

# Kinetics and Mechanisms of Aryldiazonium Ions in Aqueous Solutions



Carlos Bravo-Díaz and Elisa González-Romero

Dedicated to Prof. Laurence S. Romsted (Rutgers, the State University of New Jersey, USA) for introducing us to the very complex—yet fascinating—chemistry of aryldiazonium ions, for his continuous support, encouragement, extremely fruitful discussions, and, most importantly, for his friendship.

**Abstract** In aqueous acid solution and in mixed alcohol-water solvents ( $[H_3O^+] > 10^{-2}$  M), in the dark and in the absence of reductants, the spontaneous decomposition of aryldiazonium,  $ArN_2^+$ , salts proceeds through borderline  $S_N1$  ( $D_N + A_N$ )- $S_N2$  mechanisms. The rate constant values depend strongly on the nature of the substituents attached to the aromatic ring of  $ArN_2^+$  and, for those with electron-withdrawing substituents, on solution composition. The product distribution is proportional to the composition of the solvation shell of the *ipso* carbon, which reflects the composition of the water/cosolvent mixture. However, upon decreasing moderately the acidity, reactions involving the formation of diazohydroxides,  $ArN_2OH$ , diazoethers,  $ArN_2OR$ , and diazoates,  $ArN_2O^-$ , become competitive and may even be the main decomposition pathway. The stability of  $ArN_2OH$ ,  $ArN_2OR$ , and  $ArN_2O^-$  species (which may coexist with  $ArN_2^+$  in solution) is intimately related to the *Z-E* (*syn-anti*, *cis-trans*) isomerization of the O-adducts, so that they may undergo further reactions when they are components of a Lewis acid-base equilibrium, or undergo homolytic scission to produce homolytic reduction products. In this book chapter, we aim to provide the reader with a practical and (hopefully) useful view of the complex chemistry of  $ArN_2^+$  in aqueous and mixed alcohol-water solutions, mainly covering the kinetics and mechanisms of the reactions. In a last section, we introduce some analytical methods for the determination of diazonium salts and their degradation products.

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## 1 Introduction

Aryldiazonium,  $\text{Ar-N}_2^+$ , and ions played a major role in organic chemistry since their discovery in 1858 by Peter Griess [1, 2]. From a historical perspective, the chemistry of aryldiazonium salts has been developed, in most instances, in aqueous media, and classical applications of arenediazonium salts include the Sandmeyer, Balz-Schieman, Gomberg-Bachman, Pschorr, and Meerwein reactions [3–5]. In the last decades, there has been renewed interest in their use as reactants in solvents other than water and alcohols, in catalytic cross-coupling reactions, [6, 7] in the chemical-biological field through modifications of amino acids, peptides, and proteins, [8] with functionalization of surfaces [9–12] and as chemical probes for probing interfacial concentrations of nucleophiles in a variety of colloidal systems [13, 14].

The utility of aryl diazonium salts in the solid-state may be, however, diminished by their potential instability, which is often governed by the nature of the counterion, [3, 15] and during the second half of the twentieth century, some chemists focused in developing synthetic methods to prepare more stable aryldiazonium salts, mostly in the form of tetrafluoroborates, hexafluorophosphates, tosylates, and disulfonamides (Chap. 2) [15, 16]. The tetrafluoroborates, in particular, can often be easily prepared and isolated as crystalline solids that can be stored in the dark, in the absence of water, at low temperatures for months to years without significant decomposition (Chap. 2) [3].

When in solution, aryldiazonium,  $\text{ArN}_2^+$ , ions may behave as Lewis acids, thus reacting with Lewis bases (nucleophiles  $\text{Nu}^-$  or  $\text{NuH}$  followed by loss of a proton) to yield covalently bonded adducts,  $\text{ArN}_2\text{-Nu}$ , at the electrophilic reactive center (the  $\beta$ -nitrogen of  $\text{ArN}_2^+$ ) [3, 4]. Typical examples of the  $\text{ArN}_2\text{-Nu}$  adducts are the azo dyes, which are formed through a C-coupling mechanism [3, 17]. The formation of azo dyes takes place when  $\text{ArN}_2^+$  ions react with aromatic substrates containing strong electron donors such as hydroxy or amino groups [17]. Covalently bonded adducts can also be formed with other nucleophiles leading to O-, S-, N-, and P-adducts [3, 4, 18].

This book chapter will focus exclusively on the reactivity of aryldiazonium ions in aqueous solution, with particular emphasis on the formation of O-coupling adducts of the type  $\text{ArN} = \text{NO-Nu}$  because  $\text{H}_2\text{O}$  and alcohol/water mixtures, together with  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  mixtures (in  $\text{CH}_3\text{CN}$ , the corresponding acetamides are formed [19]) are, by far, the most important solvents for diazonium salts, and where a variety of nucleophiles can be present or dissolved depending on experimental conditions [3]. Details on reactions in other solvents can be found elsewhere [3, 18]. The synthesis of  $\text{ArN}_2^+$ , their classical reactions such as the Sandmeyer reaction, and their recent applications will not be covered as this material can be found in other chapters of the present book and in specialized books or reviews [3, 4, 17, 20, 21]. In addition, the chemistry of alkanediazonium,  $\text{RN}_2^+$ , ions will not be covered here because they are of much less practical application than the aromatic ones because of their much lower stability [20, 22].

Furthermore, the present book chapter is not intended to be exhaustive in covering all literature but is rather aimed to provide the reader a broad view of the complex chemistry of  $\text{ArN}_2^+$  in aqueous solution, with special emphasis on the kinetics and mechanism of the reactions involved. Indeed, this solution chemistry has important consequences in the grafting of diazonium salts. In the next sections, we will discuss the various mechanisms in some detail.

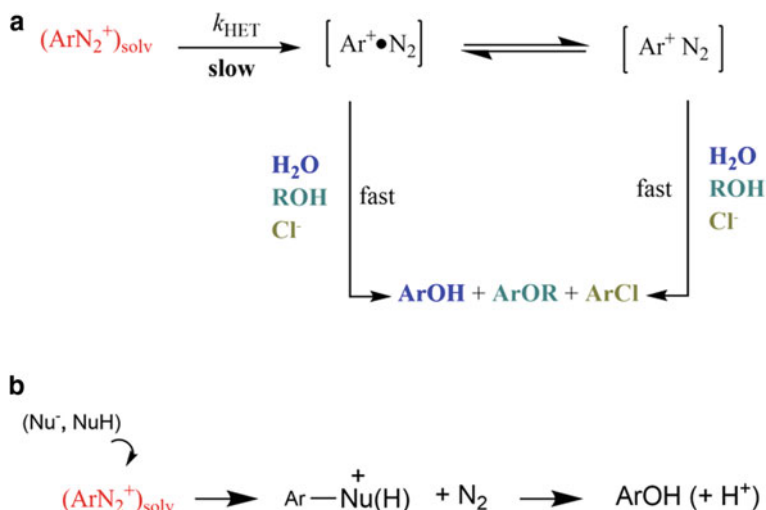
## 2 A Brief Survey of the Chemistry of Arenediazonium Ions in Aqueous Solutions

One of the most important—but mechanistically complicated—reaction is the deceptively spontaneous decomposition of ground state  $\text{Ar-N}_2^+$  in aqueous solution and in alcohol/water mixtures. Part of the complexity of the reaction arises from the fact that water and aliphatic and aromatic alcohols (ROH, ArOH) may also act as a neutral nucleophiles in addition to act as a solvents, and, depending on the pH, can even ionize so that species such as  $\text{OH}^-$  and  $\text{ArO}^-$  may be present in solution and act as potential nucleophiles [18, 23–25].

The reaction of  $\text{ArN}_2^+$  with water was first reported by Griess in the late nineteenth century and its “apparent” complexity made it to be the origin of some scientific controversy between E. Bamberger and A. Hantzsch for almost two decades (1894–1912) because of the structures of the products [3, 4, 26, 27]. In aqueous acid solution ( $\text{pH} < 2$ ), in the absence of reductants, and in the dark, the mechanism of the spontaneous decomposition of  $\text{ArN}_2^+$  is still a matter of debate, as there is not yet clear evidence if the reaction proceeds through  $\text{S}_{\text{N}}1$  ( $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ ) or  $\text{S}_{\text{N}}2$  mechanisms, Scheme 1, leading to the formation of heterolytic products [19, 28–30]. A decrease in the acidity of the solution modifies the mechanism of their spontaneous decomposition so that between  $\text{pH} \sim 4$  and  $\sim 9$ , diazohydroxides,  $\text{ArN}_2\text{OH}$ , and diazoethers,  $\text{ArN} = \text{N-OR}$ , are formed from the reaction of  $\text{ArN}_2^+$  with  $\text{H}_2\text{O}$  and ROH, respectively, which in this case act as a nucleophiles) [3, 18, 26, 27]. When phenoxide  $\text{ArO}^-$  ions are present,  $\text{ArN}_2^+$  may also react with them and diazoethers  $\text{Ar-N} = \text{N-OAr}'$  may be formed [18]. Both  $\text{ArN}_2\text{OH}$  and  $\text{ArN} = \text{N-OR}$  or ( $\text{Ar-N} = \text{N-OAr}'$ ) may undergo homolytic decomposition, leading to the formation of reduction products and, in some instances, tarry materials [4].

In aqueous alkaline solutions ( $\text{pH} > 9$ ),  $\text{ArN}_2^+$  function as Lewis acids, reacting at the terminal nitrogen with  $\text{OH}^-$ , and diazohydroxides  $\text{ArN}_2\text{OH}$  are formed which can further react with  $\text{OH}^-$  to finally form diazoates  $\text{ArN}_2\text{O}^-$ , which are quite stable and can be isolated [3, 18].

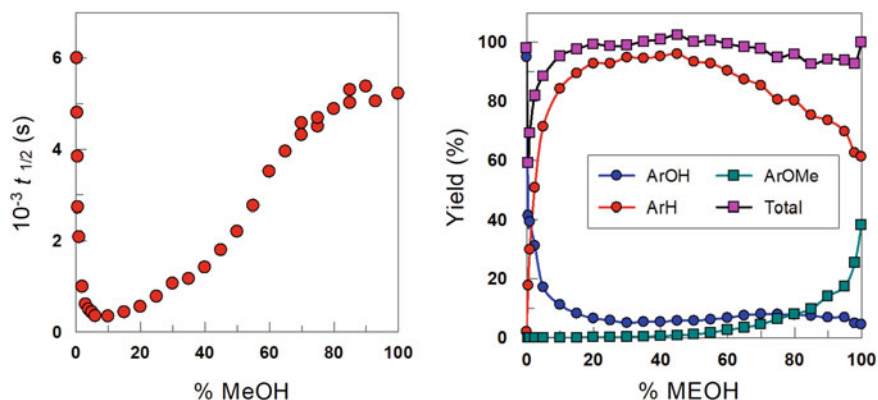
Spontaneous dediazoniations, thus, may involve a variety of mechanisms and the following example should be sufficient to illustrate how apparently minor modifications in the experimental conditions may lead to major changes in the dediazonation kinetics and in the product distributions. In aqueous acid solution, in the dark and in the absence of reductants, dediazonation of 4-nitrobenzenediazonium (PNBD)



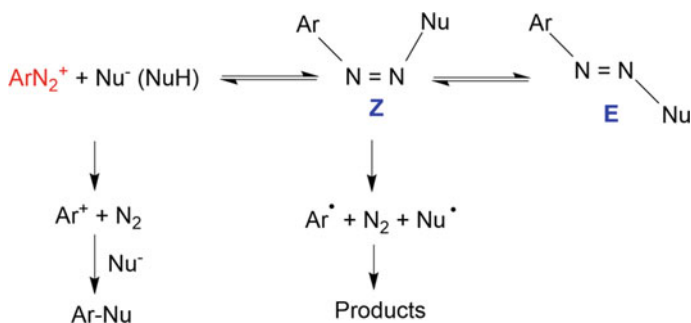
**Scheme 1** **a** Ionic or heterolytic  $\text{S}_{\text{N}}1$  ( $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ ) dediazonation mechanism in the presence of various nucleophiles illustrating the formation of an intimate ion•molecule or a solvent separated ion-molecule pair that traps all nucleophiles available in their solvation shell **b**  $\text{S}_{\text{N}}2$  dediazonation mechanism. In both cases, heterolytic products are formed. The selectivity of  $\text{ArN}_2^+$  against nucleophiles is very low, an argument commonly employed as an evidence for the  $\text{S}_{\text{N}}1$  mechanism against the  $\text{S}_{\text{N}}2$  one [3, 31, 32].

follows the  $\text{S}_{\text{N}}1$  mechanism depicted in Scheme 1, with a half-life  $t_{1/2} = 1383$  min [33]. However, addition of small amounts of MeOH leads to non-first-order kinetics compatible with a radical mechanism, so that  $t_{1/2} \approx 6$  min at 10% (v:v) MeOH, Fig. 1. Interestingly enough, a further increase in [MeOH] makes the reaction to progressively revert to a first-order behavior, slowing down the rate of dediazonation so that at percentages of MeOH higher than 90%, clean first-order kinetics are obtained with  $t_{1/2} \approx 77$  min. In the absence of MeOH, 4-nitrophenol (product from heterolytic cleavage) is formed in quantitative yield; however, at only 20% MeOH, the reduction product nitrobenzene (product from homolytic cleavage) is obtained in more than 90% and the yield of 4-nitrophenol is less than 10%. Upon increasing the MeOH content of the solution, the formation of 4-nitroanisole (obtained from the heterolytic reaction between PNBD and MeOH, Scheme 1) becomes competitive and, at 99% MeOH, both nitrobenzene (60%) and 4-nitroanisole (40%) are obtained [33]. The reduction product 4,4-dinitrophenyl (obtained from the coupling reaction of two Ar• radicals) is detected only at MeOH percentages in the range 0.5–15%.

A major feature that needs to be considered when dealing with reactions where  $\text{ArN}_2\text{ONu}$  adducts are formed is the geometrical *Z-E* (*syn-anti*) isomerism, Scheme 2, leading to the *Z*-(*anti*) and *E*-(*syn*) forms. Isomerization is possible in reactions of  $\text{ArN}_2^+$  with nucleophiles  $\text{Nu}^-$  where the nitrogen-nitrogen double-bond is retained, i.e.,  $\text{R}-\text{N}=\text{N}-\text{R}'$  (R and R' can be alkyl or aryl residues). Their formation was recognized experimentally as early as 1938 by Hartley [34] after Hantzsch and Werner [35]



**Fig. 1** Variations of the half-life (left) and of the product distribution (right) for the spontaneous decomposition of 4-nitrobenzenediazonium as a function of the percentage of MeOH (v:v) in solution. Up to four products can be detected depending on experimental conditions, 4-nitrophenol (ArOH), 4-nitroanisole (ArOMe), nitrobenzene (ArH), and 4,4-dinitrobiphenyl (only detected in the range 0.5–15%). Adapted with permission from ref. [33], copyright 2006 Wiley–VCH Verlag



**Scheme 2** *Z* (*syn*)-*E* (*anti*) isomerism following the formation of  $\text{Ar}-\text{N}=\text{N}-\text{Nu}$  adducts which may undergo homolytic scission. The competitive spontaneous decomposition of  $\text{ArN}_2^+$  through the formation of a highly reactive aryl cation ( $\text{S}_{\text{N}}1$  mechanism, Scheme 1) is also shown for illustrative purposes. Dediazoniations that follow homolytic mechanisms are always (as far as they are known today) faster than the heterolytic ones. Adapted with permission from ref. [18], copyright 2011 J. Wiley & Sons

put forward the hypothesis of their existence [3] and was investigated by employing a variety of nucleophiles such as  $\text{Nu} = \text{O}^-$  (diazoates),  $\text{Nu} = \text{RO}^-$  (diazoethers),  $\text{Nu} = \text{SO}_3^-$  (sulfonates),  $\text{Nu} = -\text{SO}_2-\text{Ar}$  (sulfones),  $\text{Nu} = \text{CONH}_2$  (carboxamides) and  $\text{Nu} = \text{S-R}$ ,  $\text{S-Ar}$  (diazothioethers),  $\text{Nu} = \text{CN}^-$  (cyanides) and  $\text{Nu} = \text{R}^1-\text{NH}-\text{R}^2$  (triazenes).  $\text{ArN}_2\text{OH}$  adducts are components of a Lewis acid-base equilibrium and react with  $\text{OH}^-$  ions to give diazoates,  $\text{ArN}_2\text{O}^-$ .

In most instances, the *Z*-isomer is the kinetically controlled product, but the *E*-isomers are thermodynamically more stable. *Z*-isomers are formed in reactions with

$\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{RO}^-$ ,  $\text{CN}^-$  and  $\text{SO}_3^{2-}$ , whereas *E*-compounds are formed with reactants such as phenols and tertiary amines. Further details on the *Z-E* isomerism can be found elsewhere [3, 4, 18].

O-adducts may also be formed when reacting with nucleophiles  $\text{Nu}^-$  other than  $\text{OH}^-$ , but their formation, identification, and isolation may be very difficult because their stability depends on the leaving ability of the nucleophile involved in the reaction. If the reactant  $\text{Nu}^-$  is a poor leaving group (even if it is a good nucleophile), such as ascorbate or gallate—3,4,5-trihydroxybenzoate- ions, some stabilization may occur by conversion to the thermodynamically stable isomer (*Z-E* isomerization) [36, 37]. If  $\text{Nu}^-$  is a good nucleophile and good leaving groups, such as halide or acetate ions, the equilibrium lies largely on the side of reactants so that formation of O-adduct is negligible and  $\text{ArN}_2^+$  undergoes spontaneous decomposition through the heterolytic mechanism [3, 23, 38]. In some instances, isomerization is not possible and the adduct splits homolytically to finally give reduction products [33, 39, 40].

### 3 Kinetics and Mechanisms of Spontaneous Decomposition of $\text{ArN}_2^+$ in Aqueous Solution and in Alcohol-Water Mixtures

#### 3.1 *Dediazoniations Under Acidic (pH < 2) Conditions*

It is generally accepted that in aqueous acid ( $\text{pH} < 3$ ) solution, in the absence of reductants and in the dark, the spontaneous hydrolysis of aryldiazonium salts afford phenols through borderline  $\text{S}_{\text{N}}1$ - $\text{S}_{\text{N}}2$  mechanisms, Scheme 1 [3, 18, 26, 31]. A variety of studies including  $\text{N}_2$  incorporation and rearrangement substituent effects, nucleophile and solvent effects have led to the widely accepted mechanism involving the rate-determining loss of  $\text{N}_2$  and formation of an extremely reactive aryl cation intermediate,  $\text{Ar}^+$ , that reacts with nucleophiles in its solvation shell in a time faster than that required for cation diffusion out of the solvent cage [3, 13, 19, 26, 28]. However, recent reports, mostly based on theoretical calculations, suggest that the formation of a free phenyl cation is not an obligatory intermediate and that a borderline  $\text{S}_{\text{N}}1$ - $\text{S}_{\text{N}}2$  mechanism is compatible with experimental results [19, 28, 29].

Table 1 collects some values for the half-lives for the spontaneous decomposition of various arenediazonium ions in different aqueous solvents. As shown,  $\text{ArN}_2^+$  decomposes spontaneously in aqueous acid and alcohol/water mixtures ( $[\text{H}_3\text{O}^+] < 10^{-2} \text{ M}$ ), with half-lives ranging from minutes to hours, depending on the substituents in the aromatic ring. Solvolytic studies in alcohol-water ( $\text{ROH}/\text{H}_2\text{O}$ ) or acetonitrile-water ( $\text{ACN}/\text{H}_2\text{O}$ ) mixtures show that, in aqueous acid solution, aryldiazonium ions undergo preferential solvation by water, [23, 40, 41] results confirmed later by classical molecular dynamics calculations of solvent distribution around  $\text{ArN}_2^+$  for

**Table 1** Values of the half-lives and activation energies for the heterolytic (HET) and homolytic (HOM) dediazonation processes of some X-ArN<sub>2</sub><sup>+</sup> in different solvents

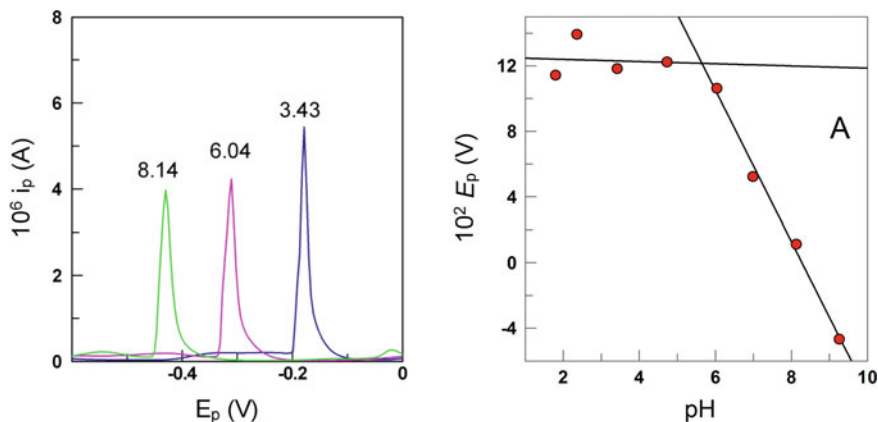
X-ArN <sub>2</sub> <sup>+</sup>	Solvent (v:v)	<i>t</i> <sub>1/2</sub> (HET) s	<i>t</i> <sub>1/2</sub> (HOM) s	<i>E</i> <sub>a</sub> (HET) kJ mol <sup>-1</sup>	<i>E</i> <sub>a</sub> (HOM) kJ mol <sup>-1</sup>
X = 4-Me	H <sub>2</sub> O	3450	–	110	–
	70–30 EtOH-H <sub>2</sub> O	359	35	116	77
	90–10 BuOH-H <sub>2</sub> O	1000	144	103	74
	75–25 BuOH	1200	4	–	76
	35–65 TFE-H <sub>2</sub> O	616	–		
	70–30 TFE-H <sub>2</sub> O	539	–		
X = 4-NO <sub>2</sub>	H <sub>2</sub> O	ca 83,000	–	119	–
	80–20 MeOH-H <sub>2</sub> O	ca 16,000	1375	–	–
	95–5 MeOH-H <sub>2</sub> O	3648	1824	–	–
X = 4-Br	H <sub>2</sub> O	ca 180,000	–	~100	–
	25–75 MeOH-H <sub>2</sub> O	–	2390	~100	71
	75–25 MeOH-H <sub>2</sub> O	–	2980	~100	74

Values compiled from Refs. [23, 33, 41, 43–45]

water/solvent mixtures [19]. The bulk product distribution reflects the relative nucleophile distribution in the solvation shell and the relative concentration of nucleophiles in solution [19, 23, 33, 40, 42].

### 3.2 Kinetics and Mechanisms of Dediazonation at Moderate Acidities (pH 3-8)

The apparently “simple” decrease of the acidity of the solution (while keeping other experimental conditions constant) leads to a completely different—and much more complex—kinetic behavior than that observed under acidic conditions, deserving a specific section for the description of the mechanistic and practical consequences of the reactions involved. Production of higher amounts of homolytic products in alcohols than in water would be anticipated based on the nucleophilicity of the solvents. However, this is not the case. Dediazoniations in alcohols usually yield three or four products (including reduction ones) and diazo tars seldom form [4]. However, in weakly acidic or alkaline aqueous solutions, tarry materials may be formed and dediazoniations produce a complex mixture of other products [3, 4, 27].



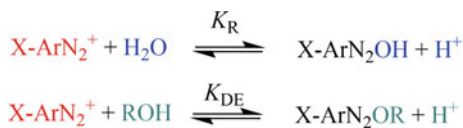
**Fig. 2** Left. Illustrative variation of the first (irreversible) reduction peak of benzenediazonium ions with pHs. Right, variation of peak potential ( $E_p$ ) of the first reduction peak of 4-methylbenzenediazonium ion with pH. Details on calculations can be found elsewhere [53]. Figures reproduced with permission from reference [53]. Copyright 2014 J. Wiley & Sons

At moderate acidities, the nucleophilic character of the solvent is reinforced, and the reactions of  $\text{ArN}_2^+$  with  $\text{H}_2\text{O}$  and  $\text{ROH}$  (as nucleophiles) lead to the formation of diazohydroxides,  $\text{ArN}_2\text{OH}$ , and diazoethers,  $\text{ArN}_2\text{OR}$ , becoming competitive so that the observed rates of the reactions are much faster than under acidic ( $\text{pH} < 2$ ) conditions and lead to the formation of a variety of products, including reduction products that in many instances are difficult to isolate or identify, suggesting that mechanisms other than the described  $\text{S}_{\text{N}}1$ - $\text{S}_{\text{N}}2$  mechanisms (Scheme 1) are operating and becoming increasingly important.

The formation of diazohydroxides  $\text{ArN}_2\text{OH}$  in aqueous solution was demonstrated on the basis of the variations of the peak currents and peak potentials ( $E_p$ ) of the first reduction peak of a number of aryldiazonium ions with acidity, Fig. 2 [39, 46–51]. The dependence of  $E_p$  on pH is typical of acid-base systems and results were interpreted according to Scheme 3 [52].

Some values for the equilibrium constants  $K_{\text{R}}$  corresponding to the formation of hydroxides are shown in Table 2, indicating that effects of the nature of the substituents in the aromatic ring of  $\text{ArN}_2^+$  are very small, suggesting an increase in the electron density on the atom adjacent to the ring during the reaction, neutralizing the positive charge on the diazonium group [54].

**Scheme 3** Nucleophilic reactions of  $\text{X-ArN}_2^+$  with  $\text{H}_2\text{O}$  and  $\text{ROH}$  to give a diazohydroxide,  $\text{X-ArN}_2\text{OH}$ , and diazoether,  $\text{X-ArN}_2\text{OR}$ , adducts. X stands for any substituent in the aromatic ring of the aryldiazonium ion





**Table 2** Equilibrium constants for the formation of diazohydroxides and diazoethers ( $K_R$  and  $K_{DE}$ , respectively) defined according to Scheme 2C

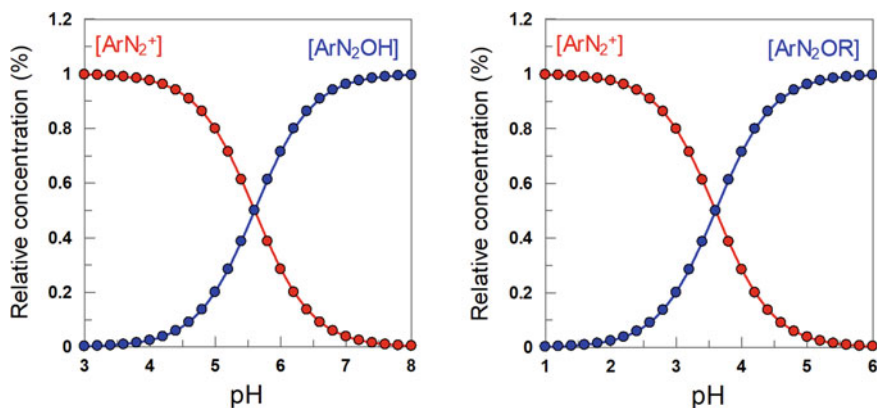
X-ArN <sub>2</sub> <sup>+</sup>	X = H	X = 4-Me	X = 4-MeO	X = 4-Br	X = 4-NO <sub>2</sub>
p <i>K</i> <sub>R</sub>	5.70	5.72	5.80	5.20	5.24
p <i>K</i> <sub>DE</sub>		3.6–5.3 <sup>a</sup>		3.5 <sup>b</sup>	4.18 <sup>c</sup>

Values from: (a) ref. [40, 55], (b) ref. [45], (c) ref. [33]

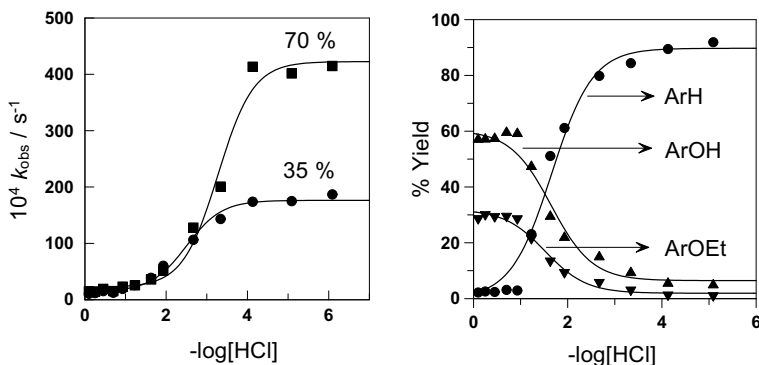
A large body of solvolytic studies shows that the formation of O-diazo adducts with neutral nucleophiles (including the solvent) is quite common [3, 18, 33, 40, 45]. The studies permitted the recognition of the dual role of H<sub>2</sub>O and ROH molecules as nucleophiles. On one side, H<sub>2</sub>O and ROH act as solvents solvating the diazonium ions and allowing them to undergo thermal heterolytic decomposition, Scheme 1. On the other hand, H<sub>2</sub>O and ROH molecules can act as nucleophiles reacting directly with arenediazonium ions to yield O-coupling adducts, Scheme 3, in the highly unstable Z configuration, i.e., Z-diazoethers. The Z-diazoethers then undergo either homolytic fragmentation, initiating radical processes leading to the formation of quantitative amounts of the reduction product, or isomerize to finally yield the E-isomer [18].

In solution, ArN<sub>2</sub><sup>+</sup>, ArN<sub>2</sub>OH, and/or ArN<sub>2</sub>OR adducts may coexist in moderate acid solutions. The variation of the relative concentrations of these species as a function of acidity is shown in Fig. 3.

A product and kinetic analyses of dediazoniations in alcohol/water mixtures show that sigmoidal variations in both the observed rate constant  $k_{\text{obs}}$  and product yields with acidity for a number of arenediazonium ions [33, 40, 43, 45] as illustrated in Fig. 4. At relatively high acidities ( $-\log([\text{HCl}]) < 2$ ), only products from ionic



**Fig. 3** Variations of the percentages of ArN<sub>2</sub><sup>+</sup>, diazohydroxides ArN<sub>2</sub>OH (left), and ArN<sub>2</sub>OR (right) in aqueous solution and in ethanol/water mixtures, respectively, upon changing the solution acidity. Average values of p*K*<sub>R</sub> = 5.6 and p*K*<sub>DE</sub> = 3.6 were employed in calculations. The large difference between p*K*<sub>R</sub> and p*K*<sub>DE</sub> values makes that the formation of ArN<sub>2</sub>OH in alcohol/water mixtures to be negligible compared to that of ArN<sub>2</sub>OR



**Fig. 4** Left: Effects of acidity on  $k_{\text{obs}}$  for the solvolytic decomposition of 4-methylbenzenediazonium, 4-Me-ArN<sub>2</sub><sup>+</sup> in 35 and 70% EtOH-H<sub>2</sub>O mixtures. Right: Effects of acidity on the dediazonation product distribution obtained in a 70% EtOH-H<sub>2</sub>O mixture. The main solvolytic products were cresol, ArOH, methylphenetole, ArOEt, and toluene, ArH. Note the quantitative formation of the homolytic (reduction) product ArH at moderate acidities (pH = 3–5). [4-Me-ArN<sub>2</sub><sup>+</sup>]  $\sim 1 \times 10^{-4}$  M,  $T = 60$  °C. Reproduced with permission from reference [18] Copyright 2010 John Wiley & Sons

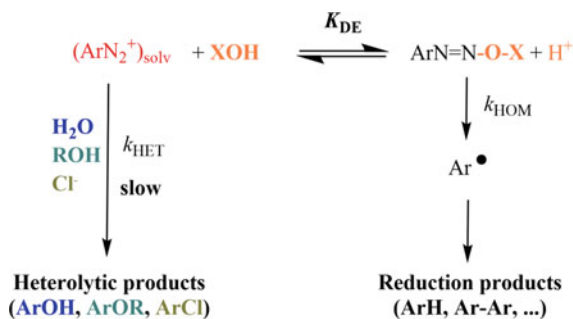
mechanisms (phenols, ArOH, ethers, ArOEt, halo derivatives, ArCl) are detected. But, upon decreasing the acidity, the homolytic product ArH becomes predominant at the expense of the heterolytic ones [40].

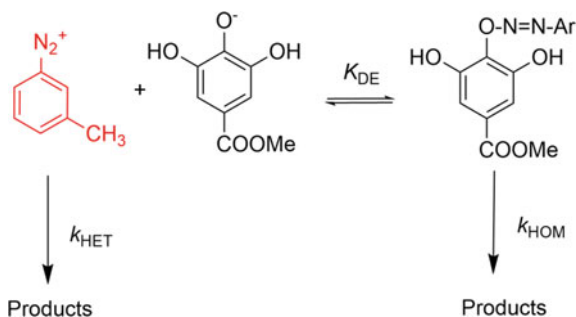
Sigmoidal variations of  $k_{\text{obs}}$  with acidity are usually observed in reactions of acid-base pairs where both forms are attainable and show different reactivities. Thus, in aqueous solutions or in alcohol/water mixtures at moderate acidities, two competing mechanisms are operating, Scheme 4, and Eq. 1 can be derived.

$$k_{\text{obs}} = \frac{k_{\text{HET}}[\text{H}^+] + k_{\text{HOM}}K_{\text{DE}}[\text{ROH}]}{K_{\text{DE}}[\text{ROH}] + [\text{H}^+]} \quad (1)$$

Two limiting situations can be considered, (i) When  $[\text{H}^+] \gg K_{\text{DE}}[\text{ROH}]$ ,  $k_{\text{obs}} \approx k_{\text{HET}}$ , i.e., the reaction proceeds wholly through the ionic D<sub>N</sub> + A<sub>N</sub> mechanism, and

**Scheme 4** Competitive heterolytic (S<sub>N</sub>1) and homolytic (O-coupling) mechanisms for the spontaneous dediazonation of ArN<sub>2</sub><sup>+</sup> with water (X = H) and alcohols (X = R) under moderately acidic conditions





**Scheme 5** Proposed reaction mechanism between 3-methylbenzenediazonium ions and methyl gallate, MG. The reaction takes place through the ionized form of MG (pKa = 8.03) and only tiny amounts of the ionized polyphenol are necessary for the reaction to proceed through the formation of the diazo ether at rates ( $k_{\text{HOM}}$ ) much higher than those of the spontaneous decomposition ( $k_{\text{HET}}$ ) [61].

only heterolytic products are obtained. On the other hand, when  $[\text{H}^+] \ll K_{\text{DE}}[\text{ROH}]$ ,  $k_{\text{obs}} \approx k_{\text{HOM}}$ , i.e., the reaction proceeds wholly through the O-diazo ether and formation of homolytic reduction products is favored. Some representative values for the average pK value, as well as those for  $k_{\text{HET}}$  and  $k_{\text{HOM}}$  are listed in Table 2.

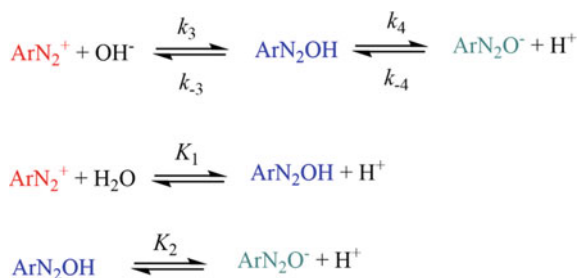
Results in the presence of molecules bearing OH groups in their molecular structure such as ascorbic acid (vitamin C, VC) [24, 36, 56–59] are also consistent with the formation of O-adducts, which were detected experimentally [36, 58, 59] and unambiguously identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as 3-O-arene-diazo ascorbic acids. [56] O-adducts are also formed in reactions of  $\text{ArN}_2^+$  with trihydric phenols such as gallic acid (GA, 3,4,5-trihydroxybenzoic acid) and methyl gallate (MG, methyl 3,4,5-trihydroxybenzoate) and catecholics such as hydroxytyrosol [25, 60–63]. For these reactions, a mechanism comprising consecutive, reversible steps, have been proposed. The first one involves a fast, bimolecular step, in which  $\text{ArN}_2^+$  ions react with  $\text{GA}^{2-}$  to form a Z-diazo ether complex, which is subsequently isomerized to the ionized form of the much more stable E-diazo ether in a second, slow, unimolecular step (Scheme 5) [25, 60, 61].

### 3.3 Dediazoniations in Alkaline (pH > 9) Aqueous Solutions

Aromatic diazonium ions behave as Lewis acids, as they can react with  $\text{OH}^-$  ions to form diazohydroxides,  $\text{ArN}_2\text{OH}$ . The diazohydroxides then became Brønsted acids and may lose a proton to yield diazoates, Scheme 6.

Reports by Wittwer and Zollinger [64] showed that the variation of the degree of neutralization with acidity is different from that expected for a dibasic acid because the equilibrium constant for the formation of the diazoate is higher than that for the formation of the diazohydroxide, that is,  $K_2 > K_1$ . This behavior is in contrast with

**Scheme 6** Equilibria showing the formation of diazoates [18]



that obtained for typical dibasic acids, where  $K_1 > K_2$ . Wittwer and Zollinger [64] estimated, from neutralization curves, that  $K_2 > 10^3 K_1$  and for this reason, it was not possible to separate, at that time, the individual values but only could be determined their product  $K_1 K_2$ . Individual values of  $K_1$  and  $K_2$  were first determined by Lewis and Suhr [65] by taking advantage of the fact that rate constant for the addition of  $\text{OH}^-$  ions to  $\text{ArN}_2^+$  ions ( $k_3$  in Scheme 6) is slower than the rate of deprotonation of the diazohydroxide ( $k_4$ ). The general conclusion that can be drawn is that  $K_2$  is greater than  $K_1$  by 3–5 orders of magnitude, depending on the nature of the substituent in the aromatic ring.

By using the corresponding equilibrium constants, Eq. 2 has been derived, which shows that  $(\text{p}K_1 + \text{p}K_2)/2 = \text{pH}_m$  equals the pH of the solution in which  $[\text{ArN}_2^+] = [\text{ArN}_2\text{O}^-]$ . The ratio  $[\text{ArN}_2^+] / [\text{ArN}_2\text{O}^-]$  changes 100 fold when the pH is changed by one [1] unit so that at  $\text{pH} = \text{pH}_m + 1$ , the reaction mixture only contains 1% of  $\text{ArN}_2^+$  and 99% diazotate. Values for the rate constants,  $\text{p}K_1$ ,  $\text{p}K_2$  for a series of arenediazonium ions, and the variations of the relative amounts of  $\text{ArN}_2^+$ ,  $\text{ArN}_2\text{OH}$ , and  $\text{ArN}_2\text{O}^-$  can be found elsewhere [3, 18].

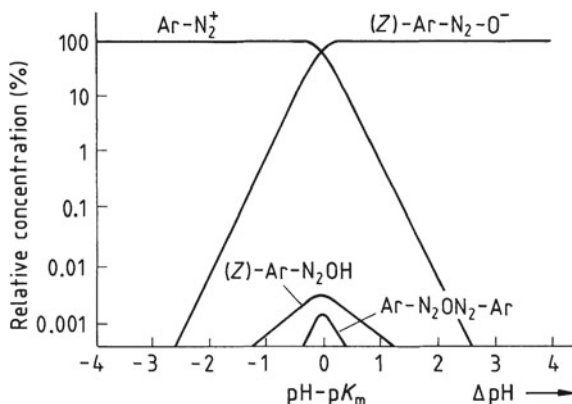
$$\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} + \log \frac{[\text{ArN}_2\text{O}^-]}{[\text{ArN}_2^+]} \quad (2)$$

The relative concentrations of the diazonium and the diazoate ions (the major equilibrium forms) are shown in Fig. 5. The equilibrium concentrations of the diazohydroxide and the diazoanhydride are usually very small at all pH values, with a maximum at  $\text{pH} = \text{p}K_m$ .

## 4 Analytical Chemistry of Diazonium Salts and Their Degradation Products

Regarding to analytical chemistry of these compounds and the chemistry around them, the identification and the quantification of the  $\text{ArN}_2^+$  itself and all by-products generated in dediazonation reactions will be the main challenge to get sufficient valuable data on these processes and to offer a convincing choice between the mechanistic

**Fig. 5** Variation of the relative concentrations of various species in equilibrium with  $\text{ArN}_2^+$  as a function of acidity. Reproduced with permission from ref. [3] Copyright 1994 J. Wiley & Sons



alternatives, in particular during surface reactions. The compounds to be identified and quantified are aromatic derivatives (typically, phenolics, haloarenes, benzene derivatives, biaryls, aromatic ethers, etc.), as well as the possible transient and stable intermediates, depending on the structural nature of  $\text{ArN}_2^+$  and the reaction media composition.

As a starting point, some of the analytical techniques are able to monitor only one component at a time, and some others are limited to narrow ranges of useful experimental conditions, once the adjustable parameters to describe the measured property in any particular solution composition have been optimized [66]. As experts in the field, the readers know well that there is not only one technique to be used. The combination of several techniques is necessary in order to get insight into complete knowledge of what is going on in the dediazonation reactions, how is the disappearance of the ion and its rate, which are the products formed and their reaction rates or the stable/transient intermediates that can be detected and monitored. On these bases, the possible degradation pathway in any matrix or composition of the reaction media (aqueous or non-aqueous solutions, colloidal and macromolecular systems, presence of different electrolytes, etc.) can be proposed. To achieve these goals, valuable and quality data that help to work out a real mechanism interpretation of dediazonation reaction will be needed. Therefore, it is easy to understand that the use of several techniques that complement each other to solve the problem is the best way to validate the results obtained. Furthermore, the analytical signal of the measured property must be correlated with the concentration of the analyte (calibration) to obtain minimum uncertainty in concentration level, and then, high-quality kinetic data can be achieved. Keep in mind that this section is not intended to be exhaustive. The proposal is to address a brief description of most popular instrumental analytical techniques used for monitoring  $\text{ArN}_2^+$  in kinetics studies up to date, with some references as representatives.

The UV-Vis spectra of ions and molecules in solution were the first instrumental methodology used to obtain both qualitative and quantitative chemical information and were widely applied to obtain kinetic data [23, 24, 33, 34, 38, 57, 58, 67, 68].

This technique is simple to use and relatively rapid, limited to transparent media and by the *cutoff point* of solvents. UV–Vis spectrophotometers with stopped-flow devices for monitoring very fast reactions are extremely valuable [69]. However, the UV region is not selective enough and most of the products involved in the dediazonation reaction absorb in the same region, being impossible to monitor the reactive loss and/or products formation at the same time. For solving this situation, the absorption band can be shifted to the visible region, more selective, by a derivatization reaction that quantitatively transforms the unreacted  $\text{ArN}_2^+$  into a compound with highly conjugated double bonds and heteroatoms. The coupling reaction with naphthols and naphthylamines to form azo dyes based on Griess reaction [7] provide the essential tool to monitor the degradation of  $\text{ArN}_2^+$  by indirect monitoring the azo dye formed, but the experimental conditions must be chosen to ensure that azo dye formation is much faster than dediazonation [17, 70]. In contrast with UV–Vis spectrophotometric technique, scant attention has been paid to the use of fluorescence for detection and monitoring dediazonation. The  $\text{ArN}_2^+$  derivatives with one aromatic ring system show a poor fluorescence, but enough for dediazonations following up [70]. This technique is more sensitive (at least by two orders of magnitude) for polyaromatic molecules with rigid planar structures as naphthalene  $\text{N}_2^+$  derivatives and much more selective than UV–Vis spectrophotometry.

Nuclear magnetic resonance, NMR, and Fourier transformed infrared, FT-IR, spectroscopies, together with Mass spectrometry by electrospray ionization, EIS-MS, are techniques that support all kinetics experiments, giving information about purity of standards, screening quantification, and structural elucidation and confirmation. They determine whether a synthetic reactant or product is the compound expected or planned. NMR and MS are remarkably close to each other in relation to the information obtained, but the advantage of MS is that it only needs small amount of sample (ng contrary to  $\mu\text{g}$  in NMR) [19, 30]. MS disadvantages are to be a destructive analytical technique and limited in solving structural isomerism, where NMR is still needed. The  $^{13}\text{C}$  NMR or  $^1\text{H}$  NMR techniques are additionally used in chemical analysis of dediazonations by monitoring the chemical shift of the products in the spectra [71, 72]. Electron paramagnetic resonance, EPR, or Electron spin resonance, ESR, spectroscopy is another spectroscopic technique used to study radical chemical species in dediazonation reactions, providing a valuable measure of how well the homolytic mechanism is going on and which are the radical intermediates found [70]. The principles of EPR are similar those to NMR, but give higher time resolution and sensitivity than NMR.

The most effective solution to prevent interferences is to use a separation technique previously to the detection. High-pressure liquid chromatography, HPLC, is a versatile technique widely used in kinetic studies of  $\text{ArN}_2^+$  for obtaining kinetic data of products formation, choosing the chromatographic mode by reverse-phase and UV or diode array detectors [23, 24, 33, 40, 57, 58, 73]. However, this technique is time-consuming, tedious, and reactive samples cannot be obviously injected. The derivatization protocol mentioned above takes advantage of quenching instantaneously the dediazonation reaction and preventing side reactions of highly reactive  $\text{ArN}_2^+$  or its intermediates with the solvents of the mobile phase or other parts of

the chromatographic system. The latter would ultimately lead to erroneous identification and quantification of dediazonation products. At that point, the coupling reactions provide the best performance in the HPLC system and HPLC column and avoid pitfalls that can impact in the HPLC analysis [74]. Gas chromatography with flame-ionization detector, GC-FID, is one of the fastest and most useful separation techniques available [37, 72, 75], but limited to organic compounds that are volatile and not thermally labile. This is why HPLC has been gaining followers up to date. The most sophisticated detection system for both qualitative and sensitive quantitative analysis in GC or HPLC systems is Mass Spectrometry, MS, which provides retention-time data and peak area measurements, but structural information obtained from the fragmentation patterns can be used to positively identify the mixture components and to determine the products of the reactions with higher sensitivity and selectivity [76, 77]. However, this methodology requires several steps for sample preparation, expensive instrumentation, and trained professionals to operate the equipment.

The investigation of dediazoniations by electroanalysis showed that a variety of polarographic and voltammetric peaks can be chosen to obtain kinetic information of  $\text{ArN}_2^+$  [46–48, 51, 78]. In this context, the selective detection is possible through the electroreduction on drop mercury electrode, DME, of the  $\text{ArN}_2^+$  and products formed by differential pulse polarography, DPP, and the electrooxidation on carbon electrodes of some products (i.e., phenolics) by DP voltammetry [39, 47]. An interesting statement of these techniques, in comparison with all others reported herein, is that the reaction of 4-hexadecylbenzenediazonium ions, 16- $\text{ArN}_2^+$ , is used as probe to better understand the colloidal interfaces and the distribution of antioxidants in very complex matrix as emulsions, can be directly monitored by linear sweep voltammetry, LSV [78, 79]. The advantages of these techniques rely on short analysis time, low cost, and simple sample preparation steps (unique dilution in electrolyte). Moreover, electroanalysis stands out for being useful for simultaneously detecting  $\text{ArN}_2^+$  loss, transient intermediates as diazoethers [36], and products formed by dediazonation with high sensitivity (detection limits lower than those obtained by the aforementioned techniques, except MS) and with similar selectivity to HPLC techniques in some dediazoniations [39, 46]. Furthermore, the electroanalysis can be applied not only in transparent solutions but also in both opaque solutions and suspensions.

## 5 Conclusions and Future Perspectives

The unique multimodal reactivity of  $\text{ArN}_2^+$ , while offering multiple options for the preparation of new compounds (Pd-catalyzed reactions, thermal or photosensitized radical chain reactions, and azo-coupling reactions) and materials, can also be fine-tuned via the appropriate choice of experimental conditions and reaction partners. This overview shows a great potential for the formation of a wide variety of azo compounds and their use in chemistry. However, it should also be mentioned that protocols involving the use of arenediazonium salts have the drawbacks of  $\text{ArN}_2^+$

being unstable in solution, highlighting the need for a careful control of experimental conditions, since apparently minor changes may lead to substantial modifications in the kinetics and mechanisms of their spontaneous decomposition, leading to large modifications in their effective concentrations in solution.

In this review, we focused on the main kinetic and mechanistic consequences of changing experimental conditions in the spontaneous decomposition of aryldiazonium salts to draw the attention of scientists interested in future applications of  $\text{ArN}_2^+$  in solution. Indeed, the various applications of aryldiazonium salts, which are readily obtained from inexpensive anilines, will continue to attract attention of chemists, but the spontaneous reaction of diazonium salts in various solvents will need to be considered anyway as it may be competitive with the other processes involved.

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**Credit authorship contribution statement.** C. B-D. Sections 1–3 and 5: conceptualization, visualization, writing, review & editing.

E. G-R. Section 4: conceptualization, visualization, writing, review & editing.

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