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$$^+$ from kinetic measurements but not with H$_2$O ($K_0$). Here, we have exploited the electrochemical properties of ArN$_2$$^+$ 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 $K_R$ values are 5–6, and they are somewhat higher than those obtained for the reaction of ArN$_2$$^+$ with alcohols ROH ($pK_{DE} = 3–5$) 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.

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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.$^{[2,3]}$ 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, Pschor, Mervin, 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)$^{[15]}$ 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.$^{[14,16]}$

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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products. In aqueous acid solutions (pH < 4), dediazoniations proceed almost exclusively through the \( \text{D}_{\text{N}} + \text{ArN}_2^+ \) mechanism, that is, rate-limiting formation of a highly unstable aryl cation \( \text{Ar}^+ \) that reacts immediately with nucleophiles Nu or NuH present in its solvation shell, Scheme 1.\(^{[4,14]}\) However, in strongly alkaline solutions (pH > 9), \( \text{ArN}_2^+ \) reacts with \( \text{OH}^- \) to give diazohydroxide, which can further react finally yielding diazoate \( \text{ArN}_2\text{O}^- \), which is quite stable, Scheme 2(A).\(^{[4,15,16]}\) Both diazohydroxides and diazoates may exist as \( \text{Z} \)-isomer and \( \text{E} \)-isomer, Scheme 2(B).\(^{[14]}\) The competitive spontaneous decomposition of \( \text{ArN}_2^+ \) ions (Scheme 1) is much slower than the reaction with \( \text{OH}^- \) or \( \text{H}_2\text{O} \) and is not displayed for clarity.

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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–ArN₂⁺BF₄⁻, 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. 4-nitrobenzenediazonium tetrafluoroborate was purchased from Aldrich (97%) and recrystallized twice from cold ether.

All solutions were made with Milli-Q grade water. Britton–Robinson 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–ArN₂⁺BF₄⁻ solutions were kept in the dark at low temperature to minimize its decomposition. The purity of X–ArN₂⁺ was checked periodically by employing UV–vis spectroscopy.

RESULTS AND DISCUSSION

Previous investigations on the electrochemical behavior of X–ArN₂⁺ in aqueous solution show that the chemical process associated with the electrochemical reduction of X–ArN₂⁺ is irreversible. 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 ArN₂⁺ 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 ± 0.12)% °C⁻¹ at pH = 2.37 and w = (0.25 ± 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. Therefore, the calculated w values suggest that the rate of transport of ArN₂⁺ from the bulk solution to the surface of the electrode is determined by its diffusion, in accordance with the previous electrochemical results and the corresponding peak currents are a measure of [ArN₂⁺] in the bulk solution. Figure 2(B) is representative and shows that the diffusion currents are proportional to [ArN₂⁺] according to the Ilkovic equation. Thus, the first reduction peak of ArN₂⁺ is irreversible, and the variation of i_p values with [ArN₂⁺] is linear at least up to [ArN₂⁺] ~10⁻⁸ M, in accordance with the literature results.

Figure 1 shows that the peak potentials E_p of the first reduction peak of ArN₂⁺ depend on the pH of the medium. Figure 3 is illustrative and shows the variation of E_p for two representatives X–ArN₂⁺. Two linear segments with a break point at pH 5–6 are obtained. The slope of the first segment, S₁, 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, S₂, 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$_2$OH through the reaction of ArN$_2$O$^+$ with OH$^-$ [Scheme 2(A)] is negligible from pH 2 to 10.[4]

When $[\text{H}^+] \gg \gg K_R$, ArN$_2^+$ is the dominant species in solution, that is, $[\text{ArN}_2^+] \gg \gg [\text{ArN}_2\text{OH}]$, and the concentration of ArN$_2$OH is negligible, and hydrogen ions are not involved in ArN$_2$O$^+$ reduction. However, at higher pH, ArN$_2$O$^+$ and ArN$_2$OH are in dynamic equilibrium, and the rate of proton transfer is much faster than the rate of electron transfer to ArN$_2$O$^+$ (or ArN$_2$(OH)$_2$)$^+$. $E_p$ values, which are measured under conditions of dynamic equilibrium, depend (Nernst equation) on both $[\text{ArN}_2^+]$ and $[\text{ArN}_2\text{OH}]$ and thus on the values of equilibrium constant $K_R$ (Scheme 4) and $[\text{H}^+]$. At a given pH, $E_p$ values do not depend on $[\text{ArN}_2\text{OH}]$ (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 electrochemical process is given by Eqn 1[34]

$$i_p = Bke^{-\frac{EF_o - E_p}{RT}}$$

where B is the product of a number of constants that includes, among others, the number of electrons $n$ involved and the Faraday constant $F$, $ke$ is the heterogeneous rate constant for the electrode process, which is given by Eqn 2, and $[\text{ArN}_2^+]$ is the concentration of the oxidized form at the surface of the electrode.

The stoichiometric concentration of the oxidized form is

$$[\text{ArN}_2^+] = [\text{ArN}_2^+] + [\text{ArN}_2\text{OH}]$$

and using the equilibrium constant $K_{OE}$, Eqn 3, the measured peak potential is given by Eqn 4,[34] where A is a constant.

### 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. $\sigma_p$ values are collected from H. Maskill.[37] For the sake of comparison, the equilibrium constants $K_{OE}$ for the formation of diazo ethers ArN$_2$OR from the reaction with alkanols ROH are also displayed.

<table>
<thead>
<tr>
<th>ArN$_2^+$</th>
<th>$\sigma_p$</th>
<th>$10^3 S_1$</th>
<th>$10^2 S_2$</th>
<th>p$K_R$</th>
<th>p$K_{OE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>0.00</td>
<td>$-(1.3 \pm 0.8)$</td>
<td>$-(5.1 \pm 0.6)$</td>
<td>5.70</td>
<td>—</td>
</tr>
<tr>
<td>4MBD</td>
<td>$-0.17$</td>
<td>$-(0.7 \pm 0.6)$</td>
<td>$-(4.6 \pm 0.2)$</td>
<td>5.72</td>
<td>3.6–5.3$^a$</td>
</tr>
<tr>
<td>4MeOBd</td>
<td>$-0.28$</td>
<td>$-(0.2 \pm 0.1)$</td>
<td>$-(3.5 \pm 0.1)$</td>
<td>5.80</td>
<td>—</td>
</tr>
<tr>
<td>4BrBD</td>
<td>0.23</td>
<td>$(0.3 \pm 0.4)$</td>
<td>$-(4.3 \pm 0.1)$</td>
<td>5.20</td>
<td>3.5$^b$</td>
</tr>
<tr>
<td>4NBD</td>
<td>0.78</td>
<td>$-(0.6 \pm 1)$</td>
<td>$-(14 \pm 3)$</td>
<td>5.24</td>
<td>4.18$^c$</td>
</tr>
</tbody>
</table>

$^a$Ref.[13,38] $^b$Ref.[22] $^c$Ref.[39]
The reactions of \( \text{ArN}_2\text{OH} \) with aliphatic alcohols \( \text{ROH} \), Scheme 5, and those with water (\( \text{H}_2\text{O} \)) 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 \( \text{ArN}_2^+ \) with the alkoxide ions, \( \text{RO}^- \), lead to the formation of diazo ethers of the type \( \text{Ar–N=O–R} \),\(^{[14]}\) Scheme 1, which are structurally similar compounds to those obtained from the reaction with \( \text{OH}^- \). 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 \( \text{RO}^- \) (or \( \text{OH}^- \)) ion, that is, deprotonation is not possible as in the case of dediazonidences, Scheme 2(A). Alkoxide ions are much less solvated in alcohols than the \( \text{OH}^- \) ions in water, and because the relative permittivity of the alcohols is substantially lower than that of water, the reaction of \( \text{ArN}_2^+ \) with \( \text{RO}^- \) is much faster than that with \( \text{OH}^- \), 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 \( \text{ArN}_2\text{OH} \) adducts is difficult, and we only know about their formation because of the variations in the peak potential of \( \text{X–ArN}_2^+ \) with pH. However, the results obtained here reinforce the idea that the formation of diazo ether adducts of the type \( \text{Ar–N=O–X} \) is general because diazo ethers are also formed in reactions with alcohols other than alkanols under acidic conditions.\(^{[14]}\) For instance, \( \text{ArN}_2^+ \) reacts with molecules bearing \( \text{OH} \) groups in their molecular structure such as gallic acid (3,4,5-trihydroxybenzoic acid) and some of their derivatives,\(^{[14]}\) ascorbic acid (vitamin C), and cyclodextrins.\(^{[12,25]}\) \( \text{ArN}_2^+ \) reacts with alkanols \( \text{ROH} \) (MeOH, EtOH, and BuOH) to give the corresponding adduct \( \text{ArN}_2\text{OR} \), Scheme 1, and because deprotonation is not possible, the \( \text{ArN}_2\text{OR} \) 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 \( K_{\text{DE}} \) are shown in Table 1. The \( K_{\text{DE}} \) values are not very different from those obtained in aqueous solution, but because the \( K_{\text{DE}} \) values are only known for a limited number of \( \text{ArN}_2^+ \), 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 \( \text{ArN}_2\text{OH} \) adducts are formed from nucleophilic attack of reaction of \( \text{H}_2\text{O} \) with \( \text{X–ArN}_2^+ \) under acidic conditions and to estimate, for the first time, the equilibrium constant \( K_R \) for the formation of dediazonicides \( \text{ArN}_2\text{OH} \) formed by the nucleophilic attack of \( \text{H}_2\text{O} \) at a number of 4-substituted \( \text{ArN}_2^+ \) 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 \( \text{ArN}_2^+ \) in aqueous solution. Compared with the methods used in the past to determine the ionization constants of \( \text{ArN}_2^+ \) (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 ArN₂⁺ can be negligible. Moreover, DPP has also been shown to be very useful in kinetic studies and valuable information not only on the parent ArN₂⁺ 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 ArN₂⁺ 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 industries³ 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 ArN₂⁺ in colloidal, organic, and in nanochemistry, where most of the reactions of ArN₂⁺ are carried out in aqueous or low polarity solvents, and the grafting of surfaces from ArN₂Nu adducts is being explored.²⁷

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