Solvolysis of Some Arenediazonium Salts in Binary EtOH/H_2O Mixtures under Acidic Conditions

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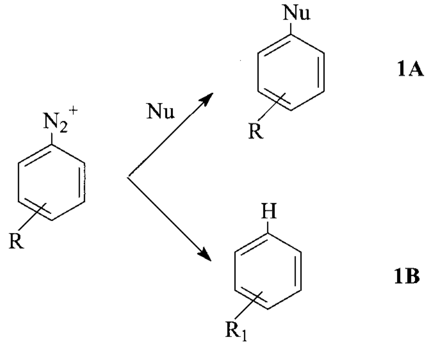
We have determined the product distribution, the rate constants for dediazoniation product formation, and the solvolytic rate constants for 2-, 3-, and 4-methylbenzenediazonium ions (2-, 3-, and 4-MBD, respectively) loss in acidic ethanol/water mixtures over the whole composition range by a combination of spectrophotometric (UV/Vis) and high performance liquid chromatography (HPLC) measurements. The observed rate constants (k_{obs}) for substrate loss are equal to those for product formation, and they remain essentially constant (2-MBD) with changing solvent composition but increase by a factor of ≈2 (4MBD) on going from water to 100% EtOH. Up to four dediazoniation products – cresols (ArOH), chlorotoluene (ArCl), methylphenetole (ArOEt), and toluene (ArH) – were detected, depending on the solvent composition; the major dediazoniation products were the ArOH and ArOEt derivatives. The product selectivity (S) of the reaction towards nucleophiles is low and essentially constant with changing solvent composition, and good linear correlations between log k_{obs} and Y_{Cl} (solvent ionizing power) were observed for the three ArN_2^+ ions. All data are consistent with the rate-determining formation of an aryl cation, which reacts immediately with available nucleophiles. The data suggest that the distribution of neutral and anionic nucleophiles in the neighborhood of the ground state arenediazonium ion remains essentially unchanged upon dediazoniation, the observed product distribution reflecting the concentrations of nucleophiles in their immediate environment (i.e., in the first solvation shells of the arenediazonium ions).

Introduction

Solvolytic dediazoniations have been studied in a number of solvents,[1−3] and it is currently believed to date that they take place through two main mechanisms: heterolytic (Scheme 1, 1A) and homolytic (1B). Literature reports[3] indicate that, in the absence of electron donors, heterolytic dediazoniations mainly take place in solvents of low nucleophilicity, such as H_2O or TFE, while homolytic dediazoniations are favored by an increase in the nucleophilicity (HMPT, pyridine).



Scheme 1. Basic representation of dediazoniation mechanisms; 1A) heterolytic; 1B) homolytic

The source of electrons in the homolytic pathway is thought to be the solvent, although the mechanism and the nature of the initiation step remains a matter of debate[3,4] because there are 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 stable E isomers, which can be isolated in some instances,[5] or may eventually give rise to homolytic rupture of the bonds, providing the initiation of a radical process.[3,6,7] In most instances analyzed, the nucleophile has to possess a charge, as in OH^-, CN^-, R-OH^-, or ascorbate ions, and so reactions are carried out under conditions in which substantial concentrations of the anionic form of the nucleophile are present.[3,6,7] Formation of Z-diazoethers with neutral nucleophiles has been reported under special circumstances under which geometric restrictions apply.[8] *p*-Nitrobenzenediazonium ions, for example, form 1:1 inclusion

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complexes with β-cyclodextrin, with the $-NO_2$ group inserted into the CD cavity, and the adopted geometry of the complex allows solvation of the ArN_2^+ ions by the secondary hydroxyl groups of β-CD, favoring further reaction to yield a highly unstable *Z*-diazo ether intermediate, which was detected experimentally, generating aryl radicals.[9]

Studies carried out in fluorinated alcohols indicate that, under acidic conditions, dediazoniations take place exclusively through the heterolytic mechanism,[10−12] in contrast with the behavior observed in non-fluorinated alcohols such as MeOH and EtOH or other solvents such as DMSO,[13−15] in which both mechanisms can be observed, depending on several factors such as pH,[3] substituents on the aromatic ring,[13,14] or even the atmosphere[13] (O_2 or N_2). Dediazoniations in ethanol/water mixtures have not been as well investigated as those in methanol,[3,12] although as early as 1864, Griess proposed a synthetic method for the replacement of aromatic amino groups by hydrogen through the formation of the corresponding diazonium ion and further treatment in boiling ethanol. Yields were variable, however, and strongly dependent on experimental conditions as well as on the nature and position of the substituents on the aromatic ring of the arenediazonium ion.[4] For a given substituent, dediazoniations in basic ethanol result in higher yields of reduction products than obtained in methanol, an effect that has been explained in terms of the higher basicity of ethoxide ion and the more facile formation of the $CH_3-C^{\cdot}HOH$ radical.[16]

Few comparative studies between dediazoniations in methanol and in ethanol under aqueous acid conditions have been carried out.[3] Rate constants and activation parameters at given solvent compositions are only available for a limited number of ArN_2^+ ions. Though considerable amounts of data on selectivities for solvolysis in alcohol/water mixtures are available,[17−19] systematic studies on individual substrates over the whole composition range are relatively rare,[20] probably because reliable results in highly aqueous or alcoholic mixtures are difficult to obtain because of the increased rates of solvolysis and decreased solubilities.[21] The ArN_2^+ ions employed in this work are soluble over the whole composition range, and the selectivity values for dediazoniations can be easily calculated if a suitable method to determine product yields is available. Determination of selectivity values at different solvent compositions provided evidence of the presence of cationic intermediates, complementing other studies involving addition of nucleophilic traps, which suffer from the disadvantage that they may induce mechanistic changes.[17,20,22,23] To expand the general understanding of dediazoniation mechanisms in alcoholic solvents, we have undertaken a physical organic chemistry investigation of the ethanolysis of 2-, 3-, and 4-methylbenzenediazonium ions under acidic conditions throughout the whole composition range. As a result, dediazoniation product distributions, selectivity values, rate constants for product formation and for arenediazonium ion loss, and activation parameters were determined. Comparisons with literature results in acidic H_2O/MeOH mixtures and other alcoholic mixtures are also pointed out.

Results and Discussion

1) Effects of Solvent Composition on the Observed Rate Constant k_{obs}

The effect of solvent composition on k_{obs} was investigated by changing the percentage of EtOH in the reaction mixture (Figure 1). With increasing ethanol content, the solvolytic rate constants for 2MBD increased smoothly, while those for 3MBD and 4MBD increased more drastically at high percentages of ethanol. The k_{obs} values at 0% EtOH are in agreement with literature values obtained by different techniques including N_2 evolution[24] at pH = 1.6−1.8, HPLC, and UV/Vis spectrophotometry.[25] The largest increase in k_{obs} is approximately twofold for 4MBD, a relatively modest increase in relation to those observed for other solvolytic reactions. Addition of electrolytes such as HCl (pH = 1−5) and NaCl ([NaCl] = 0−1 M) did not change k_{obs} significantly (data not shown).

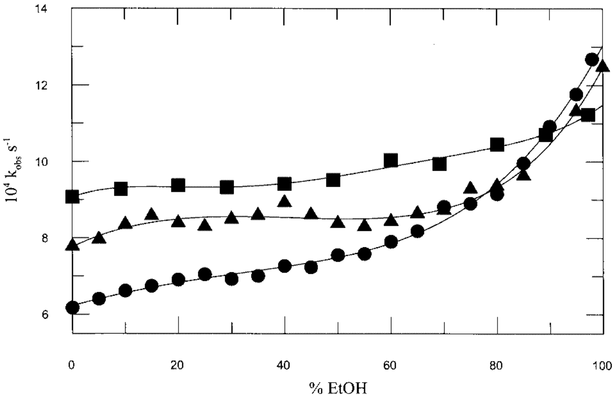


Figure 1. Variation in k_{obs} for ethanolysis of 2MBD (■), 3MBD(▲), and 4MBD(●) with increasing [EtOH]; $[ArN_2^+] \approx 2 \times 10^{-4}$ M, [HCl] = 0.01 M, T = 35 °C (2MBD and 3MBD), T = 60 °C (4MBD)

Rate constants for product formation at different solvent compositions were obtained by employment of the chromatographic technique. The results in Figure 2 are representa-

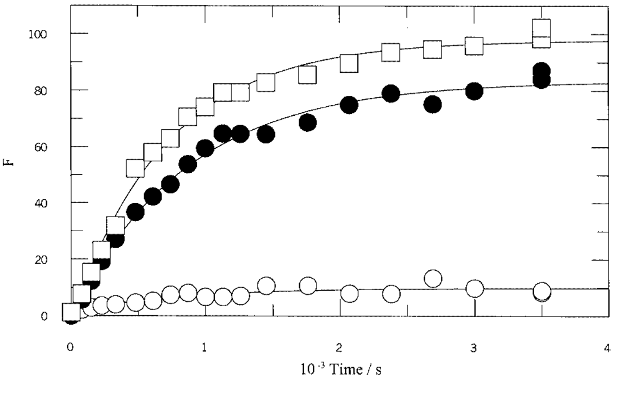


Figure 2. Variation in the percentage of formation of dediazoniation products with time at 98% EtOH for 4MBD; ● 4MB-OEt, ○ (4MB-OH), □ Total yield. [4MBD] ≈ 2×10^{-4} M, [HCl] = 0.01 M, T = 60 °C

tive and illustrate the formation of 4MBD dediazoniation products with time at 98% EtOH. Quantitative conversion into products is obtained, the major dediazoniation products being ArOEt (F = 83%) and ArOH (F = 9%). Other minor products include ArH and ArCl, but their total yield (F_{ArH} + F_{ArCl}) is lower than 5% (data not shown for the sake of clarity). Observed rate constants for ArOEt formation, $k_o = (1.19 \pm 0.04) \times 10^{-3}\ s^{-1}$, and for ArOH formation, $k_o = (1.29 \pm 0.01) \times 10^{-3}\ s^{-1}$, are equal within experimental error, and are the same as obtained spectrophotometrically for 4MBD loss. Similar results were obtained for 2MBD and 3MBD (results not shown).

2) Sensitivity of the Reaction towards Solvent Polarity

The sensitivity of dediazoniation to changes in solvent polarity can be shown by the Winstein-Grunwald equation,[26,27] which has often been applied to the correlation of solvolysis rates. Figure 3 shows the obtained linear plots, which yield slopes of $m = -0.058 \pm 0.005$ (4MBD, cc = 0.989), $m = -0.018 \pm 0.001$ (3MBD, cc = 0.997) and $m = -0.026 \pm 0.005$ (2MBD, cc = 0.935), reflecting the extraordinary insensitivity of dediazoniations to medium effects,[3] attributed to the similarities in structure and charge distribution between the parent arenediazonium ions and the corresponding aryl cations.[25,28,29]

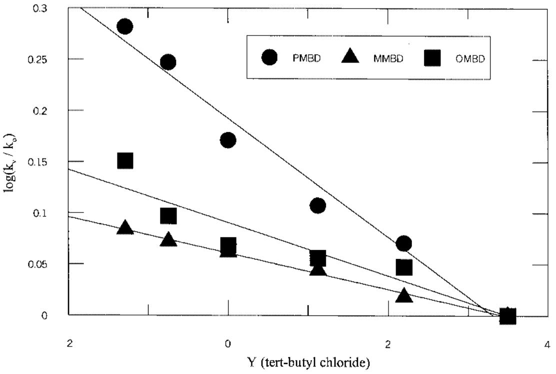


Figure 3. Winstein-Grunwald plots for 2MBD (■), 3MBD (●), and 4MBD (▲); Y values from reference[27]

3) Effects of Solvent Composition on Dediazoniation Product Distribution

Figure 4 shows the effects of solvent composition of product yields for 4MBD and 3MBD, chosen as representatives. Up to four dediazoniation products − ArOH, ArOMe, ArH, and ArCl − are formed, and quantitative conversion into products is achieved over the entire composition range. The major dediazoniation products are ArOH and ArOEt. With increasing EtOH content, yields of ArOH decrease and a concomitant increase in ArOEt yield is observed. Only traces (<4%) of ArH and ArCl dediazoniation products are detected at any solvent composition. The results for 2MBD are similar and show that yields of ArCl and ArH are even lower than those obtained for 3MBD and 4MBD.

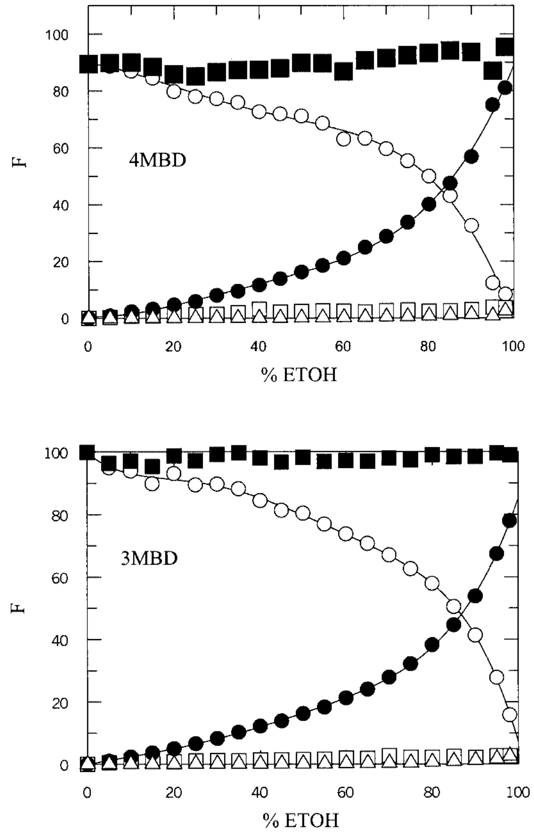


Figure 4. Effects of solvent composition on product distribution for 3MBD and 4MBD; ● ArOH, ○ Ar-OEt, □ Ar-H, ▲ ArCl, ■ total yield. [3MBD] ≈ [4MBD] ≈ 2 × 10^{-4} M, [HCl+ = 0.01 M, T = 35 °C (3MBD), T = 60 °C (4MBD).

4) Nature of the Transition State − Effects of Temperature on k_{obs}: Activation Parameters

Activation parameters were determined by measuring k_{obs} at different temperatures and at a number of solvent compositions according to the theory of absolute rates by application of Equation (1), where k_B and h stand for the Boltzmann and Plank constants respectively:

$$Ln\left(\frac{hk_{obs}}{k_B T}\right) = \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \qquad (1)$$

The data in Figure 5 are illustrative. Table 1 shows the activation parameters in 98% EtOH and the corresponding rate constants at T = 40 °C. For purposes of comparison, Table 1 also shows literature values in pure water and in 99.5% MeOH. In all cases, the values of $\Delta H^{\#}$ are relatively high in relation to those for bimolecular reactions, and the entropic term is clearly positive.[51]

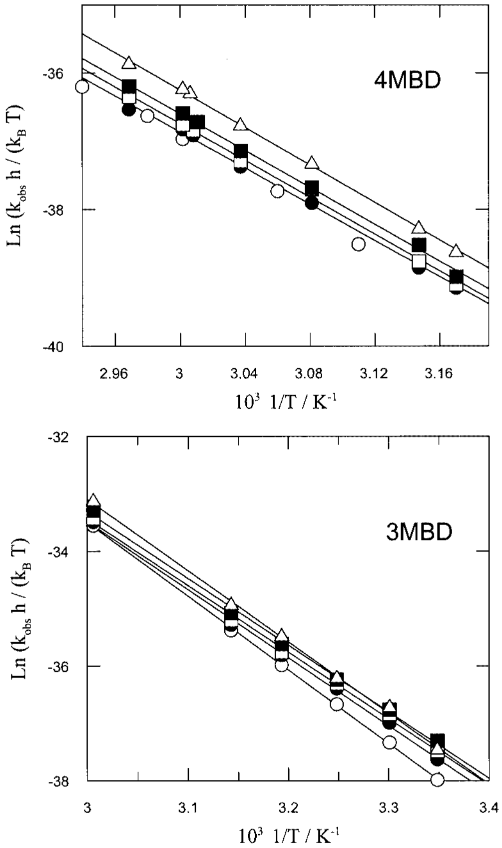


Figure 5. Arrhenius plots for 3MBD and 4MBD at ○ 0%, ● 25%, □ 50%, ■ 75%, ▲ 98% EtOH [3MBD] ≈ [4MBD] ≈ 2.0 × 10^{-4} M, [HCl] = 0.01 M

Table 1. Selectivity values for 2-, 3-, and 4MBD

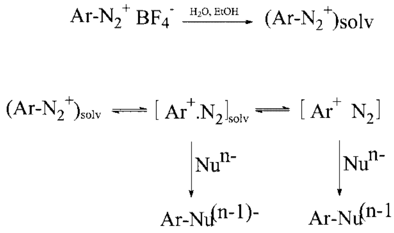
	$S_{w}^{Cl^-}$	S_{w}^{MeOH}	S_{w}^{EtOH}
2MBD	2.7±0.1[a]	0.40±0.05[b]	0.50±0.06[c]
3MBD	2.6±0.08[a]	0.60±0.05[b]	0.75±0.06[c]
4MBD	1.7−3.4[a]	0.74±0.05[b]	0.70±0.10[c]

[a] From ref.[60] [b] From ref.[8] [c] This work.

All runs obeyed first order kinetics for more than three half-lives at any solvent composition. With increasing [EtOH], observed rate constants increase only moderately, the major increase, of approximately twofold, being for 4MBD (Figure 1). Product distribution analysis shows that quantitative conversion into products is achieved at any solvent composition (Figure 4). The heterolytic ArOH and ArOEt dediazoniation products are obtained in significant yields and only traces of reduction products such as ArH were detected. The practical absence of reduction products such as ArH or biaryls (Ar-Ar) indicates that the reaction takes place through a heterolytic mechanism (Scheme 1).

A rate-limiting nucleophilic attack should produce a strong dependence of the rate constant on solvent composition, which is not observed (Figure 1), so the data suggest that dediazoniation takes place mainly through a rate-determining splitting of arenediazonium ions into N_2 and extremely reactive aryl cations that then react further with available nucleophiles (Scheme 1). Consistently with this interpretation, we have observed that at a fixed solvent composition, k_{obs} for product formation is the same as that for ArN_2^+ loss (Figure 2). Aryl cations have not to date been isolated in aqueous systems, because they are extremely short-lived intermediates (<0.5 ns[30]), owing to their extreme electrophilicity and reactivity, but Winkler et al.[31] were able to isolate them in a solid argon matrix, and literature reports indicate that photolyzed arenediazonium cations generate aryl cations that can be observed by addition to aromatics.[32]

Preassociation stepwise mechanisms like that shown in Scheme 2, in which the aryl cation has a short but finite lifetime, have been employed to describe product distribution in terms of ion-molecule or ion-nucleophile pairs.[15,33] Nucleophilic attack may occur on "free" carbocations, contact ion-molecule pairs, or contact ion-solvent pairs. Different research groups have proposed formation of ion-molecule pairs involving ground state arenediazonium ions. Zollinger et al.[34] suggested the formation of ion molecule pairs with N_2 at high N_2 pressures. More recently, transient colored complexes between arenediazonium ions and aromatic hydrocarbons have been observed and characterized.[35] Solid arenediazonium tetrachlorocuprate(II) complexes,[36] which may decompose to give ArCl in high yields,[37] have been isolated, and in some recent dediazoniation work Cuccovia et al.[38] proposed the formation of tight ground state arenediazonium ion-nucleophile pairs prior to N_2 departure in the presence of very weak nucleophiles such as alkylsulfates and alkylsulfonates.



Scheme 2. Dediazoniation mechanism showing the stepwise formation of a ion-molecule complex and a solvent-separated ion-molecule pair

Rate constants for nucleophilic attack on carbocations have been reported to be close to the diffusion control limits: 10^9-10^{13} M^{-1} s^{-1}.[32] With lifetimes in the nanosecond order of magnitude, aryl cations do not have time to diffuse away, and hypothetical preassociation of the nucleophile with the precursor would not account for much of the trapping, as it happens with other extremely short lived carbocations behave.[39] Thus, in the absence of specific interactions, arenediazonium ions will decompose mainly through the solvated aryl cations; that is, upon unimolecular removal of N_2, one nucleophile molecule of the first coordination shell will form the corresponding dediazoniation product. In other words, to obtain a specific dediazoniation product, the corresponding nucleophile molecule must be present in the solvation shell of the aryl cation prior to N_2 splitting from the precursor. Consistently with this interpretation, Scheme 1 illustrates that the formation of the aryl cation does not involve separation of charge but its redistribution, and consequently that no significant reorganization of the coordination shell is to be expected upon formation of the corresponding aryl cation.

Further support for the proposed mechanism can be obtained from analysis of the variation in the selectivity of the reaction towards nucleophiles with solvent composition. Assuming that the nucleophilic attack is under kinetic control and by denoting the specific rate constants for nucleophilic attack as k_{Nu_1} and k_{Nu_1} the selectivity S of the reaction can be defined[22,23] by Equation (2), where F stands for the percentage of formation of the corresponding reaction product, and nucleophile concentrations are assumed to refer to the reaction site.

$$S_{Nu_2}^{Nu_1} = \frac{k_{Nu_1}}{k_{Nu_2}} = \frac{F_{R-Nu_1}\left[Nu_2\right]}{F_{R-Nu_2}\left[Nu_1\right]} \qquad (2)$$

The selectivity values (Table 1) are essentially constant with solvent composition and are similar to those typically reported for aryl cations competing with different nucleophiles, which typically range from 0.4 to 6.[38] Such low values are orders of magnitude lower than those observed for nucleophiles competing with water in reactions with stabilized carbocations,[23,40,41] and they are consistent with the formation of highly reactive aryl cations and with the stepwise preassociation mechanism shown in Scheme 1. The data in Figure 4 indicate that equal amounts of ArOH and ArOEt are obtained when the solvent composition is about 80% EtOH/H_2O. Such a composition corresponds to approximate concentrations of $[H_2O] = 8.3$ M and $[EtOH] = 14.6$ M, suggesting that ArN_2^+ ions undergo preferential solvation with H_2O molecules. The barriers for capture of carbocations by the solvent[39] are sufficiently small that the product distribution reflects the solvent distribution in the first solvation shell of the reactant. This is consistent with the relatively modest variation in k_{obs} on going from water to ethanol, suggesting that the solvation of the ground state is essentially the same as that in the proximity of the transition state; that is, $\Delta G^{\#}$ is not significantly affected by solvent composition.

The assumption was confirmed by analysis of the activation parameters (Table 1); both $\Delta H^{\#}$ and $\Delta S^{\#}$ values are very similar to those found in water and in methanol. Solvolytic unimolecular reactions can show positive or negative $\Delta S^{\#}$ values. Positive $\Delta S^{\#}$ values such as those found in this work (Table 2) suggest that the transition state has greater structural freedom than the reactants, in line with the reported positive volumes of activation ($\Delta V^{\#}$) for a number on dediazoniations in different solvents.[11,42−44] Inspection of Scheme 1 shows that the parent arenediazonium ion and the aryl cation polarize the surrounding solvent molecules to similar extents, so the gain in entropy due to the loss of molecular vibrations is not compensated by the loss of entropy due to the restricted motion of the solvating molecules. On the other hand, the $\Delta H^{\#}$ values are relatively high, as in many unimolecular reactions,[40,45] and clearly contrast with those usually found for bimolecular reactions. In typical S_N2 reactions,[45] activation enthalpies are substantially lower because the breaking of old bonds, which requires energy, and the formation of the new ones, which releases energy, are highly concerted and usually synchronous. Thus, the relatively high $\Delta H^{\#}$ values found suggest a transition state that has undergone bond breaking with little compensating bond making. Positive $\Delta S^{\#}$ values, such as those found in this work, compensate for the large enthalpy term, allowing dediazoniations to proceed at considerable rates in relation to other unimolecular reactions, consistently with results for a number of dediazoniations showing much lower solvent dependence than seen with typical unimolecular reactions.[3,11,46,47]

Finally, it is worth noting the unanticipated though modest effect of the methyl groups on k_{obs}. As shown in Table 2, the presence of a methyl group in the *ortho* or *meta* positions is rate-enhancing relative to the value for benzenediazonium ion, in contrast with the effect of a *para* methyl, which is rate-retarding. Substituents on the aromatic ring have marked effects on the stabilities of arenediazonium ions;[2,3] 4-*tert*-butyl, 4-nitro, and 4-halo groups, for instance, are also rate-retarding,[10] and their effects are not understandable in terms of the Hammett equation[3,48,49] but can be interpreted in terms of a dual substituent parameter[50] separating the resonance (associated with the ability to transfer charge) and inductive (associated with the polarity) effects.[3,51−53]

When the methyl group is conjugated to an electron-deficient site through an aromatic system, the electron-deficient site can then attract charge from the carbon-hydrogen bonds of the methyl group through the π system[23] (hyperconjugation). Direct resonance interaction with the reaction site takes place only in the *para* position,[23] so high negative σ^+ values are to be expected for a *para* methyl group ($\sigma^+ = -0.25$[54] or $\sigma^+ = -0.31$[23]) in relation to those for *meta* methyl groups ($\sigma^+ = -0.06$[23]). Alternatively, the methyl group behaves as a electron-releasing group in its interaction with an electron-deficient site which is able to attract electron density from the polarizable alkyl group through the σ bonds,[40,45] an effect that decreases with distance. Therefore, *para* methyl stabilizes the parent arenediazonium ion more than the intermediate aryl cation, while *ortho* and *meta* methyl groups stabilize the corresponding aryl cation more than the parent methylbenzenediazonium ion (Scheme 1). These arguments are consistent with the observed kinetic behavior for thermal decompositions, in aqueous acid solution, of arenediazonium ions with *para* or *meta* substituents with π-donating capability, such as $-OH$ ($\sigma^+ = -1.25$[54]) or $-OCH_3$ ($\sigma^+ = -0.61$[54]): experimentally obtained rate constant values for dediazoniations with *para* $-OH$ or $-OCH_3$ substituents

Table 2. Activation parameters for the three methyl substituted benzenediazonium ion in water, 99.5% MeOH, 98% EtOH, and $k_{obs.}$ values for their thermal decomposition at T = 40 °C

	T Range/°C	10^4 k_{40}/s^{-1}	10^{-15} A/s^{-1}	E_a/ kJ·mol^{-1}	$\Delta H^{\#}$ / kJ mol^{-1}	$\Delta S^{\#}$ / J·mol^{-1} K^{-1}
0% MeOH						
BD[a]		8.50	3.23	113		
2MBD[b]	26.5−41.0	14.88	2.1	108.2	106	40.4
3MBD[b]	26.5−41.0	12.55	2.8	109.5	107	43.0
4MBD[b]	40.0−60.0	0.52	1.7	112.4	110	21.6
99.5% MeOH						
BD[a]		8.5				
2MBD	25−40	23.8	0.79	105	105	40.8
3MBD	25−40	24.05	0.94	105	106	42.5
4MBD	40−65	0.91	0.79	114	109	25.6
98% EtOH						
BD		7.4[c]		113[c]	75[d]	−64[d]
2MBD	35−53	20.5	0.96	105.7±3	103±1	34±4
3MBD	25−60	25.3	0.40	103±2	103±2	34±7
4MBD	40−65	1.0	2.6	116±2	114±2	41±4

[a] BD stands for benzenediazonium. [b] From ref.[8] [c] From ref.[61] [d] From ref.[10]

are lower than those obtained when substituents are in the *meta* position.[24,42] These results are also in agreement with a theoretical electron density analysis[52] that indicates that a *para* -NH_2 group ($\sigma^+ = -1.61$[54]) enhances the C−N bonding.

Conclusion

Our results show that solvolysis of 2MBD, 3MBD, and 4MBD in $EtOH/H_2O$ mixtures proceeds through a heterolytic $D_N + A_N$ mechanism. Only traces of products associated with radical pathways are detected, the major dediazoniation products being cresols (ArOH) and phenol ethers (ArOEt), reflecting the compositions of the first solvation shells of ground state ArN_2^+ ions. The k_{obs} values increase modestly with increasing EtOH, up to twofold for 4MBD, the k_{obs} values for product formation are the same as those for diazonium ion loss, and the selectivity values are solvent-independent. The presence of a methyl group in the *ortho* or *meta* positions is rate-enhancing in relation to the value for benzenediazonium ion, in contrast with the effect of a *para* methyl, which is rate-retarding.

Experimental Section

UV/Vis spectra and some kinetic experiments were followed on a Beckman DU-640 UV/Vis spectrophotometer equipped with a thermostatted cell carrier attached to a computer for data storage. Product analysis was carried out on a WATERS HPLC system that included a 560 pump, a 717 automatic injector, a 2487 dual wavelength detector, and a computer for data storage. Products were separated on 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 70:30 v/v $MeOH/H_2O$ containing 10^{-4} M HCl. The injection volume was 25µL in all runs and the UV detector was set at 220 nm and 280 nm.

Arenediazonium salts (ArN_2^+) were prepared under non-aqueous conditions as described elsewhere,[55] were stored in the dark at low temperature to minimize decomposition, and were recrystallized periodically. Other reagents were of maximum purity available and were used without further purification. Cresols (ArOH), chlorotoluenes (ArCl), methylphenol ethers (ArOEt), and the reagents used in the preparation of arenediazonium salts (as tetrafluoroborates) were purchased from Aldrich. 2-Naphthol-6-sulfonic acid, sodium salt (2N6S) was purchased from Pfaltz & Bauer. Other materials employed were from Riedel de Haen. All solutions were prepared with Milli-Q grade water.

Solution composition is expressed as percentage of EtOH by volume. Molar concentrations were calculated by ignoring the small excess volume of mixed solvents.[56]

Kinetic data were obtained both spectrophotometrically and chromatographically. Observed rate constants were obtained by fitting the absorbance-time or percentage yield-time data to the integrated first order Equation (3) by a non-linear least-squares method, where M is the measured magnitude of the UV/Vis absorbance or product yields.

$$Ln\left(\frac{M_t - M_\infty}{M_0 - M_\infty}\right) = -k_{obs}t \tag{3}$$

All runs were carried out at $T = 35 \pm 0.1$ °C, with the arenediazonium salts as the limiting reagents. Duplicate or triplicate experiments gave average deviations lower than 7%.

Spectrophotometric kinetic data were obtained by following the disappearance of the corresponding ArN_2^+ at an appropriate wavelength to minimize interference (mainly dediazoniation 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 ($cc \geq 0.999$). Stock solutions were prepared by dissolving

ArN_2^+ in the appropriate acidic (HCl) mixture to minimize diazotate formation,[57] to give final concentrations of about 1×10^{-4} M and [HCl] = 3.6×10^{-3} M. Stock solutions were generally used immediately or within 90 min with storage in an ice bath to minimize decomposition.

Preliminary HPLC experiments showed that only four decomposition products are formed: ArOH, ArCl, ArH, and ArOEt. Linear ($cc > 0.999$) calibration curves for conversion of HPLC peak areas (A) into concentrations for these products were obtained by use of commercial samples. Percentages of formation (F) of dediazoniation products were obtained from the ratio of the dediazoniation product concentration ([Analyte]) and the initial diazonium salt concentration, estimated by weight: $F = 100\ [\text{Analyte}]/[ArN_2^+]$.

Chromatographic kinetic data for all dediazoniation products were obtained by a well established procedure described elsewhere.[37,55,58,59] Dediazoniations were quenched at convenient times with an aliquot of a stock quenching solution prepared by dissolving 2N6S in a solution containing TRIS buffer ([TRIS]= 0.05 M) as described elsewhere. After mixing, the final 2N6S concentration was about a 20-fold excess over that of arenediazonium salt and the final pH was about pH = 8, because naphthoxide ions are much more reactive than their protonated forms but as pH increases, the competing reaction between arenediazonium ions and OH^- to form diazotates becomes significant.[57] Rate constants for a coupling reactions in a number of solvents have been reported to be higher than those in water.[3] Nevertheless, auxiliary experiments performed at different $EtOH/H_2O$ mixtures by following azo dye formation spectrophotometrically showed that under our experimental conditions the coupling reaction is essentially over in the time of mixing of the reagents, so azo dye formation is at least 100 times faster than the fastest dediazoniation.

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