Formation of diazohydroxides ArN$_2$OH in aqueous acid solution: polarographic determination of the equilibrium constant K_R for the reaction of 4-substituted arenediazonium ions with H$_2$O†

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In aqueous acid (pH <4) solutions, in the dark, and in the absence of reductants, arenediazonium ions, ArN$_2^+$ decompose spontaneously through the rate-limiting formation of the extremely unstable aryl cation that reacts with any nucleophile present in its solvation shell ($D_N + A_N$ mechanism). However, in weak acidic and alkaline solutions, ArN$_2^+$ react with H$_2$O and OH$^-$ at the terminal nitrogen to give azo adducts of the type ArN$_2$OH that are in equilibrium with the parent ArN$_2^+$. The diazohydroxide, in this case an acid, is in equilibrium with its conjugate base, and diazoate ArN$_2$O$^-$. The equilibrium constant for reaction with OH$^-$ has been determined for a limited number of ArN$_2^+$ from kinetic measurements but not with H$_2$O (K_R). Here, we have exploited the electrochemical properties of ArN$_2^+$ to determine, for the first time, the equilibrium constants K_R of formation of 4-substituted X–ArN$_2$OH (X=H, Me, MeO, Br, and NO$_2$), which can decompose in several ways including Z–E isomerization or further reaction with OH$^-$ to give diazoate ArN$_2$O$^-$. The technique applied was differential pulse polarography, which is very selective and sensitive. The determined pK_R values are 5–6, and they are somewhat higher than those obtained for the reaction of ArN$_2^+$ with alcohols ROH (p$K_{DE} = 3$–5) under similar acidic conditions. The K_R values are not very sensitive to changes in the nature of the substituent in the aromatic ring and a linear Hammett plot with a slope of $\rho = 0.58$ was obtained. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: diazohydroxide; diazonium

INTRODUCTION

Arenediazonium ions, ArN$_2^+$, are important intermediates in preparative and synthetic chemistry that became industrially significant after Griess[1] discovered the azo-coupling reaction.[2–5] They can be easily prepared from anilines in the presence of a suitable nitrosating agent in both aqueous and aprotic media under mild conditions, and their chemical structures can be easily tailored because of the wide variety of commercially aromatic amines. Their use is not restricted to organic synthesis. For instance, they are currently exploited as starting materials in nanochemistry and colloidal chemistry to modify carbon surfaces,[6,7] to probe the interfacial compositions of colloidal aggregates[8,9] and to determine the distribution of polar molecules in emulsions.[10,11]

Arenediazonium ion chemistry is very rich and complex. Some of their most important reactions are commonly included in organic chemistry textbooks, for example, the Sandmeyer, Gomberg–Bachman, Pschorr, Merwin, and Heck. Nevertheless, various aspects of its chemistry are still far from being completely understood.[12–14] Its chemistry is dominated by the electrophilic character of the –N$_2^+$ group, which behaves as a Lewis acid reacting with nucleophiles (Lewis bases, Nu$^-$ or NuH followed by a proton loss) to give covalently bonded adducts, ArN$_2$–Nu, at β-nitrogen of the ArN$_2^+$, which is the electrophilic reactive center, Scheme 1.[2,4,14,15] The examples

of covalently bonded adducts are azo dyes (C-coupling)[3] or formation of diazo ethers (O-coupling).[14] The adducts can display geometrical isomerism, leading to the Z-(*cis*, *syn*) and E-(*trans*, *anti*) forms, Scheme 1, which show different stabilities and can be interconverted by acid catalyzed processes.[4,16]

One of the most widely yet complex reactions studied is the deceptively simple combination of the terminal nitrogen with hydroxide ions, Scheme 2(A). The reaction was discovered in the late 19th century by Griess[1] and became the source of some controversy for several years (1894–1912) between A. Hantzsch and E. Bamberger[15–17] because of the structures of the

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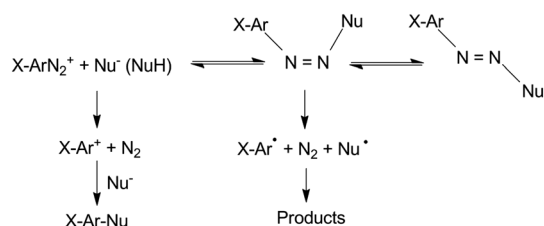
Scheme 1. Basic representation of the nucleophilic addition mechanism leading to the formation of Ar–N=N–Nu adducts in the (Z)-configuration and (E)-configuration. The competitive spontaneous decomposition of ArN_2^+, which takes place through the rate-limiting formation of a highly reactive aryl cation ($D_N + A_N$ mechanism), is also shown, Scheme 3[4,29]
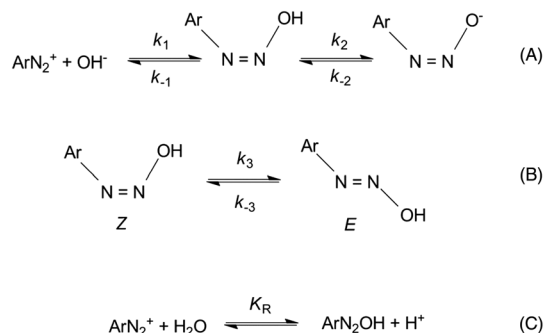
Scheme 2. Representative equilibria involved in the reaction of ArN_2^+ with OH^- ions and H_2O. A full description of the equilibria involved can be found in the recent review by C. Bravo-Díaz and in the references therein.[14] The spontaneous decomposition of ArN_2^+ ions (Scheme 1) is much slower than the reaction with OH^- or H_2O and is not displayed for clarity

products. In aqueous acid solutions (pH <4), dediazoniatons proceed almost exclusively through the $D_N + A_N$ mechanism, that is, rate-limiting formation of a highly unstable aryl cation Ar^+ that reacts immediately with nucleophiles Nu^- or NuH present in its solvation shell, Scheme 1.[4,14] However, in strongly alkaline solutions (pH >9), ArN_2^+ reacts with OH^- to give diazohydroxide, which can further react finally yielding diazoate ArN_2O^-, which is quite stable, Scheme 2(A).[4,15,16] Both diazohydroxides and diazoates may exist as Z-isomer and E-isomer, Scheme 2(B), but, for most ArN_2OH and ArN_2O^-, the rates of Z–E isomerization are orders of magnitude slower than those of the reaction between the parent ArN_2^+ and OH^-. For the sake of clarity, we will hereafter refer only to the Z-isomers, Scheme 2(A), which are the first formed as kinetically controlled products.[4,14–16]

The acid–base behavior of ArN_2^+ was extensively studied by Zollinger,[4] Lewis,[18] Ritchie,[19,20] Sterba[16,19,20], and others[21] in the years 1950s—1970s and was shown to be very complex because of different equilibria and competitive reactions involved. Here, we will summarize relevant mechanistic aspects. Further details can be found elsewhere.[2,4,14–16] On the basis of potentiometric measurements, Zollinger[4] and Sterba[16,19,20] showed that the second equilibrium constant in Scheme 2(A) is higher than the first one, that is, $K_2 >>> K_1$. As a consequence, it was not possible to determine the individual values but only their product. On the basis of kinetic experiments, Ritchie[19,20] concluded that both ArN_2^+ and ArN_2OH react with OH^- and H_2O in alkaline solution but that under the experimental conditions commonly employed in kinetic experiments to determine the rate constants k_1 and k_{-1} (pH 9–12), the reaction with H_2O is much slower than that with OH^- so that the main operating mechanism is that in Scheme 2(A) and the reaction with

H_2O (Scheme 2(C)) can be neglected.[4] If pH is increased, the forward rate constants in Scheme 2(A) became too fast to measure. On the contrary, if pH is lowered, formation of diazohydroxide may be incomplete. Depending upon the nature of the substituents, the reverse reaction (k_{-1}) and the Z–E isomerization reactions can be competitive, and the rate of diazoate formation can contribute significantly to the overall rate. As a consequence of the aforementioned and other experimental difficulties, some mechanistic aspects are still not known, and the individual K_1 and K_2 values were only determined for a few ArN_2^+.

Dediazoniations at intermediate acidities (i.e., pH 4–9) are quite different from those in aqueous acid solutions. Rate constants increase with the increasing pH, and a plethora of dediazoniation products, including diazo tars that are difficult to identify, are obtained, showing that mechanisms other than $D_N + A_N$ or the reaction with OH^- occur.[4] In previous solvolytic work, we demonstrated that aliphatic alcohols ROH react with ArN_2^+ under acidic conditions to give diazo ethers of the type $E–ArN_2OR$.[13,14,22] Formation and decomposition of such adducts were observed experimentally in the course of dediazoniations,[14] and they are usually unstable and decompose homolytically leading to the formation of reduction products. However, in some instances, they isomerize to much more stable Z-isomer, and some of them can be isolated.[23]

Here, we studied the possibility of ArN_2OH adduct formation through nucleophilic reaction between H_2O and ArN_2^+, Scheme 2 (C). We investigated adduct formation in aqueous solution under the conditions where the reaction with OH^- [Scheme 2(A)] is negligible. The difficulties mentioned earlier in kinetic investigations of ArN_2^+ in moderately acidic or alkaline solutions producing a variety of products prevent efficient and practical use of chromatographic techniques, as in the solvolytic studies with aliphatic alcohols,[14] led to a different experimental approach.

Here, we took advantage of the electrochemical properties of ArN_2^+ and determined, for the first time, the equilibrium constant K_R for the nucleophilic attack of a water molecule toward substituted ArN_2^+ in aqueous solution. Differential pulse polarography, DPP, is a convenient technique for studying dediazoniation mechanisms and to obtain valuable information not only about the parent electroactive ArN_2^+ but also on the electrochemically generated species.[24–28]

The purpose of this paper is twofold. First, to determine if azo adducts of the type ArN_2OH are formed from the nucleophilic attack of H_2O under acidic or weakly alkaline conditions just as diazo ethers are formed in reaction with alcohols ROH. We determined for the first time the equilibrium constants K_R for ArN_2OH, adduct formation, Scheme 2(C), for a number of 4-substituted ArN_2^+ with H_2O. The dependence of K_R on the Hammett σ constants indicates that K_R values are not sensitive to electronic changes induced by substituents in the aromatic ring. Second, we explored other methods besides kinetics and HPLC to expand current knowledge about the solvolytic reactions of ArN_2^+ and formation of ArN_2Nu adducts.

Previous electrochemical work shows that ArN_2^+ can be easily reduced on the surface of Hg electrode, Scheme 3.[26,30,31] In
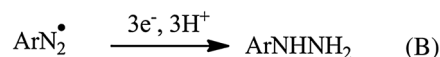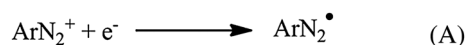
Scheme 3. Chemical processes associated with the electrochemical reduction of ArN_2^+ ions[4,29]

aprotic solvents such as CH_3CN, the reduction of ArN_2^+ is very simple, and only one single, broad, one electron wave is observed at the potentials close to 0 V versus saturated calomel electrode[6,7] showing that the aryl radical is formed directly. In aqueous solution, two polarographic waves are observed, Scheme 3.[26] The first corresponds to the transfer of one electron to yield the arenediazenyl radical, $ArN_2^\bullet$, showing a polarographic wave usually located in the potential region +0.05 V to −0.1 V (versus Ag/AgCl), a potential where a few organic compounds are electroactive, Scheme 3(A).[32] The second reduction step, Scheme 3(B), is usually detected at potentials around −0.5 V to −0.70 V involving three electrons and three protons leading to phenylhydrazine.[30] The formation of the aryl radicals in aqueous solution was confirmed by coulometry on a mercury pool and in acetonitrile (ACN) in the presence of a spin trap.[7] Figure 1 illustrates the polarographic waves of the first reduction peak of benzenediazonium ions (BD) at selected acidities.

EXPERIMENTAL

Materials

Reagents were of the maximum purity available and used as is. HCl, NaOH, the materials employed in the preparation of the Britton–Robinson buffer and arenediazonium tetrafluoroborates, $X–ArN_2^+ BF_4^-$, were from Fluka or Aldrich. BD and the substituted 4-methyl-benzenediazonium ion, 4-methoxy-benzenediazonium ion, and 4-bromo-benzenediazonium ions were prepared from the corresponding anilines (Sigma, Fluka, St. Louis, Mo, USA) following a standard non-aqueous procedure as described elsewhere.[33] 4-nitrobenzenediazonium tetrafluoroborate was purchased from Aldrich (97%) and recrystallized twice from cold water.

All solutions were made with Milli-Q grade water. Britton–Robison buffer of the desired pH was prepared by mixing solutions of 0.04 M acetic, boric, and orthophosphoric acids with the appropriate amounts of 0.2 M NaOH to obtain the desired pH. Stock $X–ArN_2^+ BF_4^-$ solutions were kept in the dark at low temperature to minimize its decomposition. The purity of $X–ArN_2^+$ was checked periodically by employing UV–vis spectroscopy.
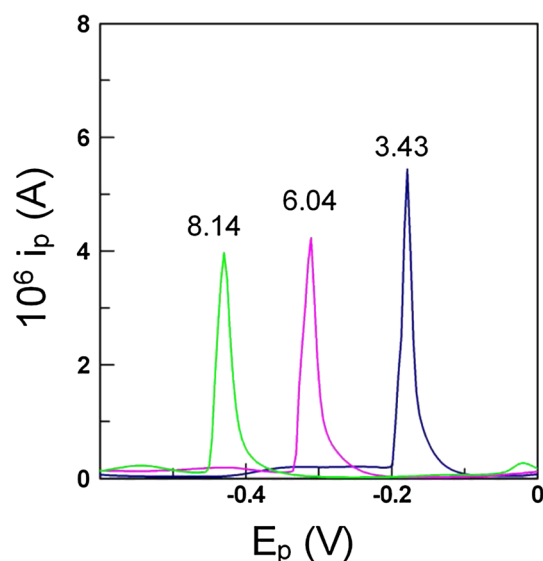
Figure 1. Representative polarograms of benzenediazonium ions obtained at different pH values. For the sake of clarity, only the first reduction peak is displayed

Instrumentation

pH values were determined from potentiometric measurements by employing a previously calibrated Elmetron CP-505 pH meter.

The DPP measurements were obtained with a computer controlled µAUTOLAB type III (Metrohm, Herisau, Switzerland) attached to a VA-stand (Mtm anko model M 165) equipped with a water jacketed voltammetric cell. Polarograms were recorded in a computer by employing the General Purpose Electrochemical Software GPES v. 4.9 (Eco Chemie, Belgium). The multimode working electrode was used in the DME mode. The three-electrode system was composed of a hanging mercury electrode, a platinum rod auxiliary electrode, and an Ag/AgCl (3 M KCl) reference electrode. All solutions used in the polarographic measurements were bubbled with N_2 gas (99.99%) for 10–15 min and kept under a N_2 atm throughout the measurements. All potentials given hereafter will be relative to the aforementioned Ag/AgCl electrode.

$X–ArN_2^+$ is thermally unstable and decompose spontaneously in aqueous acid solution ($D_N + A_N$ mechanism, Scheme 1), with half lives ranging from hours to days depending on the position and nature of the substituents in the aromatic ring.[4] At $T = 25\,°C$, 4-substituted $X–ArN_2^+$ are quite stable,[4] and no significant decomposition takes place in the time scale of a typical electrochemical experiment (0.5–3 min).

RESULTS AND DISCUSSION

Previous investigations on the electrochemical behavior of $X–ArN_2^+$ in aqueous solution show that the chemical process associated with the electrochemical reduction of $X–ArN_2^+$ is irreversible.[26] When protons are involved, as in Scheme 2(C), electron uptake may occur before or after the possible proton transfer, and it is very convenient to obtain some insights into the characteristics of the electrochemical processes and their time sequences for correct interpretation of the results. Thus, we first analyzed variations of the peak currents with temperature and concentration.
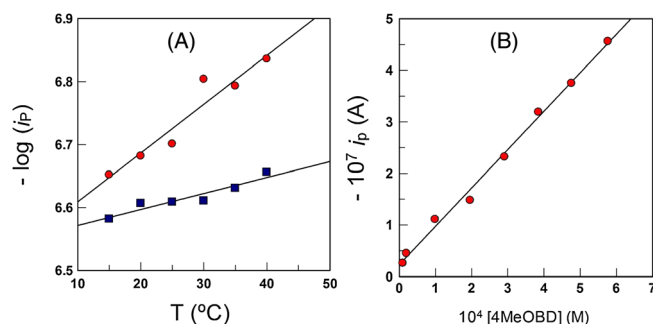
Figure 2(A) is illustrative and shows the variation of i_p with T for 4-bromo-benzenediazonium at two pH values. Similar plots were obtained for the other ArN_2^+ investigated. The slopes of the linear plots, expressed as the percentage of variation (usually denoted as the half temperature coefficient, w), yield the values of $w = (0.77 \pm 0.12)\%\,°C^{-1}$ at pH = 2.37 and $w = (0.25 \pm 0.04)\%\,°C^{-1}$ at pH = 4.7. Diffusion currents increase linearly with the temperature, with the w values much lower than those of kinetic currents, which usually range from 5 to 20% $°C^{-1}$.[34] Therefore, the calculated w values suggest that the rate of transport of ArN_2^+ from the bulk solution to the surface of the electrode is determined by its diffusion, in accordance with the previous electrochemical results,[25,26] and the corresponding peak currents are a measure of $[ArN_2^+]$ in the bulk solution. Figure 2(B) is representative and shows that the diffusion currents are proportional to $[ArN_2^+]$ according to the Ilkovic equation. Thus, the first reduction peak of ArN_2^+ is irreversible, and the variation of i_p values with $[ArN_2^+]$ is linear at least up to $[ArN_2^+] \sim 10^{-4}$ M, in accordance with the literature results.[26]

Figure 1 shows that the peak potentials E_p of the first reduction peak of ArN_2^+ depend on the pH of the medium. Figure 3 is illustrative and shows the variation of E_p with pH for two representatives $X–ArN_2^+$. Two linear segments with a break point at pH 5–6 are obtained. The slope of the first segment, S_1, is very low or negligible as shown in Table 1, indicating that the E_p values are pH-independent up to ~ pH = 5–6. However, the values of the slopes of the second linear segment, S_2, are much higher and negative, Table 1, that is, upon the
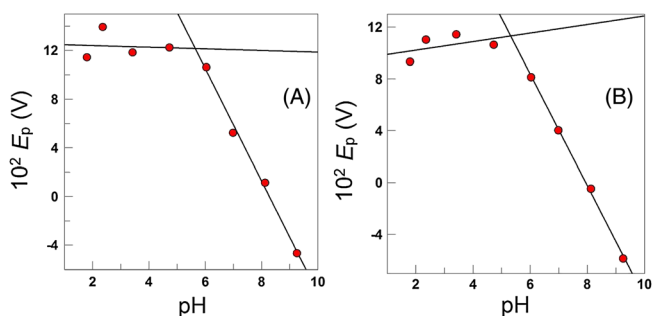
increasing pH, the E_p values are shifted in a linear fashion toward more negative values.

The results in Fig. 3 are qualitatively consistent with the hydrolysis of ArN_2^+ in dynamic equilibrium and compared with a slow rate electron transfer, Scheme 4,[34] bearing in mind that the formation of ArN_2OH through the reaction of ArN_2^+ with OH^- [Scheme 2(A)] is negligible from pH 2 to 10.[4]
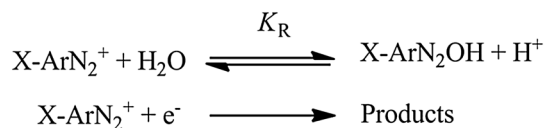
When $[H^+] >>> K_R$, ArN_2^+ is the dominant species in solution, that is, $[ArN_2^+] >>> [ArN_2OH]$, and the concentration of ArN_2OH is negligible, and hydrogen ions are not involved in

$$X\text{-}ArN_2^+ + H_2O \underset{}{\overset{K_R}{\rightleftharpoons}} X\text{-}ArN_2OH + H^+$$

$$X\text{-}ArN_2^+ + e^- \longrightarrow Products$$

Scheme 4. Dynamic equilibrium reaction of ArN_2^+ with H_2O to give ArN_2OH and a proton and its electrochemical reduction (first reduction peak)

ArN_2^+ reduction. However, at higher pH, ArN_2^+ and ArN_2OH are in dynamic equilibrium, and the rate of proton transfer is much faster than the rate of electron transfer to ArN_2^+ (or $ArN_2(OH_2)^+$).

E_p values, which are measured under conditions of dynamic equilibrium, depend (Nernst equation) on both $[ArN_2^+]$ and $[ArN_2OH]$ and thus on the values of equilibrium constant K_R (Scheme 4) and $[H^+]$. At a given pH, E_p values do not depend on $[ArN_2^+]$ (contrary to i_p); however, E_p values depend on pH. The dependence of E_p on pH shown in Fig. 3 is typical of acid–base systems in dynamic equilibrium, Scheme 4.[34,35] For such a system, the peak current for the irreversible electrodic process is given by Eqn 1[34]

$$i_p = Bk_{e^-}[ArN_2^+] \tag{1}$$

where B is the product of a number of constants that includes, among others, the number of electrons n involved and the Faraday constant F, k_{e^-} is the heterogeneous rate constant for the electrode process, which is given by Eqn 2, and $[ArN_2^+]$ is the concentration of the oxidized form at the surface of the electrode.

$$k_{e^-} = k_e^0 e^{\left(-\frac{\beta n F}{RT}\left(E_p - E^0\right)\right)} \tag{2}$$

In Eqn 2, k_e^0 is the heterogeneous rate constant of the electrode process at the standard potential E^0, β is the transfer coefficient, n is the number of electrons involved, F is the Faraday constant, and E_p is the measured peak potential.

The stoichiometric concentration of the oxidized form is

$$[ArN_2^+]_T = [ArN_2^+] + [ArN_2OH]$$

and using the equilibrium constant K_R, Eqn 3, the measured peak potential is given by Eqn 4,[34] where A is a constant.

Figure 2. (A) Effects of temperature on i_p for the first reduction peak of 4BrBD at pH = 2.37 (α) and pH = 4.7 (β), [4BrBD] ≈ 4 × 10⁻⁵ M. (B) Variation of the peak current of the first reduction peak of 4MeOBD. Experimental conditions are as follows: Britton–Robinson Buffer (0.04 M) pH = 2, ΔU = 1.25 V, v_{scan} = 0.041 V s⁻¹

Figure 3. Plots of the variation of E_p of the first reduction peak of 4MBD (A) and 4BrBD (B) with pH

Table 1. Slopes S_1 and S_2 and standard deviations of the straight lines at low (<5) pH and high (>6) pH, respectively. The S_1 values can be considered statistically 0 because the value of their standard deviation is similar or higher than the mean value. The equilibrium constant K_R values for the nucleophilic addition of water to X–ArN_2^+, Scheme 2(C), is determined from the intersection of the two straight lines, as shown in Figure 3. $σ_p$ values are collected from H. Maskill.[37] For the sake of comparison, the equilibrium constants K_{DE} for the formation of diazo ethers ArN_2OR from the reaction with alkanols ROH are also displayed

ArN_2^+	$σ_p$	$10^3 S_1$	$10^2 S_2$	pK_R	pK_{DE}
BD	0.00	−(1.3 ± 0.8)	−(5.1 ± 0.6)	5.70	—
4MBD	−0.17	−(0.7 ± 0.6)	−(4.6 ± 0.2)	5.72	3.6–5.3[a]
4MeOBD	−0.28	−(0.2 ± 0.1)	−(3.5 ± 0.1)	5.80	—
4BrBD	0.23	(0.3 ± 0.4)	−(4.3 ± 0.1)	5.20	3.5[b]
4NBD	0.78	−(0.6 ± 1)	−(14 ± 3)	5.24	4.18[c]

[a]ref.[13,38].
[b]ref.[22].
[c]ref.[39].

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$$K_R = \frac{[ArN_2OH][H^+]}{[ArN_2^+]} \quad (3)$$

$$E_p = A + \frac{RT}{nF} \ln \frac{[H^+]}{K_R + [H^+]} \quad (4)$$

When $[H^+] \gg K_R$, Eqn 4 simplifies to Eqn 5, showing that, at low pH, the slope of the variation of E_p with pH should be 0 (i.e., E_p values are pH independent) as shown in Fig. 3.

$$E_p = A \quad (5)$$

When $[H^+] \ll K_R$, Eqn 4 can be rearranged into Eqn 6, which predicts that, upon the increasing pH, the peak potentials become more negative as illustrated in Fig. 3.

$$E_p = A - \frac{RT}{nF} \ln K_R - \frac{2.3RT}{nF} pH \quad (6)$$

Note that Eqn 6 predicts that the variation of E_p values with increasing pH is linear with a negative S_2 slope and eventually, E_p values may become negative as shown in Fig. 3.

At the intersection point of the two straight lines in Fig. 3(A,B), the E_p values are the same and thus, according to Eqn 6, the equilibrium constant K_R, Scheme 4, is numerically equal to the pH at that point (i.e., pK_R = pH). The determined pK_R values are collected in Table 1. The obtained K_R values indicate that electronic changes induced by substituents are very small as illustrated in Fig. 4, where the Hammett plot is displayed. The slope of the linear plot is rather small, $\rho = 0.58$, but positive, suggestive of an increase in the electron density on the atom adjacent to the ring during the reaction.[36] That is, the positive charge on the diazonium group becomes neutral in diazohydroxide.

It may be illustrative to compare the nucleophilic reactions of ArN_2^+ with aliphatic alcohols ROH, Scheme 5, and those with water (HOH). On the basis of the nucleophilicity of the solvents, one would expect less homolytic products in water than in alcohols, but this is not the case. Dediazoniations in weakly alkaline aqueous solutions produce a complex mixture of dediazoniation products formed (sometimes diazo tars); however, in alcohols, the number of products rarely exceeds three or four and diazo tars seldom form.[4]

The reactions of ArN_2^+ with the alkoxide ions, RO^-, lead to the formation of diazo ethers of the type Ar–N=N–O–R,[14] Scheme 1, which are structurally similar compounds to those obtained from the reaction with OH^-. However, the kinetics and mechanism of these O-coupling reactions are quite different because the primary Z-diazoether product cannot further react with the other RO^- (or OH^-) ion, that is, deprotonation is not possible as in the case of diazohydroxides, Scheme 2(A). Alkoxide ions are much less solvated in alcohols than the OH^- ions in water, and because the relative permittivity of the alcohols is substantially lower than that of water, the reaction of ArN_2^+ with RO^- is much faster than that with OH^-, the reverse reaction is much slower, and the equilibrium is shifted toward the O-adducts.[4]

As discussed before, the spectroscopic or chromatographic characterization of the ArN_2OH adducts is difficult, and we only know about their formation because of the variations in the peak potential of X–ArN_2^+ with pH. However, the results obtained here
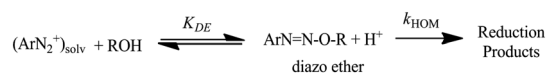
Scheme 5. Proposed reaction mechanism for the formation and decomposition of diazo ethers under acidic conditions
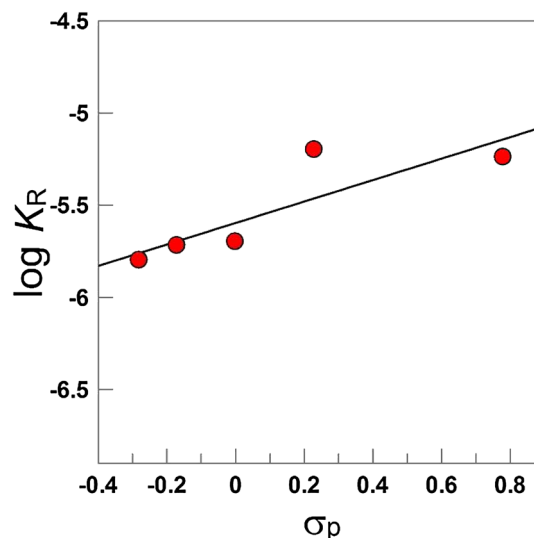
Figure 4. Effects of substituents on the formation of diazohydroxides according to Scheme 4; σ_p values are from H. Maskill[37]

reinforce the idea that the formation of diazo ether adducts of the type Ar–N=N–O–X is general because diazo ethers are also formed in reactions with alcohols other than alkanols under acidic conditions.[14] For instance, ArN_2^+ reacts with molecules bearing OH groups in their molecular structure such as gallic acid (3,4,5-tryhydroxybenzoic acid) and some of their derivatives,[14] ascorbic acid (vitamin C), and cyclodextrins.[12,25] ArN_2^+ reacts with alkanols ROH (MeOH, EtOH, and BuOH) to give the corresponding adduct ArN_2OR, Scheme 1, and because deprotonation is not possible, the ArN_2OR either isomerizes to much more stable E-diazo ether or decomposes homolytically in the rate-determining step leading to the formation of reduction products. Some representative values for the equilibrium constant K_{DE}, are shown in Table 1. The K_{DE} values are not very different from those obtained in aqueous solution, but because the K_{DE} values are only known for a limited number of ArN_2^+, no general comparisons can be performed, and more work on their formation and decomposition reactions is warranted.

CONCLUSIONS

In conclusion, we have been able to show that ArN_2OH adducts are formed from nucleophilic attack of reaction of H_2O with X–ArN_2^+ under acidic conditions and to estimate, for the first time, the equilibrium constant K_R for the formation of diazohydroxides ArN_2OH formed by the nucleophilic attack of H_2O at a number of 4-substituted ArN_2^+ by employing DPP. The K_R values, obtained from variations of the peak potential of the first reduction peak with pH, range 5–6 and are rather insensitive to substituent effect.

Differential pulse polarography has been shown to be very useful to investigate chemical behavior of ArN_2^+ in aqueous solution. Compared with the methods used in the past to determine the ionization constants of ArN_2^+ (mainly spectrometric – stopped flow

– and potentiometric), DPP has the advantage of its high selectivity and sensitivity, allowing to overcome some of the major problems found in the past. In addition, the electrochemical experiments can be performed in a short period making that the spontaneous decomposition of ArN$_2^+$ be negligible. Moreover, DPP has also been shown to be very useful in kinetic studies and valuable information not only on the parent ArN$_2^+$ but also on the electrochemically generated aryl radicals Ar$^•$, for instance, the association constants of Ar$^•$ with sodium dodecyl sulfate micelles and cyclodextrins were obtained by employing this technique.[24,25]

Our results show that the formation of diazo adducts with neutral nucleophiles is much more common than expected, and our results should also contribute to obtain a substantial body of knowledge to propose a unified, general, picture about the formation and decomposition of diazo ethers with neutral nucleophile. The determination of the equilibrium constants for the formation of adducts of the type ArN=N–OR under acidic conditions is recent in the time scale of the ArN$_2^+$ chemistry, and further work to determine the corresponding equilibrium constants and to analyze their dependence with the nature and position of the substituents in the aromatic ring is warranted.

The results are of some importance to the azo dye and pigment industries[3] because in electrophilic substitution reactions, it is the most basic form of the nucleophilic substrate (i.e., the phenoxide ion or the free aromatic amine), the one which gives rise to the highest rates of substitution, and thus the formation of diazohydroxides may be competitive. They are also of some importance to explore novel applications of ArN$_2^+$ in colloidal, organic, and in nanochemistry, where most of the reactions of ArN$_2^+$ are carried out in aqueous or low polarity solvents, and the grafting of surfaces from ArN$_2$Nu adducts is being explored.[7]

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