

pH Effects on Ethanolysis of Some Arenediazonium Ions: Evidence for Homolytic Dediazonation Proceeding through Formation of Transient Diazo Ethers

Roman Pazo-Llorente,^[a] Carlos Bravo-Diaz,^{*[a]} and Elisa Gonzalez-Romero^[b]

Keywords: Alcohols / Arenediazonium ions / Dediazonation / Kinetics / Solvolysis

The effects of pH on the observed rate constants ($k_{\text{obsd.}}$) and on the solvolytic dediazonation product distributions of ethanolysis of 2-, 3-, and 4-methylbenzenediazonium ions (2MBD, 3MBD, and 4MBD, respectively) were determined by a combination of spectrophotometric (UV/Vis) and chromatographic (HPLC) techniques. The variation of both $k_{\text{obsd.}}$ and product yields with pH follow S-shaped curves with inflection points at $\text{pH} \approx 3.6$, depending on solvent composition. With increasing pH, $k_{\text{obsd.}}$ values increase by factors of up to about 4 (2MBD), about 3 (3MBD), and about 50 (4MBD) with respect to the $k_{\text{obsd.}}$ values at low pH. HPLC analyses of the reaction mixtures show that only heterolytic products are obtained at low pH, indicating that solvolytic dediazonation takes place through an ionic mechanism, but an increase in

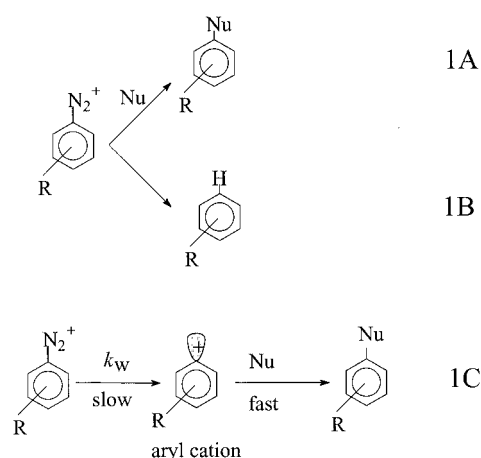
pH favors homolytic dediazonation, with quantitative conversion into the reduction product toluene being obtained at $\text{pH} \geq 6$ (4MBD), indicating that a turnover from the heterolytic to the homolytic mechanisms is taking place under experimental conditions under which insignificant amounts of EtO^- or OH^- should be present in solution. The obtained S-shaped profiles suggest that the initiation process of the homolytic pathway is the result of the formation of a highly unstable transient diazo ether complex and not by direct electron transfer from the solvent (EtOH) to the arenediazonium ions as is currently believed.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

It is now accepted that solvolytic dediazoniations take place through two main mechanisms (Scheme 1): heterolytic (1A) and homolytic (1B).^[1–3] The heterolytic dediazonation pathway involves a $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ mechanism (Scheme 1, C; i.e., a rate-limiting loss of N_2 and formation of an extremely reactive aryl cation that reacts with available nucleophiles on a timescale faster than that required for cation diffusion). The homolytic dediazonation pathway requires an electron transfer to the arenediazonium ions, which can be accomplished in different ways,^[2,3] including reductive methods at an electrode^[4–7] or by employment of nucleophilic anions or nucleophilic neutral molecules such as alcohols.^[8,9] The variety of methods and reducing agents that can be employed to generate intermediate aryl radicals ($\text{Ar}^\cdot$) and the multiplicity of steps open to radical reactions

makes the homolytic pathway of greater synthetic value than the heterolytic one, in which only solvolytic products $\text{Ar}-\text{Nu}$ are attainable.^[2]



Scheme 1. Basic representation of dediazonation mechanisms: 1A) heterolytic, 1B) homolytic, 1C) the $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ heterolytic dediazonation mechanism

Solvolytic studies carried out in a variety of solvents^[1–3] indicate that heterolytic dediazoniations mainly take place in solvents of low nucleophilicity such as H_2O or TFE,

^[a] Universidad de Vigo, Facultad de Ciencias, Dpto. Química Física, 36200 Vigo, Spain
Fax: (internat.) + 34-986-812556
E-mail: cbravo@uvigo.es

^[b] Universidad de Vigo, Facultad de Ciencias, Dpto. Química Analítica y Alimentaria, 36200, Vigo, Spain

while homolytic dediazoniations are favored by an increase in the nucleophilicity of the solvent (HMPT, pyridine, etc.). There exist, however, a number of solvents, such as MeOH, EtOH, and DMSO, usually considered borderline solvents in which both mechanisms may be observed simultaneously. For a given solvent, electron-withdrawing substituents in the aromatic ring favor homolytic dediazoniations.^[1–3]

Many investigators have sought to determine the mechanisms by which the diazonium group is replaced by hydrogen in solvolytic dediazoniations to yield ArH derivatives.^[1–3,10–14] The source of electrons in solvolytic dediazoniations is thought to be the solvent,^[12,14,15] but in contrast to other dediazoniations, no obvious reductants are employed in those experiments to initiate the radical process, so the mechanism and nature of the initiation step remain a matter of debate,^[2,3,13,14] because what is lacking in these cases is a single and still convincing piece of evidence in favor, or against, the different proposed mechanistic alternatives.^[10,16] Bunnet et al.^[10,17] postulated that, in alkaline methanol solutions, the source of radicals is the homolytic decomposition of a (Z)-diazo methyl ether, which is formed rapidly, yielding the aryl radical, N₂ and the methoxy radical, while under acidic conditions they favor initiation by direct electron transfer from MeOH to the arenediazonium ion.^[10,17] Recent solvolytic investigations also appear to favor direct electron transfer from the solvent (EtOH) to initiate the radical reaction, and alternative radical mechanisms proceeding through the formation of intermediate aryl diazo ethers have been deemed less likely.^[13,14]

There exist, however, a variety of reactions in which nucleophiles add to diazonium ions at N_β to give (Z) adducts as kinetically controlled products. These (Z) adducts may undergo subsequent isomerization to the thermodynamically more stable (E) isomers, which in some instances can be isolated,^[18] or may eventually give rise to homolytic rupture of the bonds providing the initiation of a radical process.^[3,9,19,20] This bond-rotating mechanism to transform the (Z) into the (E) isomers has recently been described for Sandmeyer hydroxylations and chlorination reactions.^[19] In most instances analyzed, the nucleophile must possess a charge, such as OH[−], CN[−], RO[−] or ascorbate ions, and experimental conditions are chosen such that substantial concentrations of the anionic form of the nucleophile are present,^[3,9,19,20] but formation of (Z)-diazo ethers with neutral nucleophiles has also been reported.^[5,21]

Following previous solvolytic work,^[5,26] we have undertaken a study to investigate the effects of pH (0–7) on the ethanolysis of 2-, 3- and 4-methylbenzenediazonium ions (2MBD, 3MBD, and 4MBD, respectively) by a combination of spectrophotometric (UV/Vis) and chromatographic (HPLC) techniques to seek for evidence of the nature of the initiation step in solvolytic radical dediazoniations. As we will show, the obtained results provide support for a radical initiation mechanism proceeding through formation of a transient diazo ether, namely Ar–N=N–OEt. The substrates were chosen because substantial knowledge on their solvolytic dediazonation mechanisms under acidic

conditions in H₂O, MeOH, and EtOH over the whole composition range is available^[22–26] and because these ArN₂⁺ ions bear electron-donating substituents in the aromatic ring, which makes them less prone to decompose through homolytic pathways.^[3]

Results and Discussion

Observed rate constants for loss of ArN₂⁺ were obtained spectrophotometrically, and first-order kinetics were obtained for more than 3 half-lives in all runs. Figure 1, chosen as representative, shows the variation in *k*_{obsd.} with pH (HCl) for dediazonation of 4MBD at 20 and 80% EtOH/H₂O; *k*_{obsd.} being essentially constant and independent of solvent composition up to pH ≈ 3. An increase in pH produces a sharp increase in *k*_{obsd.} (up to 50 times its value at low pH), which reaches a plateau region at pH ≥ 6 depending on solvent composition. Similar kinetic S-shaped profiles were obtained for 2- and 3MBD over the same pH range and at the same solvent compositions (results not shown), but the extents of the increase in *k*_{obsd.} were lower than that seen for 4MBD: about 4 times for 2MBD and about 3 times for 3MBD. These results are consistent with reported data for homolytic dediazonation rates in MeOH indicating that they are 4–32 times higher than the heterolytic ones.^[3,10] Replacement of HCl by H₂SO₄ did not result in significant changes in the *k*_{obsd.} values, suggesting that the observed S-shaped profiles are not due to nucleophile (Cl[−], SO₄^{2−}) effects.

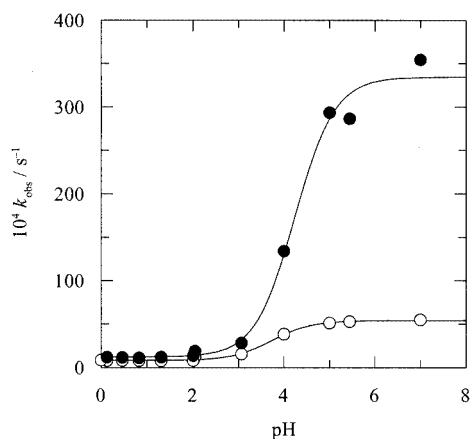


Figure 1. pH effects on *k*_{obsd.} for dediazonation of 4MBD in 20% (open circles) and 80% (black circles) EtOH/H₂O (v/v); [4MBD] ≈ 10^{−4} M, *T* = 60 °C

In addition to the kinetic analyses, an HPLC analytical study of the dediazonation product distribution was performed over the same pH range. Up to four dediazonation products – cresols (ArOH), methylphenetoles (ArOEt), toluene (ArH), and chlorotoluenes (ArCl; only obtained when HCl was employed as source of H⁺ ions) – were detected (Figures 2 and 3, A), their relative yields depending on pH and solvent composition. In the pH = 0–2

range, significant amounts only of the heterolytic ArOH and ArOEt products are obtained, with yields similar to those previously reported,^[26] but with increasing pH a noticeable decrease in ArOH and ArOEt yields is detected with a concomitant increase in the yield of ArH, such that at $\text{pH} \geq 6$ formation of the ArH derivative is about half the total yield (20% EtOH/H₂O, v/v), and it is essentially quantitative when an 80% EtOH/H₂O mixture is employed. Note that the inflection points of the S-shaped curves in Figures 1 and 2 are identical independently of the measured (k_{obsd} , or product yield) parameter. Similar variations in the product distribution for dediazonation of 2- and 3MBD were obtained over the same pH range and at the same solvent compositions.

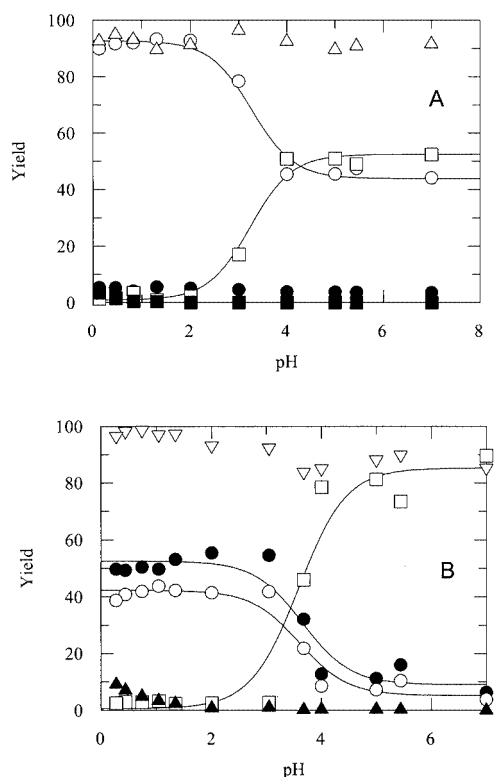


Figure 2. pH-dependent product distribution for dediazonation of 4MBD at 20% (A) and 80% (B) EtOH/H₂O (v/v); experimental conditions as in Figure 1; ArOH (black circles), ArOEt (open circles), ArH (squares), ArCl (black triangles), total (ArOH + ArOEt + ArH + ArCl) (open triangles)

Arenediazonium ions may function as one-electron oxidizing agents, and free radicals are generated in reactions with suitable electron donors.^[3,9,20,27–29] Two particular mechanisms, outer- and inner-sphere, have been proposed for these reactions.^[3,30] The outer-sphere mechanism assumes a direct electron transfer from a reducing agent to ArN_2^+ ions, yielding a radical from the reducing agent and an aryl diazenyl radical ($\text{ArN}_2\cdot$), which subsequently decomposes spontaneously in aqueous solution to yield N_2 and the corresponding aryl radicals. In the alternative inner-sphere mechanism, reduction of the arenediazonium

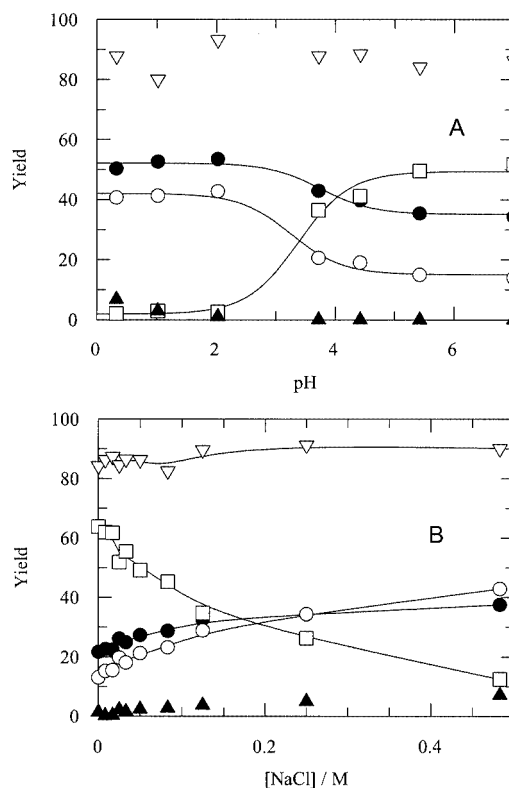
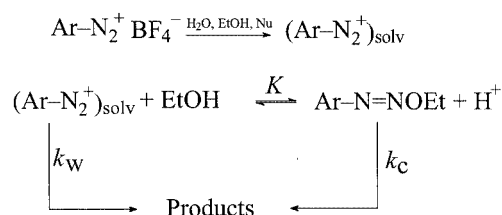


Figure 3. A) Effects of pH on product distribution of 3MBD in a 80% EtOH/H₂O mixture; B) effects of [NaCl] on product distribution for dediazonation of 3MBD in a 80% EtOH/H₂O mixture in the absence of added acid; [3MBD] $\approx 1 \times 10^{-4}$ M; ArOH (black circles), ArOEt (open circles), ArH (squares), ArCl (black triangles), total (ArOH + ArOEt + ArH + ArCl) (open triangles)

ion is preceded by the formation of a complex, namely Ar-N=N-O-R , which was detected experimentally in some dediazonations.^[9,20,21]

S-shaped curves such as those shown in Figures 1, 2, and 3 (A) are usually observed in reactions of acid-base pairs in which both forms are attainable and show different reactivities.^[31] Under our experimental conditions, only two specimens may undergo acid-base processes: the ArN_2^+ ions and EtOH. The pK_a of EtOH is about 15 and the pK_a values of the 2-, 3-, and 4-methyl derivatives have been reported to be about 12,^[32] so ArN_2^+ ions reacting with EtO^- or with OH^- ions, as in alkaline media,^[10,17] appear unlikely under the experimental conditions employed. A more plausible mechanism is proposed in Scheme 2, which involves two competitive mechanisms: The thermal decomposition of the solvated ArN_2^+ ions through the heterolytic $\text{D}_\text{N} + \text{A}_\text{N}$ mechanism and the inner-sphere mechanism in which the slow step is the rate-limiting decomposition of a transient diazo ether (ArN_2OEt) formed from reaction between ArN_2^+ ions and EtOH in a rapid pre-equilibrium step.

The proposed mechanism is consistent with experimental results shown in Figures 1 and 2 because ArN_2^+ ions are solvated by EtOH and H₂O molecules,^[26] and so formation of the presumed complex should depend on solvent composition and on pH. A similar mechanism has been proposed to interpret the reactivity of arenediazonium ions with a



Scheme 2. Proposed reaction mechanism for solvolysis of ArN_2^+ in EtOH/ H_2O mixtures; the reactive EtOH molecule is one of those in the solvation shell of the ArN_2^+ ions; k_w and k_c stand for the thermal rate constant and for the first-order rate constant for the decomposition of the ArN_2OEt complex, respectively, and K stands for the equilibrium constant for complex formation

number of ascorbate ions, for which the formation of such an intermediate was detected experimentally by employment of electrochemical methods.^[9,20] The assumption of a rate-limiting decomposition of the diazo ether is also consistent with reported results for other *O*-coupling reactions^[1,3,33,34] and was experimentally examined in reactions of arenediazonium ions where geometric restrictions apply.^[21,35]

From Scheme 2, Equation (1) can be derived, where k_w and k_c are the rate constants for the spontaneous thermal decomposition of ArN_2^+ and the rate constant for decomposition of the complex, respectively, and $K_1 = K[\text{EtOH}]$ with K standing for the equilibrium constant for complex formation.

$$k_{\text{obsd.}} = (k_w[\text{H}^+] + k_c K_1)/([\text{H}^+] + K_1) \quad (1)$$

This equation is typical of processes in which an S-shaped dependence of $k_{\text{obsd.}}$ on pH is achieved.^[31] From Equation (1) and by considering limits, it can be seen that when $[\text{H}^+] \gg K_1$, $k_{\text{obsd.}} \approx k_w$ (i.e., the reaction proceeds through the $\text{D}_\text{N} + \text{A}_\text{N}$ mechanism and only heterolytic products are obtained), while when $[\text{H}^+] \ll K_1$, $k_{\text{obsd.}} \approx k_c$ (i.e., the reaction proceeds through the ArOEt complex and formation of reduction products is favored). The solid lines in Figures 1, 2 and 3 (A) were obtained by fitting the corresponding data to a Henderson–Hasselbach-type equation, from which values of $\text{p}K_1 = 3.3$ (20% EtOH) and 3.6 (80% EtOH) can be obtained for 3- and 4MBD. Table 1 shows the k_w , k_c , and the average $\text{p}K_1$ values obtained for the ArN_2^+ ions employed in this work. The K_1 values, and

Table 1. k_w , k_c , and $\text{p}K_1$ values for diazo ether formation

	2MBD	3MBD	4MBD
$10^4 k_w [\text{s}^{-1}]$	7.3 ^[a] 7.4 ^[b]	8.6 ^[a] 10.3 ^[b]	8.3 ^[a] 11.9 ^[b]
$10^4 k_c [\text{s}^{-1}]$	12.6 ^[a] 28.8 ^[b]	19.6 ^[a] 27.6 ^[b]	54.9 ^[a] 354.3 ^[b]
$\text{p}K_1$	3.3 ^[a] [c] 3.6 ^[b,c]	3.2 ^[a,c] 3.5 ^[b,c]	3.4 ^[a,c] 3.6 ^[b,c]

[a] 20% EtOH/ H_2O . [b] 80% EtOH/ H_2O . [c] Average value from HPLC and spectrophotometry.

hence the equilibrium constants K for ArN_2OEt formation, appear to be independent of the position of the substituent in the aromatic ring, but depend on the solvent composition. However, the rate constant for ArN_2OEt breakdown k_c is strongly dependent both on the position of the substituent and on solvent composition.

Further evidence for the proposed mechanism was obtained when NaCl was intentionally added to reaction mixtures (80% EtOH/ H_2O) in which no acid was initially present (see B in Figure 3). With increasing $[\text{NaCl}]$, Cl^- ions become part of the solvation shell of the parent ArN_2^+ ions, competing with EtOH and H_2O molecules, and thus inhibiting the formation of the presumed ArN_2OEt complex, hence inhibiting the formation of ArH derivatives and favoring an increase in heterolytic product formation (i.e., addition of Cl^- ions favors the ionic mechanism). These results are consistent with previous work indicating that the observed product distribution reflects the concentrations of nucleophiles in their immediate environment (i.e., in the first solvation shell of ArN_2^+ ions).^[8,26]

Diazo ethers of the general structure $\text{ArN}=\text{NOR}$ (with R = alkyl, aryl) are rarely formed as stable products.^[3,10,33,34] The diazo ether formally derived from 1-naphthol and the benzenediazonium ion, for example, is sensitive to acid and base as well as to light. Previous studies^[3,10,33,34] concerning reactions between arenediazonium ions and alkoxide or phenoxide compounds, which yield diazo ethers, provide further support for the proposed mechanism but suggest that the decomposition of the diazo ether complex may not be as simple as indicated in Scheme 1.

Fundamentally, reactions between arenediazonium ions and methoxide ion occur in two phases. The first is the very rapid formation of a (*Z*)-diazo methyl ether, and in a second one following this step some of the (*Z*)-diazo ether decomposes to yield reduction products (usually hydrodediazonation) and the rest is converted into the (*E*)-diazo ether. Investigations developed by Broxton et al.^[36] confirmed that the initial reaction of the arenediazonium ions takes place in such a way that the (*Z*)-diazo ether is directly formed almost exclusively, and part of it is transformed to the (*E*) isomer by an ionization-recombination mechanism.^[3,19] Given that almost quantitative yields of the reduction product ArH are obtained at $\text{pH} > 6$, it is likely that the initially formed (*Z*)-diazo ether undergoes homolytic fragmentation to give $\text{EtO}^\bullet$ and the arenediazenyl radical $\text{ArN}_2^\bullet$, which immediately decomposes to yield the aryl radical $\text{Ar}^\bullet$ and N_2 . Once the radicals are formed, an $\text{H}^\bullet$ atom from $\text{EtO}^\bullet$ is abstracted, giving rise to the ArH derivative.^[3,10,12]

Conclusion

In conclusion, our data strongly suggest that there is no need to invoke direct electron transfer from the solvent in order to explain homolytic dediazoniations in EtOH, but that the reaction proceeds through two competitive mechanisms: the thermal $\text{D}_\text{N} + \text{A}_\text{N}$ mechanism and a rate-limiting

decomposition of a transient ArN_2OEt diazo ether formed from ArN_2^+ ions and EtOH molecules in their solvation shells. The data in Table 1 suggest that the position of the substituent has an effect both on k_c values and on the dediazonation product distribution, but not on the values of the equilibrium constant K for diazo ether formation, which appears to be solvent-dependent.

Experimental Section

Instrumentation: UV/Vis spectra and some kinetic experiments were monitored with a Beckman DU-640 UV/Vis spectrophotometer fitted with a thermostatted cell carrier attached to a computer for data storage. Product analysis was carried out with a WATERS HPLC system including a 560 pump, a 717 automatic injector, a 2487 dual wavelength detector and a computer for data storage. Products were separated with a Microsorb-MV C-18 (Rainin) reversed-phase column (25 cm length, 4.6 mm internal diameter and 5 μm particle size) with a mobile phase of MeOH/H₂O (70:30, v/v), containing 10^{-4} M HCl. The injection volume was 25 μL in all runs and the UV detector was set at 220 nm and 280 nm.

Materials: Arenediazonium salts (ArN_2^+) were prepared under non-aqueous conditions as described elsewhere^[37] and were stored in the dark at low temperature to minimize decomposition and recrystallized periodically. Other reagents were of maximum purity available and were used without further purification. Cresols (ArOH), chlorotoluenes (ArCl), methylphenetoles (ArOEt), and the reagents used in the preparation of arenediazonium salts (as tetrafluoroborates) were purchased from Aldrich. Other materials employed were from Riedel-de Haën. All solutions were prepared with Milli-Q grade water. Solution composition is given by percent of EtOH by volume. Molar concentrations were calculated by ignoring the small excess volume of mixed solvents.^[38]

Methods: Kinetic data were obtained spectrophotometrically. Observed rate constants were obtained by fitting the absorbance/time data to the integrated first-order Equation (2) by a nonlinear least-squares method.

$$\ln [(M_t - M_\infty)/(M_0 - M_\infty)] = -k_{\text{obsd}} t \quad (2)$$

All runs were carried out at $T = 35 \pm 0.1$ °C (2MBD, 3MBD) and at $T = 60$ °C (4MBD) with arenediazonium salts as the limiting reagents. Duplicate or triplicate experiments gave average deviations lower than 7%. Spectrophotometric kinetic data were obtained by monitoring the disappearance of the corresponding ArN_2^+ at an appropriate wavelength to minimize interference (mainly dediazonation products or intentionally added electrolytes). Beer's law plots (not shown) for ArN_2^+ aqueous and ethanolic solutions up to 2.00×10^{-4} M are linear (correlation coefficient $cc \geq 0.999$). Stock solutions were prepared by dissolving ArN_2^+ in the appropriate acidic (HCl) mixture to minimize diazotate formation,^[39] to give final concentrations of about 1×10^{-5} M and $[\text{HCl}] = 3.6 \times 10^{-3}$ M. Stock solutions were generally used immediately or within 90 min with storage in an ice bath to minimize decomposition. Reactions were initiated by addition of an aliquot (< 100 μL) of the ArN_2^+ stock solution to the previously thermostatted reaction mixture. Preliminary HPLC experiments showed that only four decomposition products are formed: ArOH, ArCl, ArH, and ArOEt. Linear ($cc > 0.999$) calibration curves for converting HPLC peak areas (A) into concentrations

were obtained for these products by use of commercial samples. Percentages of formation (F) of dediazonation products were obtained from the ratio of the dediazonation product concentration ($[\text{Analyte}]$) and the initial diazonium salt concentration, estimated by weight (i.e., $F = 100 [\text{Analyte}]/[\text{ArN}_2^+]$) as described elsewhere.^[23,24,26]

Acknowledgments

Financial support from the following institutions is acknowledged: MCyT (BQU2003-04775-C02-02), FEDER, Xunta de Galicia (PGDIT03TAL30101PR) and Universidad de Vigo. R. P.-L. thanks Xunta de Galicia for a postgraduate research training grant.

- [1] A. F. Hegarty, "Kinetics and Mechanisms of Reactions Involving Diazonium and Diazo Groups", in *The Chemistry of Diazonium and Diazo Compounds* (Ed.: S. Patai), John Wiley & Sons, New York, **1978**.
- [2] C. Galli, *Chem. Rev.* **1988**, *88*, 765.
- [3] H. Zollinger, *Diazo Chemistry I, Aromatic and Heteroaromatic Compounds*, VCH, Weinheim, Germany, **1994**.
- [4] M. E. Romero-Nieto, C. Bravo-Díaz, E. González-Romero, *Int. J. Chem. Kinet.* **2000**, *32*, 419.
- [5] C. Bravo-Díaz, E. González-Romero, "Reactivity of Arenediazonium ions in Micellar and Macromolecular Systems", in *Current Topics in Colloid & Interface Science*, Research Trends, Trivandrum, India, **2001**, vol. 4.
- [6] C. Bravo-Díaz, E. González-Romero, *Electroanalysis* **2003**, *15*, 303.
- [7] C. Bravo-Díaz, E. González-Romero, "Electrochemical behavior of arenediazonium salts – New trends and applications", in *Current Topics in Electrochemistry*, Research Trends, Trivandrum, India, **2003**, vol. 9.
- [8] I. M. Cuccovia, M. A. da Silva, H. M. C. Ferraz, J. R. Pliego, J. M. Riveros, H. Chaimovich, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1896.
- [9] U. Costas-Costas, E. Gonzalez-Romero, C. Bravo Díaz, *Helv. Chim. Acta* **2001**, *84*, 632.
- [10] J. F. Bunnet, C. Yijima, *J. Org. Chem.* **1977**, *42*, 639.
- [11] F. W. Wassmundt, W. F. Kiesman, *J. Org. Chem.* **1997**, *62*, 8304.
- [12] S. J. Canning, K. McCrudden, H. Maskill, B. Sexton, *Chem. Commun.* **1998**, 1971.
- [13] P. S. J. Canning, K. McCrudden, H. Maskill, B. Sexton, *J. Chem. Soc., Perkin Trans. 2* **1999**, *12*, 2735.
- [14] P. S. J. Canning, H. Maskill, K. McCrudden, B. Sexton, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 789.
- [15] T. J. Broxton, J. F. Bunnet, *Nouv. J. Chim.* **1979**, *3*, 133.
- [16] I. Szele, H. Zollinger, *Helv. Chim. Acta* **1978**, *61*, 1721.
- [17] T. J. Broxton, J. F. Bunnet, C. H. Paik, *J. Org. Chem.* **1977**, *42*, 643.
- [18] M. P. Doyle, C. L. Nesloney, M. S. Shanklin, C. A. Marsh, K. C. Brown, *J. Org. Chem.* **1989**, *54*, 3785.
- [19] P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1135.
- [20] U. Costas-Costas, C. Bravo-Díaz, E. González-Romero, *Langmuir* **2004**, *20*, 1631.
- [21] E. González-Romero, B. Malvido-Hermelo, C. Bravo-Díaz, *Langmuir* **2002**, *18*, 46.
- [22] R. Pazo-Llorente, M. J. Rodríguez-Sarabia, E. González-Romero, C. Bravo-Díaz, *Int. J. Chem. Kinet.* **1999**, *31*, 73.
- [23] R. Pazo-Llorente, M. J. Sarabia-Rodríguez, E. González-Romero, C. Bravo-Díaz, *Int. J. Chem. Kinet.* **1999**, *31*, 531.
- [24] R. Pazo-Llorente, E. González-Romero, C. Bravo-Díaz, *Int. J. Chem. Kinet.* **2000**, *32*, 210.
- [25] R. Pazo-Llorente, C. Bravo-Díaz, E. González-Romero, *Fresenius J. Anal. Chem.* **2001**, *369*, 582.
- [26] R. Pazo-Llorente, C. Bravo-Díaz, E. González-Romero, *Eur. J. Org. Chem.* **2003**, *17*, 3421.

- [27] K. J. Reszka, C. F. Chignell, *J. Am. Chem. Soc.* **1993**, *115*, 7752.
- [28] K. J. Reszka, C. F. Chignell, *Chem.-Biol. Interact.* **1995**, *96*, 223.
- [29] K. C. Brown, M. P. Doyle, *J. Org. Chem.* **1988**, *53*, 3255.
- [30] K. H. Saunders, R. L. M. Allen, *Aromatic Diazo Compounds*, Edward Arnold, Baltimore, MD, **1985**.
- [31] R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, VCH Publishers, New York, **1991**.
- [32] V. Sterva, *Diazonium-Diazo Equilibrium*, John Wiley & Sons, New York, **1978**.
- [33] W. J. Boyle, T. Broxton, J. F. Bunnet, *Chem. Comm.* **1971**, 1470.
- [34] J. F. Bunnet, H. Takayama, *J. Org. Chem.* **1968**, *33*, 1924.
- [35] E. González-Romero, B. Fernández-Calvar, C. Bravo-Díaz, *Prog. Colloid Polym. Sci.*, in press.
- [36] T. J. Broxton, D. L. Roper, *J. Org. Chem.* **1976**, *41*, 2157.
- [37] M. C. García-Meijide, C. Bravo-Díaz, L. S. Romsted, *Int. J. Chem. Kinet.* **1998**, *30*, 31.
- [38] H. Yamamoto, K. Ichikawa, J. Tokunaga, *J. Chem. Eng. Data* **1994**, *39*, 155.
- [39] H. Zollinger, C. Wittwer, *Helv. Chim. Acta* **1952**, *35*, 1209.

Received March 15, 2004