Competitive Homolytic and Heterolytic Dediazoniation Mechanisms: Rate Constants and Product Distribution of Methoxy-, Hydroxy-, and Hydro-Dediazoniation of 3- and 4-Methylbenzenediazonium Salts in Acidic MeOH/H_2O Mixtures

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ABSTRACT: The rates and product distribution for methoxy-, hydroxy- and hydro-dediazoniation and the rate constants for disappearance of 3- and 4-methylbenzenediazonium tetrafluoroborate in acidic MeOH/H_2O mixtures, in the presence and absence of electrolytes like HCl, NaCl, and $CuCl_2$, are reported. Data were obtained by using a combination of VIS-UV and

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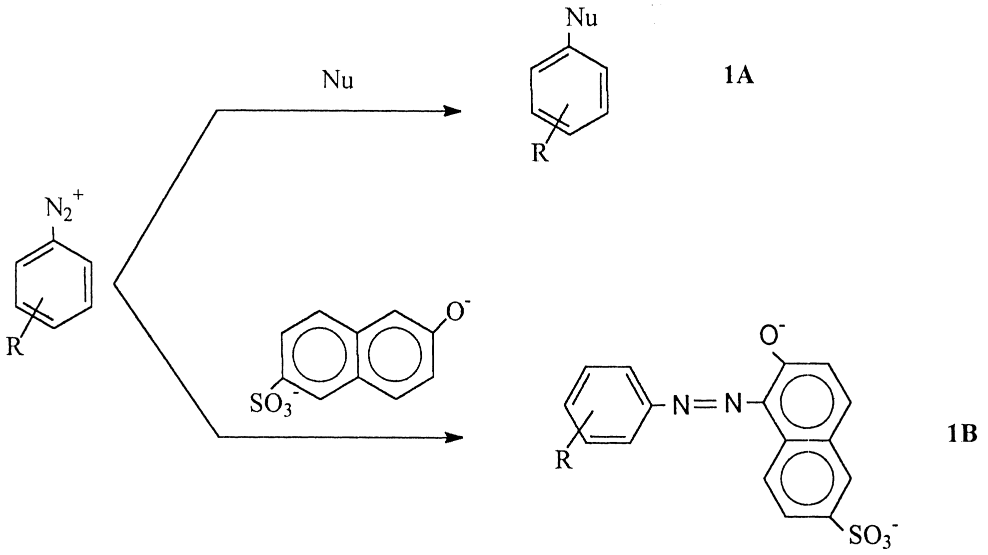
HPLC techniques. The kinetics and product distributions are completely consistent with competitive homolytic and heterolytic mechanisms, the heterolytic one being predominant at any solvent composition. Heterolytic data are in agreement with the predictions of a $D_N + A_N$ mechanism; that is, rate determining formation of an aryl cation that reacts immediately with available nucleophiles. Selectivity values, determined from product yields, are low and independent of solvent composition. Product formation is discussed in terms of a preassociation step between aryl cations and the nucleophile, which does not account for much of the trapping, and a nucleophilic attack on a "free" arenediazonium cation. Activation parameters were also determined at 99.5% MeOH: enthalpies of activation are high and entropies of activation are positive, and they are similar to those reported for pure water. Int J Chem Kinet 32: 210–220, 2000

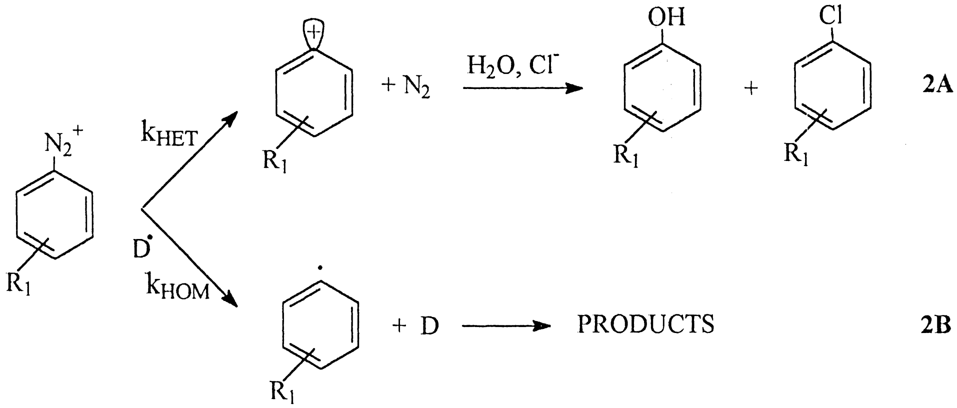
INTRODUCTION

The reactions of arenediazonium ions, ArN_2^+, Scheme I, have attracted considerable attention [1–3], both from a synthetic and from a mechanistic point of view, because of their extraordinary sensitivity to environmental changes [4,5]. In spite of the fact that a substantial body of knowledge about their reactions is available, some of their mechanisms are not completely understood. Electron density analysis [6] of a number of diazonium ions has shown that both aliphatic and aromatic diazonium ions are best thought of as carbenium ions closely associated with an internally polarized N_2 molecule, which implies a dative C—N bond (N→C σ donation and C→N π backdonation).

Solvolytic dediazoniations have been studied in a number of solvents [4,5] and, to date, it is believed that they take place through two main mechanisms, Scheme II, heterolytic, and homolytic. Literature reports [5] indicate that, in the absence of electron donors, heterolytic dediazoniations mainly take place in solvents of low nucleophilicity like H_2O or TFE; meanwhile, homolytic dediazoniations are favored by an increase in the nucleophilicity (HMPT, Pyridine). MeOH, EtOH, and DMSO have been reported as borderline solvents where both mechanisms can be observed, depending on several factors like pH [5], substituents of the aromatic ring [7,8], or even the atmosphere [8] (O_2 or N_2). The source of electrons is thought to be the solvent (i.e., D = MeOH), although the mechanism and the nature of the initiation step is unclear [5]. Bunnet et al. [7,8] postulated that, in alkaline methanol solutions, the source of radicals is the homolytic decomposition of a (Z)-diazo methyl ether, which is formed rapidly, yielding the aryl radical, N_2, and the methoxy radical; meanwhile, under acidic conditions they favor initiation by direct electron transfer from MeOH to the arenediazonium ion [7]. A particularly interesting aspect is the gradual changeover from heterolytic to homolytic dediazoniation, which led to the question of a common intermediate for these



Scheme I Reactions of arenediazonium ions. (a) Dediazoniation. (b) Representative nucleophilic addition: coupling reaction with 2-napthol-6-sulphonic, sodium salt.



Scheme II Dediazoniation mechanisms. (a) Heterolytic. (b) Homolytic.

two types of mechanisms [9]. Investigations developed by Bunnet et al. [7,8] and by Kuokkanen [10] suggest that there is no need to invoke such a common intermediate and that the formation of both homolytic and heterolytic products can be explained in terms of competitive mechanisms that are taking place simultaneously.

Evidence for the involvement of free radicals in dediazoniations has been obtained primarily by product analyses (primarily by HPLC and GC-MS) and from EPR measurements [11–13], and evidence for aryl cation intermediates in dediazoniations has been reported by several authors [5,14,15]. Experiments developed by Swain et al. [16] suggest that the aryl cation is formed reversibly, and a molecular orbital study of the benzenediazonium cation in water [17] is consistent with the formation of stable molecule-ion pairs. Zollinger and coworkers [18] concluded that molecular nitrogen reacts reversibly with the phenyl cation intermediate, and a number of flash photolysis studies [19] confirm that aryl cations are real intermediates in heterolytic dediazoniations although their lifetimes are extremely short, on the order of a few nanoseconds. The selectivity, S, of the reaction toward nucleophiles can be defined by Eq. 1, where C stands for percent of conversion to the corresponding dediazoniation product, and nucleophile concentrations are assumed to refer to the reaction site.

$$S_{\mathrm{Nu_2}}^{\mathrm{Nu_1}} = \frac{k_{\mathrm{Nu_1}}}{k_{\mathrm{Nu_2}}} = \frac{C_{\mathrm{R-Nu_1}}[\mathrm{Nu_2}]}{C_{\mathrm{R-Nu_2}}[\mathrm{Nu_1}]} \qquad (1)$$

Dediazoniations in MeOH [7–9] were mainly studied under alkaline conditions, usually at one fixed solvent composition, in contrast to the relatively few number of studies done under acidic conditions [20]. The lack of studies under such acidic conditions, and the relatively few data published on rates of product formation and on alcohol/water selectivities for the highly unstable arenediazonium cations, encouraged us to examine the kinetics and mechanism of the dediazoniation of 3- and 4-methylbenzenediazonium tetrafluoroborate (MMBD and PMBD, respectively) in binary methanol-water acid solutions over the whole composition range. The aim of the manuscript is twofold: to complement studies concerning nucleophilic attack on the short-lived aryl cations and to use it as a starting point for future solvolytic dediazoniations in binary mixtures and in colloidal systems [21–23] and in macromolecular systems [4,5,24]. Colloidal systems show significant gradients of polarity on going from the bulk phase to the core of the aggregate; meanwhile, macromolecular systems show relatively hydrophobic microscopic environments where arenediazonium ions can be located [21,25], thus competing with solvents for the macromolecular cavity or micellar sites. Therefore, those systems can determine the arenediazonium chemical reactivity by governing their contact with other substrates, which include the nucleophilic solvent molecules, incorporated in the system [21–23] and by governing the polarity of their immediate environment, which can be decisive for unimolecular decomposition reactions [24,26]. Few references about activation parameters of dediazoniations in methanol [9,10] can be found in the literature, although a number of them involve other solvents [9,27–29], so we have also determined their activation parameters to get insights into the nature of the transition state.

EXPERIMENTAL

Instrumentation

UV-VIS spectra and some kinetic experiments were followed on a Beckman DU-640 UV-VIS spectrophotometer equipped with a thermostated cell carrier attached to a computer for data storage. Product analysis was carried out on a WATERS HPLC system, which included a 510 pump, a 717 automatic injector, a 486 VIS-UV detector, and a computer for data storage. Products were separated on a Microsorb-MV C-18 (Rainin) reverse-phase column (25 cm length, 4.6 mm internal diameter, and 5 μm particle size) using 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 210 nm (PMBD) or 220 nm (MMBD).

Materials

Reagents were of the maximum purity available and were used without further purification. Toluene, ArH, cresols, ArOH, chlorotoluenes, ArCl, anisoles, ArOMe, copper (II) chloride (99.999%), and the reagents used in the preparation of diazonium 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 Häen. All solutions were prepared by using Milli-Q grade water.

Diazonium salts were prepared under nonaqueous conditions [30] and were stored in the dark at low temperature to minimize its decomposition and recrystallyzed periodically. Stock solutions were prepared dissolving the diazonium salt in the appropriate acidic (HCl) mixture to minimize diazotate formation [31], to give final concentrations of about 1×10^{-4} M and [HCl] $= 3.6 \times 10^{-3}$ M and were generally used immediately or within a short period of time with storage in an ice bath to minimize decomposition. Beer's law plots (not shown) for MMBD and PMBD aqueous and methanolic solutions up to 2.00×10^{-4} M are linear (cc = 0.999).

Methods

Kinetic data were obtained from spectrophotometric and chromatographic (HPLC) data by employing a well-established methodology [21,30,32–35]. Observed rate constants were obtained by fitting the absorbance-time, percent yield-time data to the integrated first-order equation (2) using a nonlinear least squares method provided by a commercial computer program, where M is the measured magnitude.

$$\ln\left(\frac{M_t - M_\infty}{M_0 - M_\infty}\right) = -k_o t \qquad (2)$$

All runs were done at $T = 35 \pm 0.1$°C (MMBD) and at $T = 60 \pm 0.1$°C (PMBD) with diazonium salts as the limiting reagents. Duplicate or triplicate experiments gave average deviations lower than 5%.

Spectrophotometric kinetic data were obtained by following the disappearance of diazonium salt at an appropriate wavelength to minimize interference mainly by chlorocuprate(II) complexes. Preliminary HPLC experiments showed that only four decomposition products are formed: ArOH, ArCl, ArOMe, and ArH. Linear (cc $>$ 0.999) calibration curves for converting HPLC peak areas, A, into concentrations were obtained for these products by employing commercial samples. The equations used were for MMBD (λ = 220 nm): A $= 2.06 \times 10^9$ [ArH], A $= 8.78 \times 10^9$ [ArOH], A $= 1.30 \times 10^{10}$ [ArOMe], A $= 9.16 \times 10^9$ [ArCl]; and for PMBD (λ = 210 nm): A $= 8.46 \times 10^9$ [ArH], A $= 9.78 \times 10^9$ [ArOH], A $= 1.24 \times 10^{10}$ [ArOMe], A $= 1.31 \times 10^{10}$ [ArCl].

Chromatographic kinetic data for all dediazoniation products were obtained following a published procedure [30] by quenching the dediazoniation reaction 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) to give, after mixing, final 2N6S concentrations about 20-fold excess over that of arenediazonium salt and final pH about pH = 8. Details of the method are given elsewhere [30]. Extra precautions have been taken to minimize MeOH evaporation when working at temperatures close to its normal boiling point or when studying the effect of temperature. Auxiliary experiments indicate that negligible evaporation, if any, takes place under our experimental conditions. Percentages of MeOH will be given hereafter by volume, and molar concentrations were calculated by ignoring the small excess volume of mixed solvents [36].

RESULTS

(a) Effects of Solvent Composition and Added Electrolytes on the Observed Rate Constant k_0

The effect of solvent composition on k_o, in the absence of added electrolytes, was investigated by changing the percentage of MeOH in the reaction mixture, Figure 1. For both MMBD and PMBD, k_o increases smoothly from $k_o = 7.97 \times 10^{-4}$ s^{-1} and $k_o = 6.11 \times 10^{-4}$ s^{-1} up to $k_o = 14.1 \times 10^{-4}$ s^{-1} and $k_o = 14.2 \times 10^{-4}$ s^{-1} at 99.6 % MeOH/H_2O, respectively. The k_o values at 0% MeOH are in agreement with those obtained with different techniques [30,32,34].

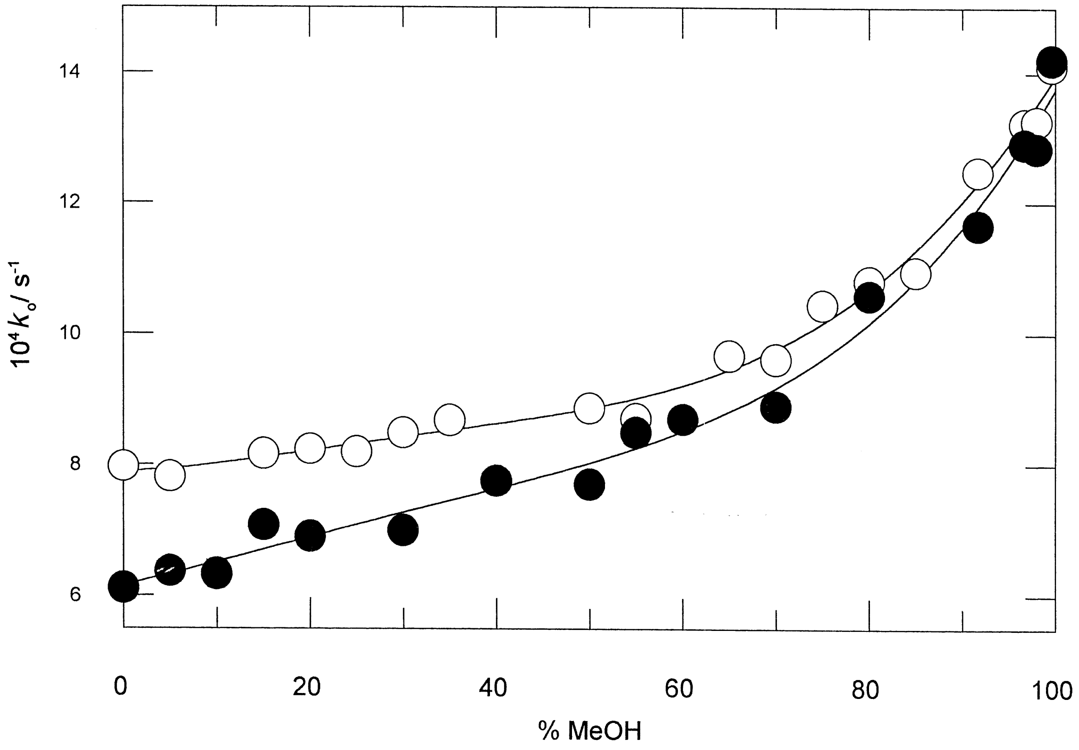


Figure 1 Variation of the observed dediazoniation rate constant, k_o, with solvent composition. ○ MMBD, ● PMBD. [MMBD] = [PMBD] = 1.0-2.0 $\times 10^{-4}$ M, [HCl] = 0.01 M, T = 35°C (MMBD), T = 60°C (PMBD)

The rate constants for product formation at different solvent compositions were obtained by HPLC. Results in Figures 2 and 3 are representative. Figure 2 shows the variation in the percent of conversion of PMBD to ArOMe (2A), ArOH, and ArH (2B) with time and the corresponding first-order plots in 98% MeOH: k_o values for product formation are the same, k_{ArOMe} = 13.8×10^{-4} s^{-1}, k_{ArOH} = 13.2×10^{-4} s^{-1} and k_{ArH} = 13.7×10^{-4} s^{-1}, thus indicating that both homolytic and heterolytic mechanisms are competitive, in agreement with previous reports. Figure 3A shows the variation in the amount of ArOMe formed with time for MMBD and the corresponding first-order plot, which yields k_o = 13.60×10^{-4} s^{-1}, a value equal, within experimental error, to that obtained monitoring ArOH formation (not shown) and to that obtained for MMBD loss from the variation of the absorbance of the corresponding azo dye with time (Fig. 3B).

The sensitivity of the dediazoniation to changes in solvent polarity can be shown by means of the Grunwald-Winstein equation [37–40], Figure 4, yielding slopes of −0.037 (MMBD) and −0.07 (PMBD), consistent with the low selectivity of dediazoniations to medium effects [4,5], which has been attributed to the similarity in structure and charge distribution between the parent arenediazonium ion and the corresponding aryl cation [32].

The effect of added electrolytes like HCl (0–1.0 M), NaCl (0–1.0 M), and $CuCl_2$ (0–0.01 M) on k_o was investigated at different MeOH/H_2O mixtures (20, 40, 80 and 99.5% v/v). Tabulated data are given as supplementary material. The observed rate constants do not change significantly upon addition of any of those electrolytes, exhibiting a similar variation as that observed for other arenediazonium ions in water [30,32]. It has been reported that $CuCl_2$ has a negligible effect on the observed rate constants of methylbenzenediazonium ions [30,32] but catalyzes the spontaneous decomposition of p-nitrobenzenediazonium in aqueous solutions [33]. $CuCl_2$ forms a number of chlorocomplexes in solution whose relative concentration depends on a number of factors such as halide concentration, temperature, and solvent [41], and up to four complexes can be formed in aqueous solutions containing Cl^- ions [41]: $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$, $CuCl_3^-$ and $CuCl_4^{2-}$ being predominant at high chloride ion concentrations [42]. However, the main copper(II) complexes formed in pure methanol [43] are $CuCl^+$ and $CuCl_2$. Therefore, our results are consistent with those expected from the interaction be-

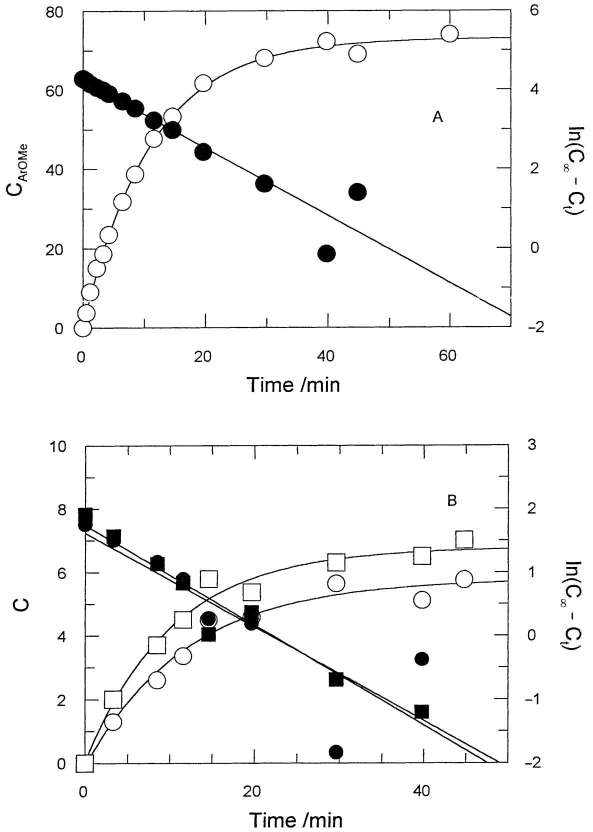


Figure 2 (a) Variation in the yield of PMB-OMe with time (○) and first-order plot (●). (b) Variation in the percent of conversion to PMB-OH (○) and PMB-H (□) and first-order plots (● and ■ respectively). [PMBD] = 1.3 × 10^{-4} M, [HCl] = 0.01 M, 98% MeOH, T = 60°C

tween positive or neutral Cu(II) chlorocomplexes with ArN_2^+ ions.

(b) Effects of Solvent Composition and Added Electrolytes on Dediazoniation Product Yields

Figure 5 shows the effects of solvent composition on MMBD and PMBD dediazoniation product yields in the absence of added electrolytes. Figure 5A shows that for MMBD only two dediazoniation products, ArOH and ArOMe, are formed in significant yields. The reduced ArH dediazoniation product is detected in highly alcoholic solutions, but its yield is very low compared with those of heterolytic products. Quantitative conversion to products is achieved in all composition ranges. For PMBD (Fig. 5B), quantitative conversion to products is achieved in all composition ranges and product distribution is similar to that for MMBD, but the formation of the corresponding reduced product, ArH, is a little more favored than for MMBD, in agreement with literature reports [5]. Results in pure water for OMBD and PMBD are in agreement with published data [30,32,34].

Table I shows that the selectivity of the MMBD and PMBD dediazoniation, S_W^{MeOH}, as defined by Eq. 1, is low and essentially independent of the percentage of MeOH in the reaction mixture, suggesting that the ratio of rates involved in Eq. 1 is insensitive to solvent composition and polarity. The average S values, S_W^{MeOH} = 0.63 (MMBD) and S_W^{MeOH} = 0.74 (PMBD), are similar to those reported for other dediazoniations in butanol [22], S_W^A = 0.28 at T = 40°C.

The effect of added electrolytes like HCl (0–1.0 M), NaCl (0–1.0 M), and $CuCl_2$ (0–0.01 M) on product yields was investigated at different MeOH/H_2O mixtures up to 75% MeOH v/v. Tabulated data are given as supplementary material. Three heterolytic dediazoniation products, ArOH, ArCl, and ArOMe, are obtained. Upon increasing the percentage of MeOH, ArOMe yield increases with a concomitant decrease

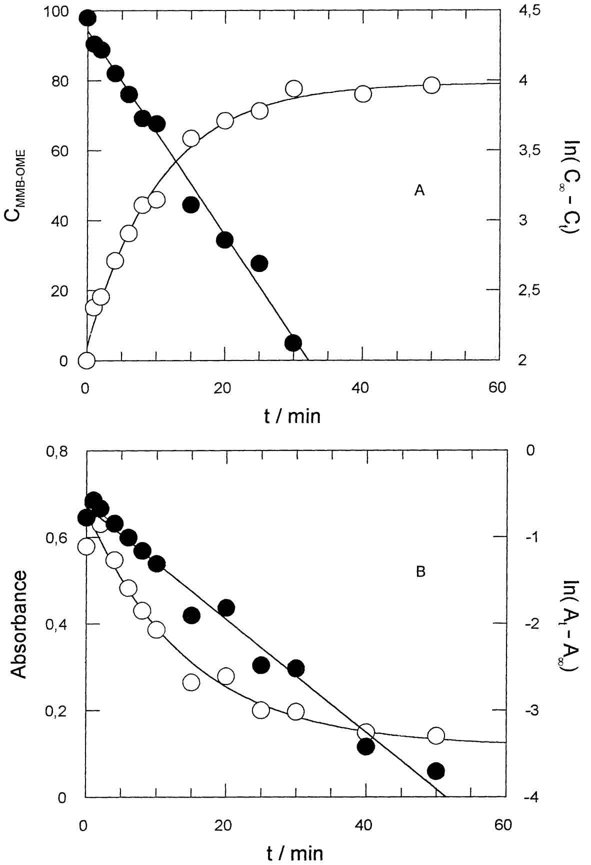


Figure 3 (a) Variation in the yield of MMB-OME with time (○) and ln plot (●). (b) Variation in the absorbance of the azo dye (see text) with time (○) and ln plot (●) for MMBD. [MMBD] = 1.5 × 10^{-4} M, [HCl] = 0.01 M, 99% MeOH, T = 35°C.

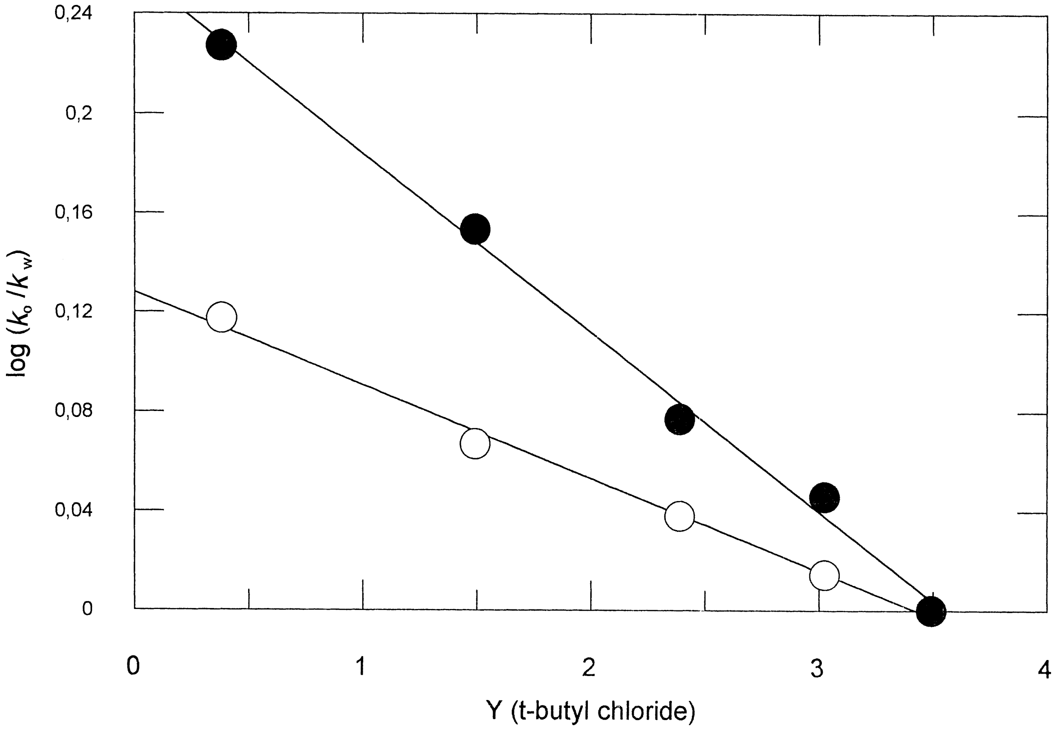


Figure 4 Winstein-Grunwald plots for MMBD (○) and PMBD (●). Y values from reference 37.

in ArOH yield. Conversions to ArCl as low as 8% are obtained at $[Cl^-] = 1.0$ M (75% MeOH/H_2O), and the reduction product ArH is only detected at high percentages of MeOH, its yield being essentially independent of electrolyte concentration.

(c) Effect of Temperature on k_0: Activation Parameters

Experimental activation parameters were determined by measuring k_o at different temperatures for MMBD at 99.5% MeOH, (Fig. 6A), and for PMBD at a number of solvent compositions, (Fig. 6B). Activation parameters were obtained according to the theory of absolute rates by means of Eq. 3, where k_B and h are the Boltzmann and Planck constants, respectively.

$$\ln\left(\frac{k_{\mathrm{obs}}}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \qquad (3)$$

Table II shows the activation energy and the activation parameters for the three methylbenzenediazonium ions at 99.5% MeOH: values of $\Delta H^{\#}$ are relatively high compared with those for bimolecular reactions [44,45], and the entropic term is substantially positive. For the sake of comparison, we have included published activation parameters in pure water and MeOH and k_o values for the three methylbenzene derivatives at one fixed temperature ($T = 40$°C) at 99.5 % MeOH.

DISCUSSION

Observed rate constants of formation of homolytic and heterolytic dediazoniation products are equal and equal to those obtained for diazonium ion loss (Figs. 1, 2, and 3), thus the products are generated with the same half-life. As noted, there is no need to invoke a common intermediate [7,8] for homolytic and heterolytic dediazoniation mechanisms; therefore, our results are consistent with the competitive dediazoniation mechanism indicated in Scheme II. HPLC data (Fig. 5), show that quantitative conversion to products is achieved in the whole composition range. At low percentages of MeOH, two heterolytic products are formed: ArOH and ArCl; however, at high methanol content the reduction product ArH is detected in relatively significant amounts, its yield being very low compared to that of ArOMe. ArH formation is favored by a *para*-methyl compared with a *meta*-methyl and

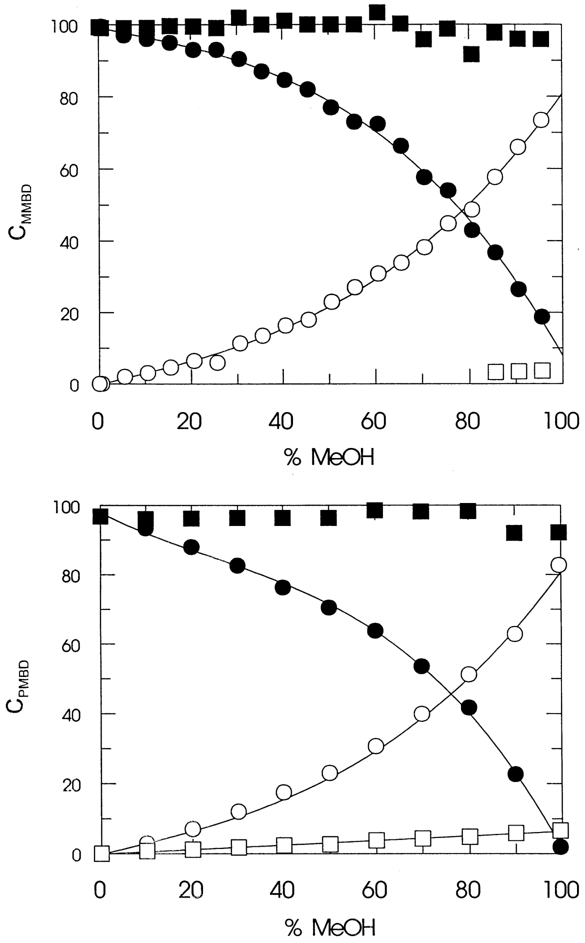


Figure 5 Influence of solvent composition on dediazoniation product yields. ● ArOH, ○ Ar-OME, □ Ar-H, ■ Total yield.

Table I Selectivity Values According to Equation 1 for MMBD and PMBD at Different Solvent Compositions. Data from Figure 5

% MeOH	S_W^{MeOH} (MMBD)	S_W^{MeOH} (PMBD)
10	0.63	0.67
20	0.62	0.77
30	0.65	0.77
40	0.65	0.75
50	0.66	0.75
60	0.63	0.73
70	0.63	0.73
80	0.62	0.70
90	0.60	0.70

ortho-methyl, in agreement with literature reports [5,11], but for both MMBD and PMBD diazonium salts, ArH yields are very low compared with those of the heterolytic products (ArOH or ArOMe), and therefore the predominant mechanism is the heterolytic one in the whole composition range. Therefore, assuming the competitive mechanism indicated in Scheme II, $k_o = k_{HOM} + k_{HET}$. For PMBD, the ratio of the rate constants for the homolytic and heterolytic mechanisms at 100% MeOH is given by $k_{HET}/k_{HOM} = (C_{ArOH} + C_{ArOMe})/C_{ArH} \approx 14$ (Fig. 5B). The value of the k_{HET}/k_{HOM} ratio increases upon decreasing the percentage of MeOH, and because of this, we considered that the homolytic process is not significant for these arenediazonium salts at any solvent composition and focused our attention on the heterolytic mechanism by assuming that $k_o \approx k_{HET}$.

Spectrophotometric kinetic data (Fig. 1) indicate that the rates of dediazoniation do not change signifi-

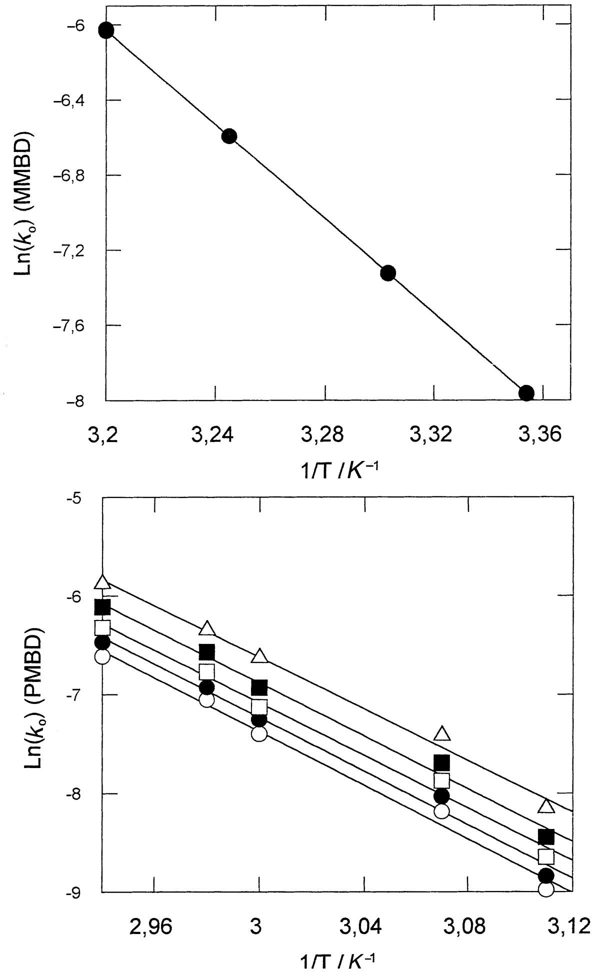


Figure 6 Arrhenius plots for MMBD at 99.5% MeOH and for PMBD at: ○ 0%, ● 25%, □ 50%, ■ 75%, △ 99.5% MeOH. [MMBD] = [PMBD] = 1.0 – 1.5 × 10^{-4} M, [HCl] = 0.01 M.

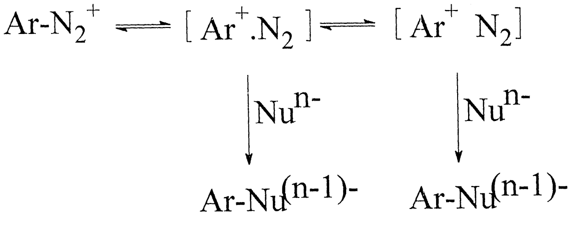
Table II Activation Parameters for the Three Methyl Substituted Benzenediazonium Ion in Water and 99.5% MeOH and Dediazoniation k_0 Values at T = 40°C

	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		
OMBD	26.5–41.0	14.88	2.1	108.2	106	40.4
MMBD	26.5–41.0	12.55	2.8	109.5	107	43.0
PMBD	40.0–60.0	0.52	1.7	112.4	110	21.6
99.5% MeOH						
BD		8.5				
OMBD	25–40	23.8	0.79	105 ± 1	105 ± 2	40.8
MMBD	25–40	24.05	0.94	105 ± 1	106 ± 1	42.5
PMBD	40–65	0.91(1.0)(DeTar)	0.79	114 ± 2	109 ± 2	25.6

* BD stands for benzenediazonium.[9]

cantly on going from water to methanol. A unimolecular reaction in which the nucleophilic attack of the solvent is rate-determining would lead to a strong dependence of k_o on nucleophile concentration, which is not observed. On the other hand, dediazoniation rate constants are insensitive to added electrolytes, and HPLC kinetic data (Figs. 2 and 3) indicate that the rate constant of formation of dediazoniation products is the same as that of disappearance of diazonium ion. Therefore, our results are consistent with a rate-determining step formation of a highly reactive aryl cation intermediate.

Selectivity values, as defined by Eq. 1, remain essentially constant on going from water to methanol (Table I), the average value for MMBD being $S_W^{MeOH} = 0.63$ and that for PMBD $S_W^{MeOH} = 0.74$. Such values are orders of magnitude lower than those observed for anionic nucleophiles competing with water in reactions with stabilized carbocations [38,39,46] but very similar to those reported for other arenediazonium ions in alcohols [22,23]. Low selectivity values are consistent with the formation of a highly reactive cation, that is, with the reactivity-selectivity principle. The nucleophilic attack on carbocations [38] may occur on "free" carbocations, on solvent-separated ion pairs, or on "intimate" contact ion pairs. The low S values obtained are consistent with a preassociation stepwise mechanism, Scheme III, in which the aryl cation, which has a short but finite lifetime, forms a "complex" with the nucleophile before the product is formed [47]. The rates of nucleophilic attack on aryl cations [19] have been reported to be close to the diffusion-control limit (i.e., ~10^9 M^{-1} s^{-1}) and, since lifetimes of aryl cation intermediates [19], although currently unknown, are ≤2–4 nanoseconds, most of the reaction of the aryl cation with the added nucleophile is occurring through the "free" ion, and preassociation of the nucleophile with the aryl cation does not account for much of the trapping. Therefore, all evidence is consistent with a heterolytic $D_N + A_N$ mechanism; that is, rate-determining formation of a "free" aryl cation, which reacts immediately, with very low selectivity, with available nucleophiles.



Scheme III

The low variation in k_o on going from water to methanol (Fig. 1) suggests that the solvation of the ground state is essentially the same as that in the proximity of the transition state; that is, the free energy of activation is not significantly affected by solvent composition. Analysis of activation parameters (Table II) indicates that $\Delta H^{\#}$ values are as high as in many unimolecular reactions [38,45], suggesting a transition state that has undergone bond breaking with little compensating bond making. Solvolytic unimolecular reactions can exhibit both positive and negative $\Delta S^{\#}$ values [39,46]. Positive $\Delta S^{\#}$ values, as we have found, suggest that the transition state has a greater structural freedom than reactants. These results are consistent with the reported positive volumes of activation, $\Delta V^{\#}$, for a number of dediazoniations in methanol [28,48–50], providing further support to the $D_n + A_n$ mechanism. On the other hand, since $\Delta S^{\#}$ values are positive, they compensate the large enthalpy term, making dediazoniations proceed at a considerable rate compared with other unimolecular reactions, as found for a number of dediazoniations in different solvents [5]. This term, however, does not contribute significantly to $\Delta G^{\#}$ because dediazoniation, as described in Scheme 3, suggests that formation of the aryl cation does not involve separation of charge but its redistribution, in agreement with electronic structure analysis studies [6]; thus, the parent arenediazonium ion and the aryl cation polarize to a similar extent the solvent. Consequently, dediazoniations show a much lower solvent dependence [5] than typical unimolecular reactions in agreement with our data and with independent experimental observations: in 19 solvents [51] the rates of heterolytic dediazoniation vary by a factor of only 9.

CONCLUSIONS

We have studied the solvolysis of 3- and 4-methylbenzenediazonium ions over the whole methanol-water composition range employing a methodology that allows simultaneous determination of rate constants for product formation and diazonium ion loss and estimations of product yields. Observed rate constants and product yields are completely consistent with competitive homolytic and heterolytic dediazoniation mechanisms, although the heterolytic one is predominant at any solvent composition. Enthalpies of activation are high and entropies of activation are positive, making dediazoniations proceed at a considerable rate compared with typical unimolecular reactions. Their values are very similar to those found in pure water, consistent with the slight increase in dediazoniation rate constants observed on going from water to methanol. Therefore, all evidence is consistent with a $D_N + A_N$ mechanism; that is, rate-determining formation of a “free” aryl cation that reacts immediately with available nucleophiles.

SUPPLEMENTARY MATERIAL

Tabulated data of the observed rate constants and of the dediazoniation product yields at a number of solvent compositions, in the absence and presence of added electrolytes (4 pages), are available. Ordering information is provided at any current masthead.

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REFERENCES

1. Klamann, D. Methoden der Organischen Chemie, 4th ed.; Houben-Weyl: Thieme, Stuttgart, 1990; Vol. E16a, Part II.
2. Hertel, H. Ullman’s Encyclopedia of Industrial Chemistry, 5th ed.; VCH: Weinheim, 1987; Vol. A8.
3. Herbs, W.; Hunger, K. Industrial Organic Pigments; VCH: Weinheim, 1993.
4. Saunders, K. H.; Allen, R. L. M. Aromatic Diazo Compounds; 3rd ed.; Edward Arnold:, 1985.
5. Zollinger, H. Diazo Chemistry I, Aromatic and Heteroaromatic Compounds; VCH: Weinheim, 1994.
6. Glaser, R.; Horan, C. J.; Lewis, M.; Zollinger, H. J Org Chem 1999, 64, 902.
7. Broxton, T. J.; Bunnet, J. F.; Paik, C. H. J Org Chem 1977, 42, 643.
8. Bunnet, J. F.; Yijima, C. J Org Chem 1977, 42, 639.
9. DeTar, D. F.; Kosuge, T. J Am Chem Soc 1958, 80, 6072.
10. Kuokkanen, T. Finn Chem Lett 1984, 38.
11. Galli, C. Chem Rev 1988, 88, 765.
12. Hanson, P.; Jones, J. R.; Gilbert, B. C.; Timms, A. W. J Chem Soc, Perkin Trans. 2 1991, 1009.
13. Hanson, P.; Hammond, R. C.; Goodracre, P. R.; Purcell, J.; Timms, A. W. J Chem Soc, Perkin Trans 2, 1994, 691.
14. Scaiano, J. C.; Kim-Thuan, J. J Photochem 1983, 23, 269.
15. Cacace, F. Science 1990, 250, 292.
16. Swain, C. G.; Sheats, J. E.; Harbison, K. G. J Am Chem Soc 1975, 97, 783.
17. Gamba, A.; Simonetta, M.; Suffritti, G. B.; Szele, I.; Zollinger, H. J Chem Soc, Perkin Trans 2 1980, 493
18. Ravenscroft, M. D.; Tagaki, K.; Weiss, B.; Zollinger, H. Gazz Chim Italiana 1978, 117, 353.
19. Steenken, S.; Ashokkumar, M.; Maruthamuthu, P.; McClelland, R. A. J Am Chem Soc 1998, 120, 11925.
20. Pazo-LLorente, R.; Sarabia-Rodriguez, M. J.; Gonzalez-Romero, E.; Bravo-Díaz, C. Int J Chem Kin 1999, in press.
21. Bravo-Diaz, C.; Soengas-Fernandez, M.; Rodriguez-Sarabia, M. J.; Gonzalez-Romero, E. Langmuir 1998, 14, 5098.
22. Chauduri, A.; Loughlin, J. A.; Romsted, L. S.; Yao, J. J Am Chem Soc 1993, 115, 8351.
23. Chauduri, A.; Romsted, L. S.; Yao, J. J Am Chem Soc 1993, 115, 8362.
24. Bravo-Díaz, C.; Sarabia-Rodriguez, M. J.; Barreiro-Sio, P.; Gonzalez-Romero, E. Langmuir 1999, 15, 2823.
25. Bartsch, R. A. Complexation of Aryl Diazonium ions by polyethers, in The Chemistry of Triple-Bonded Functional Groups; J. Wiley & Sons: New York, 1983; Vol. 2.
26. Bravo-Díaz, C.; Romero-Nieto, M. E.; Gonzalez-Romero, E. Langmuir 1999, accepted for publication.
27. Ishida, K.; Kobori, N.; Kobayashi, M.; Minato, H. Bull Chem Soc Jpn 1970, 43, 285.
28. Kuokkanen, T. Finn Chem Lett 1981, 52.

29. Kuokkanen, T. Finn Chem Lett 1981, 81.
30. Garcia-Meijide, M. C.; Bravo-Diaz, C.; Romsted, L. S. Int J Chem Kinet 1998, 30, 31.
31. Zollinger, H.; Wittwer, C. Helv Chim Acta 1952, 35, 1209.
32. Pazo-LLorente, R.; Rodriguez-Sarabia, M. J.; Gonzalez-Romero, E.; Bravo-Díaz, C. Int J Chem Kinet 1999, 31, 73.
33. Bravo-Diaz, C.; Romsted, L. S.; Harbowy, M.; Romero-Nieto, M. E.; Gonzalez-Romero, E. J Phys Org Chem 1999, 12, 130.
34. Bravo-Diaz, C.; Gonzalez-Romero, E. Anal Chim Acta 1999, 385, 373.
35. Romero-Nieto, M. E.; Bravo-Diaz, C.; Gonzalez-Romero, E. Submitted for publication (Int J Chem Kin) 1998.
36. Yamamoto, H.; Ichikawa, K.; Tokunaga, J. J Chem Eng Data 1994, 39, 155.
37. Leffler, J. E.; Grunwald, E. Rates and Equilibria of Organic Reactions; Dover: New York, 1989.
38. Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry, 3rd ed.; Harper-Collins Pub.: New York, 1987.
39. Pross, A. Theoretical & Physical Principles of Organic Reactivity; J. Wiley & Sons: New York, 1995.
40. Grunwald, E.; Winstein, S. J Am Chem Soc 1948, 70, 846.
41. Schwing-Weill, M. J. Bull Soc Chim France 1973, 3, 823–830.
42. Salmon, P. S.; Neilson, G. W.; Enderby, J. E. J Phys C, Solid State Phys 1988, 21, 1335–1349.
43. Manahan, S. E.; Iwamoto, R. T. J Electroanal Chem 1967, 13, 411–417.
44. Isaacs, N. Physical Organic Chemistry, 2nd ed.; Longman Scientific & Technicals:, 1995.
45. Maskill, H. The Physical Basis of Organic Chemistry; Oxford Univ. Press: Oxford, 1995.
46. Ritchie, C. D. Physical Organic Chemistry: The Fundamental Concepts, 2nd ed.; Marcel Dekker: New York, 1990.
47. Jenks, W. P. Chem Soc Rev 1981, 10, 345.
48. Brower, K. R. J Am Chem Soc 1960, 82, 4535–4537.
49. Kuokkanen, T. Finn Chem Lett 1980, 189.
50. Kuokkanen, T. Finn Chem Lett 1980, 192.
51. Szele, I.; Zollinger, H. Helv Chim Acta 1978, 61, 1721.