figures and equations.)

Chromatographic kinetic data for all dediazoniation products were obtained by using an established methodology,[25] i.e. by quenching the dediazoniation reaction at convenient time intervals with an aliquot of a stock standard quenching solution. This solution was prepared by dissolving 2-naphthol-6-sulfonic acid sodium salt (2N6S) in NaOH and acetic acid–sodium acetate buffer to give final concentrations of 0.01 M 2N6S, 0.1 M NaOH, 0.035 M AcOH and 0.007 M NaOAc. After addition of the

Table 2. Effects of added HCl and NaCl on k_0 for dediazoniation of PNBD at 60 °C[a], $\lambda = 350$ nm

10^4[PNBD](M)	[HCl](M)	[NaCl](M)	$10^5\ k_0(s^{-1})$
1.30	0.02	—	3.68
1.30	0.10	—	3.67
1.30	0.20	—	3.56
1.30	0.30	—	3.54
1.30	0.40	—	3.58
1.30	0.50	—	3.64
1.30	0.70	—	3.67
1.30	0.90	—	3.83
1.30	1.00	—	3.67
1.30	1.20	—	3.74
1.30	0.02	—	3.58
1.30	0.02	0.10	3.67
1.30	0.02	0.20	3.53
1.30	0.02	0.30	3.71
1.30	0.02	0.40	3.58
1.30	0.02	0.50	3.64
1.30	0.02	0.60	3.54
1.30	0.02	0.70	3.74
1.30	0.02	0.83	3.40
1.30	0.02	1.00	3.58
1.30	0.02	1.10	3.56

[a] ArOH formation was followed spectrophotometrically at 350 nm for 3–4 half-lives with correlation coefficients ≥0.999.

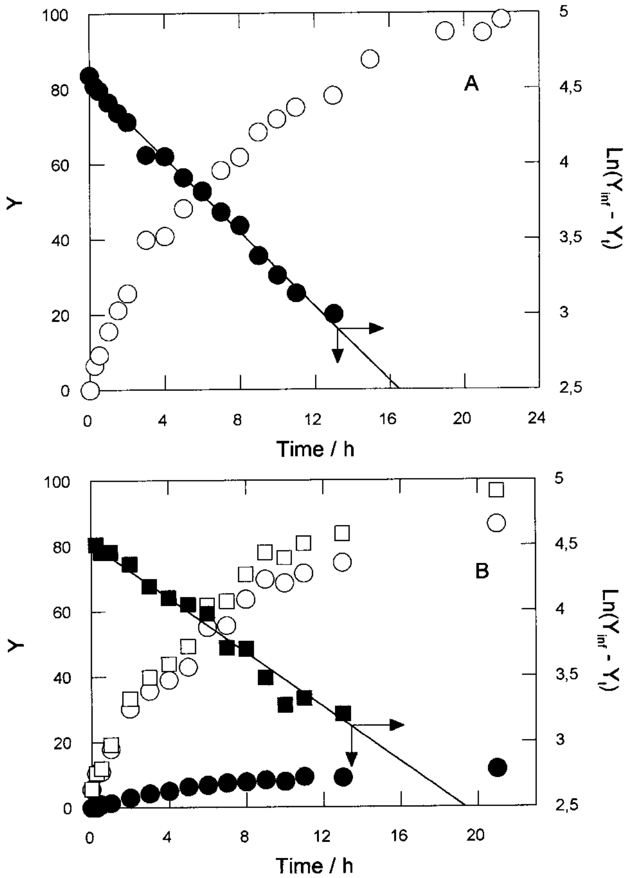


Figure 1. Variation of product yield with time and first-order plot for ArOH formation obtained from quenching experiments. (A) ○, ArOH; ●, logarithmic plot. $T = 60\,°C$; [PNBD] = 1.64×10^{-4} M; [HCl] = 0.01 M. (B) ○, ArOH; ●, ArCl; □, total; ■ logarithmic plot of ArOH. $T = 60\,°C$; [PNBD] = 1.64×10^{-4} M; [HCl] = 1.0 M

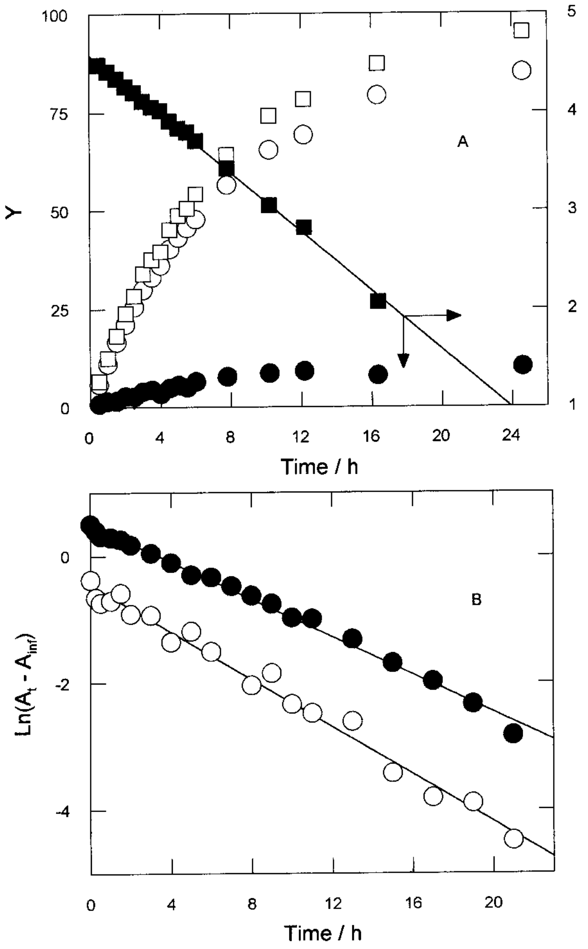


Figure 2. (A) Variations in product yields obtained from quenching experiments (○, ArOH; ●, ArCl; □, total) with time and logarithmic plot for ArOH formation (■). $T = 60\,°C$; [PNBD] = 1.0×10^{-4} M; [HCl] = 0.01 M; [NaCl] = 1.0 M. (B) Typical plots of $\ln(A_t - A_\infty)$ versus time for formation of the azo dye. $T = 60\,°C$; [PNBD] = 1.64×10^{-4} M; ●, [HCl] = 0.01 M; ○, [HCl] = 1.0 M

quenching solution, the final 2N6S concentration was in about a 10-fold excess over that of the arenediazonium salt and the final pH was 4.5–5.0. After dediazoniation was complete, the solutions were cooled to room temperature and diluted with MeOH to ensure that the ArOH and particularly ArCl, which has a limited solubility in water, were completely dissolved. Aliquots of these solutions were transferred to HPLC vials and analyzed in triplicate. The relative standard deviation of the peak areas was less than 2%. Details about the protocol have been published.[25]

Control experiments show that pH ≈ 4.5 is the optimum value for ther coupling reactions under these conditions. The coupling rates change dramatically with pH because naphthoxide ions are much more reactive than their parent naphthols,[1,3,4] but as the pH increases, Cu(II) hydroxide formation becomes significant, as does the competing reaction of arenediazonium ions with OH$^-$ to form diazotates.[27] The use of a coupling reaction to stop the dediazoniation reaction requires that its rate be significantly faster than the dediazoniation rate. Control experiments performed by following azo dye formation spectrophotometrically show that at pH 4.5 at 25 °C the quenching reaction is over one order of magnitude faster than the fastest CuCl$_2$-catalyzed reaction observed. To check for possible interactions between 2N6S and Cu(II), we monitored the effect of added 2N6S on the absorbance at 800 nm [λ_{max} for Cu(II)[28]]. The spectrum remained unchanged, indicating that added 2N6S had no effect on Cu(II) absorbance under the experimental conditions used.

RESULTS

Dediazoniation in the absence of CuCl$_2$. Effect of HCl and NaCl on the observed rate constant, k_0, and on product yields

Values of k_0 were obtained by monitoring ArOH

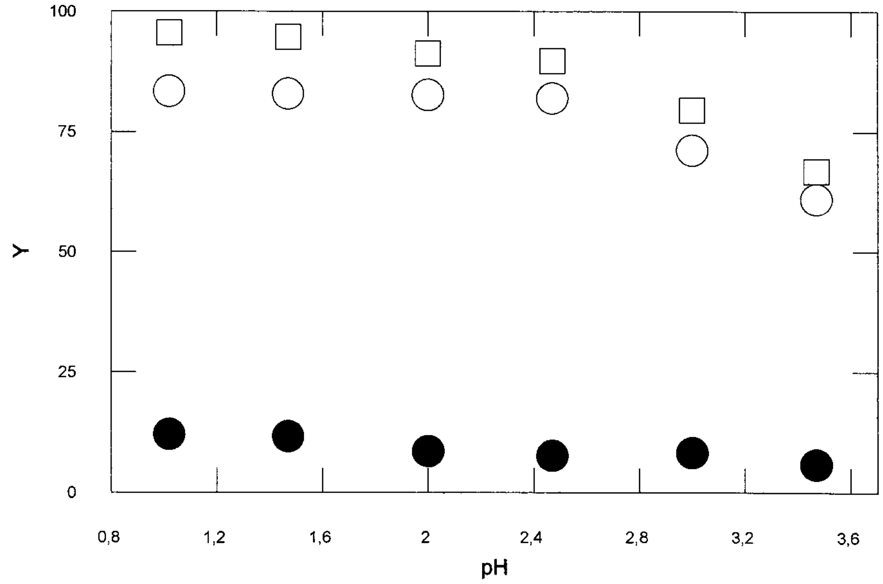


Figure 3. Effect of pH, defined as pH = −log[H^+], on product yields in the absence of $CuCl_2$. ○, ArOH; ●, ArCl; □, total. T = 60 °C; [PNBD] = 1.0 × 10^{-4} M; [NaCl] = 1.0 M

formation spectrophotometrically and were independent of acidity (0.02–1.2 M HCl) and Cl^- concentration([Cl^-] = [HCl] + [NaCl] = 0.02–1.10 M) (Table 2). The average value of k_0 is (3.6 ± 0.2 × 10^{-5} s^{-1}, in agreement with literature values of $k_0 = 3.3 \times 10^{-5}$ s^{-1} obtained by N_2 evolution[22] (T = 60.0 °C, pH = 1.6–1.8) and $k_0 = 3.22 \times 10^{-5}$ s^{-1} (T = 60.3 °C), obtained by measuring changes in rate with pressure.[23]

Rates of formation of dediazoniation products and, indirectly, the rate of decomposition of arenediazonium ions were also obtained by quenching the dediazoniation reaction at increasingly longer periods of time and measuring product yields by HPLC. Figures 1 and 2A show the variation of product yields with time and logarithmic plots based on Eqn 1 (only for ArOH) under different experimental conditions. From the slopes of these linear plots we obtained values of k_0 for ArOH formation, yielding an average value of $k_0 = 3.8 \times 10^{-5}$ s^{-1}, in good agreement with the average value obtained spectrophotometrically (Table 2).

Values of k_0 for loss of arenediazonium ion were also obtained from the decrease in absorbance of the azo dye obtained from PNBD coupling with 2N6S [Fig. 2B]. The average value is $k_0 = (3.54 \pm 0.27) \times 10^{-5}$ s^{-1} for four

Table 3. Effect of added $CuCl_2$ on k_0 for dediazoniation of PNBD[a]

10^4[PNBD](M)	[HCl](M)	[NaCl](M)	10^3 [$CuCl_2$](M)	$10^5 k_0(s^{-1})$	$\tau_{1/2}$ (min)[b]
1.40	1.00	—	0.66	3.31	
1.40	1.00	—	1.00	3.49	
1.40	1.00	—	1.30	3.62	
1.40	1.00	—	2.98	3.74	
1.40	1.00	—	6.60	3.79	
1.40	1.00	—	8.95	4.22	
1.40	1.00	—	12.00	5.48	
1.40	1.00	—	15.00	5.96	
1.00	0.01	1.00	0.00		363
1.00	0.01	1.00	0.57		150
1.00	0.01	1.00	1.27		80
1.00	0.01	1.00	2.87		50
1.00	0.01	1.00	3.40		30
1.00	0.01	1.00	4.00		25
1.00	0.01	1.00	4.60		25
1.00	0.01	1.00	5.20		20

[a] Formation of ArOH was monitored spectrophotometrically at 350 nm and 60 °C.
[b] Half-lives for formation of ArOH in 0.01 M HCl (see text).

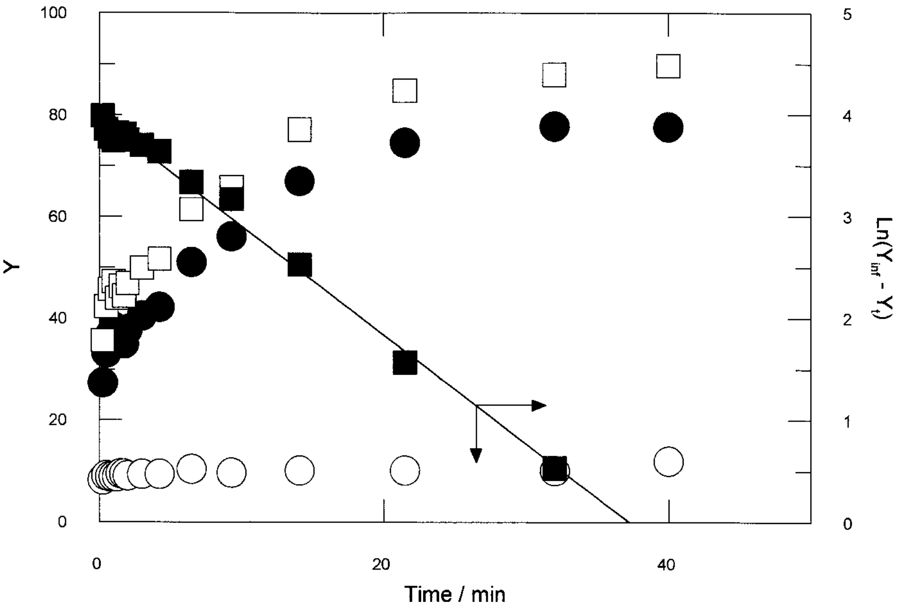


Figure 4. Variation of product yields (○, ArOH; ●, ArCl; □, total) with time and a first-order plot for ArCl (■). $T = 60\,°C$; [PNBD] = 1.0×10^{-4} M; [HCl] = 0.01 M; [NaCl] = 1.0 M; [$CuCl_2$] = 15×10^{-3} M

runs and is the same, within experimental error, as those obtained spectrophotometrically and chromatographically. Figures 1 and 2A also show that only ArOH and ArCl are formed with ArOH being the major product. The total yield is almost 100% in all cases.

We also determined the effect of H^+ on product yields. Preliminary experiments in dilute H_2SO_4 in the absence of NaCl (not shown) indicate a large decrease in the ArOH yield at about pH 5–6, suggesting a change in mechanism. A careful study in 1.0 M NaCl across a range of HCl concentrations (Fig. 3) shows that quantitative conversion to ArOH is achieved at $[H^+] \geq 0.1$ M and that the total and ArOH yields drop significantly above about pH 2.5 (unlike ArCl). The chromatograms showed no extra peaks other than the ArOH and the void volume peak, so the unknown product probably elutes with the salts in the void volume. This decrease in the ArOH yield is probably caused by a competing reaction between unreacted arenediazonium ion and *p*-nitrophenol (see below).

Dediazoniation in the presence of $CuCl_2$. Effect of pH and $CuCl_2$ on the observed rate constant and product yields

The effect of added $CuCl_2$ on k_0 was obtained by monitoring ArOH formation at 350 nm (see Experimental) as a function of different $[H^+]$, but keeping the total chloride ion concentration constant ($[Cl^-]_{tot} = 1.0$ M). Cl^- forms a number of complexes with copper ions that depend on $[Cl^-]$[29,30] and to ensure that the distribution of complexes was the same in all experiments, sufficient NaCl was added such that $[Cl]_{tot} = 1.0$ M. The spectrophotometric method is only useful over a limited range of solution compositions because (a) $CuCl_2$ chloro complexes absorb strongly across the wavelength region in which ArOH absorbs[29] and (b) the yield of ArOH decreases significantly with added $CuCl_2$.

Table 3 shows the effect of added $CuCl_2$ at $[H^+] = 1$ M and $[H^+] = 0.01$ M. At $[H^+] = 1$ M, k_0 almost doubles on going from 0 to 15×10^{-3} M $CuCl_2$. At this acidity, all runs showed first-order behavior. At lower acidities, $CuCl_2$ is more catalytically active and the rate of ArOH formation depends more strongly on added $CuCl_2$. Compare Figs 1 and 2A (in the absence of $CuCl_2$) with Fig. 4 (in the presence of 15×10^{-3} M $CuCl_2$), in which reactions are first order, and Fig. 5 (chosen as representative), in which non-first-order behavior is observed at intermediate $CuCl_2$ concentrations ($[H^+] = 0.01$ M and $[CuCl_2] = 2.46 \times 10^{-3}$ M). For this reason, we report approximate half-lives instead of observed rate constants with added $CuCl_2$ in 0.01 M HCl (Table 3), simply to ilustrate that added $CuCl_2$ catalyzes the dediazoniation of PNBD.

All HPLC traces in both 0.01 and 1 M HCl showed signals for only two dediazoniation products, ArOH and ArCl, and small amounts of ArH. Figures 6 and 7 show the effect of added $CuCl_2$ on product yields at $[H^+] = 0.01$ and 1 M respectively ($[Cl]_{tot} = 1.0$ M). At both acidities, added $CuCl_2$ increases the relative amount of ArCl formed with a concomitant decrease in the yield of ArOH. Figure 6 shows that in the absence of $CuCl_2$ and at low $CuCl_2$ concentrations ArOH is the major product, but at high $CuCl_2$ concentrations ArCl is the major product. The total yields are essentially quantitative, >90%, except at low $CuCl_2$ concentrations at $[H^+] = 0.01$ M (Fig. 6). At this acidity, the ArOH yield

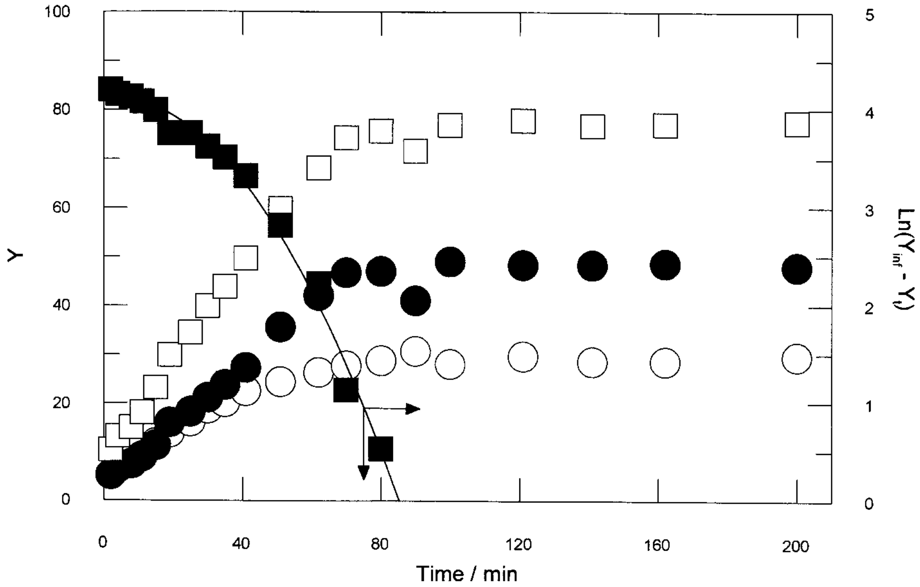


Figure 5. Variation of product yields (○, ArOH; ●, ArCl; □, total) with time and first-order plot for ArOH (■). $T = 60\,°C$; [PNBD] = 1.0×10^{-4} M; [HCl] = 0.01 M, [NaCl] = 1.0 M; [$CuCl_2$] = 2.46×10^{-3} M

decreases rapidly at low $CuCl_2$ concentrations from an initial yield of 86% in the absence of $CuCl_2$ and then more gradually at higher $CuCl_2$ concentrations to about 6% at 50 mM $CuCl_2$. The yield of ArCl is 8.2% in the absence of $CuCl_2$ but it rises rapidly and then more slowly up to 92% at 50 mM $CuCl_2$. The total yield passes through a minimum of about 60% conversion at 0.3–0.4 mM $CuCl_2$ (about 3–4 times [PNBD]). Figure 7 shows that when the acid concentration is increased 100-fold up to $[H^+] = 1.0$ M, the minimum in the total yield disappears and ArCl again becomes the major product at higher $CuCl_2$ concentrations. As noted before, the chromatograms showed only peaks for ArOH and ArCl, so whatever product is formed it probably comes off with the salts in the void volume, which is why it is not observed in the chromatograms. These strong pH-dependent product distributions have not been reported previously and were investigated further.

Figure 8 shows the effect of increasing pH at 3.96×10^{-4} M $CuCl_2$, the concentration at the minimum

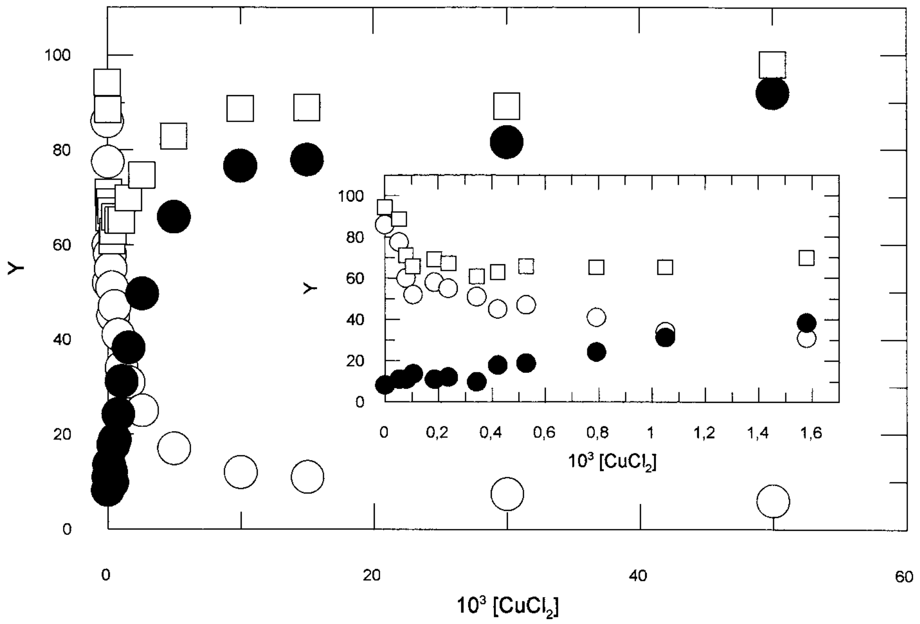


Figure 6. Variation of product yields (○, ArOH; ●, ArCl; □ total) with [$CuCl_2$]. $T = 60\,°C$; [PNBD] = 1.0×10^{-4} M; [HCl] = 0.01 M; [NaCl] = 1.0 M. Inset shows yields between [$CuCl_2$] = 0 and 1.6×10^{-3} M

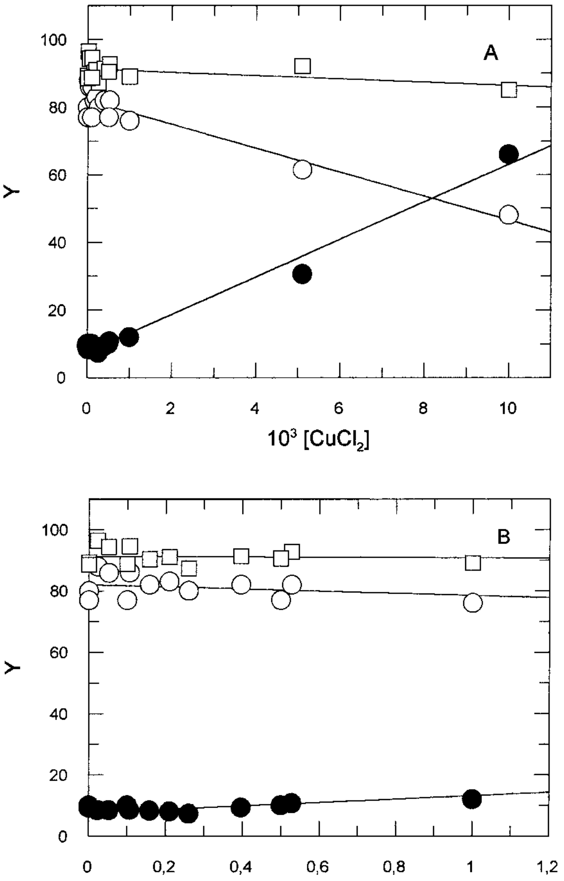


Figure 7. Variation of product yields (○, ArOH; ●, ArCl; □, total) with [CuCl$_2$]. $T = 60$ °C; [PNBD] = 1.0×10^{-4} M; [HCl] = 1.0 M. (B) shows yields between [CuCl$_2$] = 0 and 1.0×10^{-3} M

of total yield in Fig. 6. The yield of ArCl increases significantly above pH 2 and the decrease in ArOH yield follows a sigmoidal curve with an inflection point at about pH 2. A similar pH dependence is observed in the absence of CuCl$_2$ (Fig. 3), but the inflection point is higher. Note that total yields are almost quantitative below pH 1 (Figs 3 and 8). Whatever reaction is responsible for this decrease in total yield, the yields of ArOH and ArCl are the same as those in Figs 1 and 2A in 1.0 and 0.01 M HCl, respectively.

One possible explanation for the decrease in total yield (Fig. 8) and the observation of non-first-order behavior (Fig. 6) is that PNBD reacts with ArOH as it is formed. To demonstrate this assumption, we ran several experiments in the presence of added ArOH at two different CuCl$_2$ concentrations at pH 2. If PNBD reacts with ArOH, then added ArOH should reduce the ArOH yield. The net ArOH yield was determined by subtracting the added ArOH concentration from the total ArOH concentration as measured by HPLC, i.e. $Y = 100([\text{ArOH}]_{\text{measured}} - [\text{ArOH}]_{\text{added}})/[\text{PNBD}]$. Figure 9 shows that the yield of ArCl is constant but that of ArOH decreases significantly. This result confirms our assumption that a competing side-reaction is taking place.

DISCUSSION

Substituents have marked effects on the stability of arenediazonium ions in solution.[3] Substituent effects are not correlated by the Hammett equation, but they fit the Swain–Lupton equation, which separates resonance and polar effects.[9,10]. Our experiments were carried out at

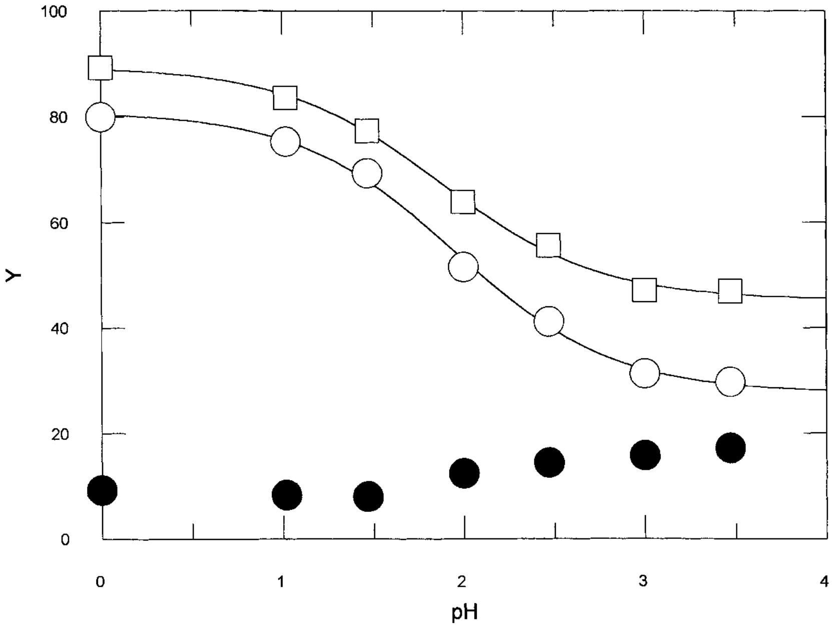


Figure 8. Effect of pH, defined as pH = $-\log[\text{H}^+]$, on product yield in the presence of 3.96×10^{-4} M CuCl$_2$ at $[\text{Cl}^-]_{\text{tot}} = 1.0$ M (○, ArOH; ●, ArCl; □, total). $T = 60$ °C; [PNBD] = 1.0×10^{-4} M

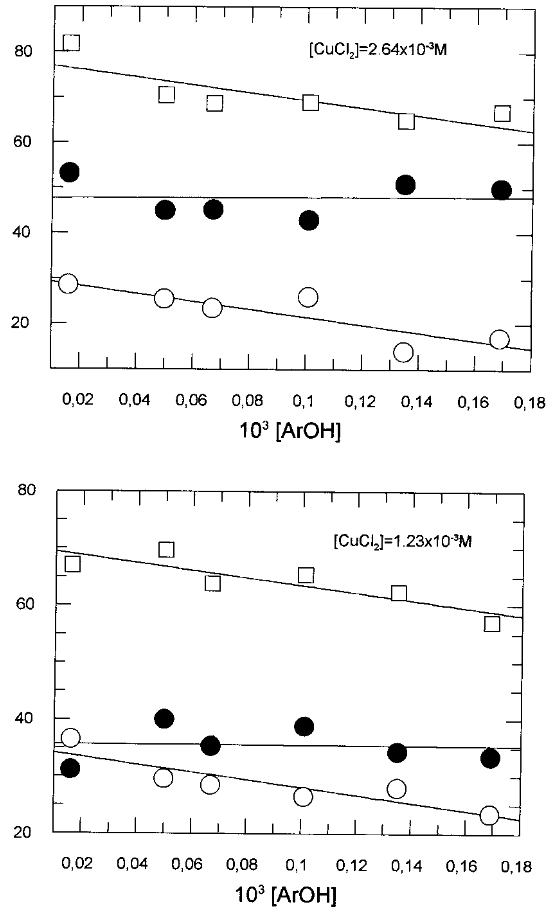


Figure 9. Effect of added ArOH on product yields (○, ArOH; ●, ArCl; □ total) at two $CuCl_2$ concentrations. $T = 60\,°C$; [PNBD] = 1.0×10^{-4} M; [HCl] = 0.01 M; [NaCl] = 1.0 M; (A) [$CuCl_2$] = 2.64×10^{-3} M; (B) [$CuCl_2$] = 1.23×10^{-3} M

60 °C because *para* and *meta* substituents, including electron-withdrawing, e.g. *p*-NO_2, and electron-donating groups, e.g. $N(CH_3)_2$ and CH_3, usually slow dediazoniation.[3,31]

All our results are consistent with Cu(II) catalysis of the heterolytic dediazoniation of PNBD (Scheme 1). Cu(I) catalyzes homolytic dediazoniation reactions.[3,14] To prevent the reduction of Cu(II) to Cu(I) we carefully purified the *p*-nitrobenzenediazonium tetrafluoroborate, avoided using organic solvents that may act as reducing agents, and did not deoxygenate the water because disolved O_2 rapidly oxidizes Cu(I) to Cu(II) in aqueous solutions.[32] Consequently, insignificant amounts of Cu(I) should be present. Dediazoniations in the presence of reductants and Cu(II) are known to proceed homolytically, generating significant yields of reduction products such as ArH, ArAr, ArN=NAr and tars[13,14] [Scheme 2B]. The only two products formed in significant yields in these experiments in aqueous HCl solutions in the presence and absence of $CuCl_2$ are ArOH and ArCl. Small amounts (<1.5%) of ArH are sometimes formed, but its yield is independent of the $CuCl_2$ concentration. Thus our results are consistent with the competitive formation of dediazoniation products via the heterolytic [Scheme 2A] and not the homolytic pathway [Scheme 2B].

In the absence of $CuCl_2$, dediazoniation of PNBD is first order. Spectrophotometric and HPLC kinetic data show that the rate constant for the formation of dediazoniation products is the same as that of the disappearance of arenediazonium ion and that it is not affected by [H^+] or [Cl^-]. The k_o values obtained are in agreement with those in the literature.[22] In the absence of $CuCl_2$, the yield of ArOH decreases and that of ArCl increases with increasing [Cl^-], HPLC kinetic data [Figs 1 and 2A] show that the observed rate constants for the formation of ArCl and ArOH are essentially the same, but the yields of ArCl are low compared with that of ArOH, consistent with the low selectivity of arenediazonium ions towards different nucleophiles compared with water as shown in other dediazoniation reactions.[25] A yield of 86% for ArOH at [Cl^-]:[H_2O] = 1:55 agrees with that of Pfeil,[24] who reported a yield of 81% at a [Cl^-]:[H_2O] ratio of 1:47. The selectivity of this reaction was estimated from product yields [Figs 1 and 2A] by using the equation[25]

$$S_w^{Cl} = \frac{(Y_{ArCl})[H_2O]}{(Y_{ArOH})[Cl^-]} \tag{3}$$

yielding a value of $S_w^{Cl} = 5.2$ ([H_2O] = 54.5 in 1.0 M NaCl[33]). This low selectivity is similar to literature values of $S_w^{Cl} = 3$ for benzendiazonium ion, $S_w^{Cl} = 4$ for 2,4,6 -trimethylbenzenediazonium ion and $S_w^{Cl} = 1.7$ for *p*-methylbenzenediazonium ion.[25] The selectivities are dependent on ionic strength, as found by Chauduri *et al.*[34] All these results are consistent with rate-determining loss of N_2 to give a highly reactive aryl cation intermediate that is trapped by a nucleophile in a subsequent, fast step [Scheme 2A].

It has been reported[29,30] that the stepwise formation constants, K_n, for the replacement of H_2O by Cl^- in the coordination sphere of Cu(II) are low, but appreciable concentrations of the chlorocomplex $CuCl_4^{2-}\cdot 2(H_2O)$ are present in solution containing excess of Cl^-.[35,36] Added $CuCl_2$ increases the ArCl yield at the expense of ArOH (Figs 4–7) and the dediazoniation reaction is accelerated about 18-fold from [$CuCl_2$] = 0 to 5.2×10^{-3} M in 0.01 M HCl (Table 3). At high $CuCl_2$ concentrations (Figs 6 and 7), the formation of ArCl is almost quantitative and the yield of ArOH approaches zero, suggesting that ArCl formation takes place primarily through the interaction of PNBD with the chlorocuprate complex $CuCl_4^{2-}\cdot 2(H_2O)$. A small fraction of ArCl is probably produced by reaction of PNBD with Cl^- as observed in the experiments in absence of $CuCl_2$ (Figs 1 and 2). ArOH is probably formed primarily by reaction of water with the 'free' arenediazonium ions.

The one conundrum in these results is why the kinetics become non-first order and the ArOH yields decrease at low acidities. Lowering the acidity reduces the ArOH yield in the absence and in the presence of $CuCl_2$, but increasing the acidity of the medium leads to quantitative conversion to products (Figs 3 and 8). The sigmoidal decrease in ArOH yield with increasing pH in the presence of $CuCl_2$ (Fig. 8) and the shift in the inflection point in its absence (Fig. 3) suggest that PNBD is reacting with a nucleophile whose concentration is increased by chlorocuprate(II) complexes, e.g. the conjugate base of ArOH, $pK_a = 7.14$. One possible explanation for the loss of ArOH at lower acidities is that PNBD couples with ArO^- and that chlorocuprate complexes accelerate the reaction, perhaps enhancing the acidity of ArOH. Arenediazonium salts are electrophiles that react with benzene derivatives having at least one nucleophilic center.[3,4] This coupling reaction is facilitated by electron-withdrawing groups such as NO_2 in *ortho* or *para* positions of the arenediazonium ring. Coupling reactions between arenediazonium salts and phenols have been known for over 100 years.[1,3] The coupling reaction is probably much faster with ArO^- because rate constants for some coupling reactions with ArO^- approach diffusion control.[3] Thus, because dediazoniation of PNBD is slow even at 60 °C ($\tau_{\frac{1}{2}} = 30–150$ min, Table 3) and that the pK_a of ArOH is about 7, the coupling reaction might compete with dediazoniation at pHs that are orders of magnitude below the pK_a of ArOH, i.e. pH 2–3. Indeed, the ArOH yield is very sensitive to solution acidity, as shown in Figs 3 and 8. The strongest evidence of a competing side reaction is demonstrated by the addition of ArOH (Fig. 9). Added ArOH reduces the ArOH yield from dediazoniation at two different $CuCl_2$ concentrations. A competing bimolecular reaction between ArO^- and PNBD also accounts for the non-first-order kinetics observed at low acidities spectrophotometrically and by HPLC at low to moderate $CuCl_2$ concentrations (Fig. 5). The effect of the competing reaction is negligible at high acidities, at low $CuCl_2$ concentrations, and at high $CuCl_2$ concentrations when the ArOH yield is low.

CONCLUSIONS

Our results show the following characteristics of the Cu(II)-catalyzed dediazoniation: (a) reducing agents and ligand transfer agents are not needed to obtain quantitative yields of the haloarene using $CuCl_2$; (b) $CuCl_2$ catalyzes the dediazoniation of PNBD and the increase in the rate constant is pH dependent; (c) dediazoniation of PNBD is first order in acidic solutions in the absence of $CuCl_2$ but in the presence of $CuCl_2$ a competing, pH-dependent reaction occurs and in 0.01 M HCl and at low to moderate $CuCl_2$ concentrations the reaction is not first order; and (d) the non-first-order kinetics are attributed to a competing bimolecular reaction between PNBD and ArO^- formed during dediazoniation. The methodology works with Cu(II)-catalyzed dediazonation reactions and should be applicable to other metal-catalyzed dediazoniation reactions that are not too fast. The results should provide a more detailed picture of the Sandmeyer reaction. Our results do not provide information on which of the possible chlorocomplexes $CuCl_n^{(2-n)} \cdot (6-n)\ (H_2O)$, with $n = 0–4$, are catalytically active. Determining the identity of the unknown product and the details of the mechanism in the pH 2–6 region is part of future work.

The results also suggest a new approach for preparing haloarenes from arenediazonium salts in high yields under mild conditions, i.e. low acidity and using Cu(II) instead of Cu(I) as catalyst, avoiding the use of reducing or ligand transfer agents. For example, a low molecular weight chloroarene such as ArCl might be produced almost quantitatively by gradually adding a diazonium salt solution to a boiling solution at optimum pH, NaCl and $CuCl_2$ concentrations. The chlorocuprate(II) complexes will always be in large excess and the chloroarene can be removed continuously by steam distillation.

Acknowledgements

This work was supported by the Spanish Ministry of Education (DGICYT, PB94-0741), Xunta de Galicia (XUGA 38305A94) and University of Vigo. M. Harbowy and L. S. Romsted appreciate support from the National Science Foundation (CHE-9526206).

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