Hydroxy- and Chloro-Dediazoniation of 2- and 3-Methylbenzenediazonium Tetrafluoroborate in Aqueous Solution

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ABSTRACT: We have measured the rates and product yields of dediazoniation of 2- and 3methylbenzenediazonium tetrafluoroborate in the presence and absence of electrolytes like HCl, NaCl, and CuCl₂ using a recently reported methodology that allows simultaneous determination of product concentrations and rates of product formation and, indirectly, loss of starting material. Activation parameters were also obtained: enthalpies of activation are high, and entropies of activation are positive. All results are consistent with a heterolytic mechanism involving the fragmentation of the arenediazonium ion into a very reactive phenyl cation. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31 73–82, 1999

INTRODUCTION

Use of arenediazonium ions as chemical trapping reagents has increased notably in the last years. They are currently been used as assay to measure proteases activities [1], to probe interfacial compositions of micelles and microemulsions [2,3], to determine counterion selectivities and co-ion concentrations in micelles, [4,5] and to determine other chemicals like

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diuretics, sulphonamides [6,7], phenols, and arylamines [8]. All those methods are based on arenediazonium derivatization employing reactions that occur either at the arene nucleus (dediazoniation reactions, Scheme 1A) or at the terminal nitrogen of the diazonium group (nucleophilic addition, 1B) to form stable compounds that can be analyzed quantitatively. The arrow in Scheme 1 indicates a bonding model that implies a C—N dative bond (synergistic C \leftarrow N σ bond and C \rightarrow N π backdative bond) as found by theoretical studies, [9] and will be used hereafter in all schemes to represent such bond model.

Addition reactions, Scheme 1B, are the classical route to obtain azo dyes and pigments [10]. In principle, all aromatic and heteroaromatic diazonium salts can be used as electrophilic reagents; its electrophilicity depends on substituents: electro-withdrawing

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Scheme 1 Basic representation of reactions of arenediazonium ions. (A) Dediazoniation; (B) nucleophilic addition.

substituents increase their electrophilicity, meanwhile, electrodonating substituents decrease it. Therefore, the coupling components must be substances that possess structures able to build up very high electron densities at one or more carbon atoms. This requirement is usually achieved by the presence of hydroxy or amino groups, which increases the C-nucleophilicity of the coupling component. Dediazoniations of aromatic diazonium ions involve a number of mechanisms leading to a wide range of products [11,12]. They can take place with a variety of nucleophiles, Scheme 1A, via both spontaneous, for example, the Griess $(Y = Cl^{-}, Br^{-}, I^{-})$, Schieman $(Y = F^{-})$, and catalyzed, for example, the Sandmeyer ($Y = Cl^{-}, Br^{-},$ CN⁻) reactions. They are believed [11,12] to occur by either heterolytic (Scheme 2A), or, in the presence of an electron donor, D, homolytic pathways (Scheme 2B). In the absence of catalysts, with weakly basic nucleophiles, in the presence of O_2 , in aqueous acid, and in the dark, dediazoniations are believed to proceed via rate determining loss of N2, generating a highly reactive phenylcation that reacts rapidly and with very low selectivity with available nucleophiles [12]. In nonaqueous solvents, products associated with free radicals, for example, biphenyl derivatives and replacement of $-N_2^+$ by -H, are often observed, especially when electron-withdrawing groups are present on the arenediazonium ion [11–13].

The present article describes part of a recent and on-going investigation of the effects of added electrolytes and other compounds on dediazoniation rates and product yields of arenediazonium ions employing a novel, recently reported, methodology [14] that allows simultaneous determination of dediazoniation product vields, rate constants for the formation of all dediazoniation products, and, indirectly, the rate constant for the disappearance of the diazonium salt. To expand the scope of its applicability we examined the kinetics and mechanism of the dediazoniation of 2- and 3methylbenzenediazonium salts (OMBD and MMBD, respectively) in water. Few references about activation parameters of dediazoniations in water [15] can be found in the literature, but a number of them can be found in other solvents [16-19], so we have also determined their activation parameters.

EXPERIMENTAL

Instrumentation

UV-VIS spectra and some kinetic experiments were obtained 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 that included a 560 pump, a 747 automatic injector, a 486 VIS-UV detector, and a computer for data storage and analysis. Products were separated on a Microsorb-MV C-18 (Rainin) reverse-phase column (25-cm length,



Scheme 2 Simplified dediazoniation mechanisms. (A) Heterolytic; (B) homolytic.

4.6-mm internal diameter, and 5- μ m particle size) using a mobile phase of 65/35 v/v MeOH/H₂O containing 10⁻⁴ M HCl. The injection volume was 25 μ L in all runs, and the UV detector was set at 220 nm. pH was measured using a previously calibrated Metrohm 713 pH-meter.

Materials, Reagents, and Solutions

Reagents were of the maximum purity available and were used without further purification. Cresols, ArOH, chlorotoluenes, ArCl, 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 Pflatz & Bauer. Other materials employed were from Riedel de Haen. All solutions were prepared by using Milli-Q grade water.

Diazonium salt preparation was done following an anhydrous method [20] and stored in the dark at low temperature to minimize its decomposition. Their stock solutions were prepared dissolving the appropriate amount of the diazonium salt in aqueous HCl to minimize diazotate formation [12] and 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.

Methods

Kinetic data were obtained both spectrophotometrically and chromatographically. Observed rate constants were obtained by fitting the absorbance-time or percent yield-time data to the integrated first-order eq. (1) using a commercial nonlinear least-squares method, where M is the measured magnitude, either absorbance or yields. (The word "yield" will be used to represent percent yield here and throughout the text, except in figures and equations where we will employ the symbol "Y").

$$\ln(M_t - M_{\infty}) = \operatorname{Ln}(M_o - M_{\infty}) - k_{obs}t \qquad (1)$$

All runs were done at $T = 35 \pm 0.1$ °C, except when investigating the influence of temperature, with diazonium salts as the limiting reagent.

Spectrophotometric kinetic data were obtained by following the disappearance of diazonium ion at an appropriate wavelength to minimize interferences mainly by chlorocuprate (II) complexes. The Beer's law plots (Fig. 1) for aqueous MMBD and OMBD solutions up to 2.00×10^{-4} M are linear (cc. = 0.999)



Figure 1 Beer law plot OMBD and MMBD. Experimental conditions: [HCl] = 0.01 M, $\Box \lambda = 260$ nm, $\bullet \lambda = 320$ nm, $\bigcirc \lambda = 247$ nm, $\blacktriangle \lambda = 310$ nm.

yielding $\epsilon_{260} = 9664 \pm 137 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{320} = 1906 \pm 46 \text{ M}^{-1} \text{ cm}^{-1}$ (OMBD) and $\epsilon_{247} = 4674 \pm 82 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{310} = 1502 \pm 26 \text{ M}^{-1} \text{ cm}^{-1}$ (MMBD).

Preliminary HPLC experiments showed that only two decomposition products are formed: ArOH and ArCl. Calibration curves for converting HPLC peak areas into concentrations were obtained simultaneously for all dediazoniation products, ArOH and ArCl, by employing commercial samples dissolved in solutions of similar composition to those used in the HPLC analysis of dediazoniation products (see below). The equations used to convert peak areas into concentrations and their typical retention times (t_r/min) were: area = 8.11×10^9 [OMB-OH] $(t_r = 6.1);$ area = 8.07 × 10⁹ [OMB-C1] $(t_r =$ 27.4); area = 8.62×10^9 [MMB-OH] ($t_r = 5.8$); and area = 8.90×10^9 [MMB-Cl] ($t_r = 29.0$). Yields of dediazoniation products were obtained from the ratio of the dediazoniation product concentration, [Analyte], and the initial diazonium salt concentration, [DS], estimated by weight, eq. (2).

$$Y = \frac{[\text{Analyte}]}{[\text{DS}]} \tag{2}$$

Chromatographic kinetic data for all dediazoniation products were obtained following a published procedure [14]. Dediazoniation was quenched at convenient times with an aliquot of a stock quenching solution prepared by dissolving the coupling reagent 2-naphthol-6-sulphonic acid, sodium salt (2N6S), with an approximately 20-fold excess of 2N6S after mixing, in water containing TRIS buffer (C = 0.05 M) to give a final pH of about pH = 8 after mixing. This pH was chosen to maximize the rate of azo dye formation [10,21] because phenoxide ions are much more reactive than their parent phenols [11], but as pH increases, the competing reaction of arenediazonium ions with OH⁻ to form diazotates becomes significant [21,22]. The use of a coupling reaction to stop the dediazoniation reaction requires that its rate be faster than the dediazoniation rate [14]. Auxiliary experiments done by following azo dye formation spectrophotometrically shows that under our experimental conditions the coupling reaction is essentially over in the time of mixing reagents. All samples were analyzed in duplicate, being the relative standard deviation of the peak areas was less than 2%.

We have also estimated k_{obs} for the disappearance of diazonium ions by adding sufficient concentrated HCl dropwise to each volumetric flask to give a final [H⁺] ≈ 0.2 M, and measuring the absorbance of each solution at λ_{max} of the corresponding azo dyes: $\lambda_{max} = 529$ nm (OMBD), $\lambda_{max} = 484$ (MMBD). The added HCl ensures that only the protonated form of the azo dye is present, and that the measured absorbance is directly proportional to the concentration of the azo dye and, therefore, the concentration of unreacted diazonium salt.

RESULTS

Influence of NaCl and HCl on k_{obs}

The effects of NaCl and HCl on k_{obs} were determined by monitoring the decrease in absorbance of arenediazonium ions with time at different NaCl and HCl concentrations (Table I) and fitting the kinetic data to eq. (1). Table I shows that k_{obs} is not affected by changing NaCl concentration or the acidity of the medium in the concentration ranges employed ([NaCl] = 0–1.0 M, [HCl] = 0–1.0 M), yielding average values of $k_{obs} = 10.31 \times 10^{-4} \text{ s}^{-1}$ (OMBD) and $k_{obs} = 8.04 \times 10^{-4} \text{ s}^{-1}$ (MMBD). These values are in good agreement with the ones in the literature [15] obtained by N₂ evolution.

Influence of $CuCl_2$ on k_{obs}

The effect of CuCl₂ concentration on k_{obs} was studied by keeping the total chloride ion concentration constant ([Cl⁻]_{tot} = 1.0 M) to hold the relative amount of chloro complexes in the medium constant [23–25]. k_{obs} values (Table I) are not affected by changing Cu(II) concentration from [CuCl₂] = 0–50 × 10⁻³ M, and they are virtually identical to those obtained in NaCl or HCl. The effect of higher CuCl₂ concentrations could not be studied by UV-VIS spectroscopy because of the absorbance of Cu(II) complexes [23,24].

Estimates of k_{obs} by HPLC and Quenching

Yields of ArOH, ArCl and their total ($Y_T = Y_{ArOH} + Y_{ArCl}$) as a function of time were determined by HPLC analysis of the products. Results in Figure 2(A) (OMBD) and 2(B) (MMBD) are representative. In all cases, we obtained only two dediazoniation products: ArOH and ArCl. Only yields of ArOH were used to calculate k_{obs} because products are formed competitively and because conversion to ArOH is almost quantitative in the absence of CuCl₂ and is reduced only slightly by added CuCl₂ (see later). Figure 2(A) and (B) also shows the first-order plots according to eq. (1). k_{obs} values were $k_{obs} = 10.13 \times 10^{-4} s^{-1}$ (OMBD) and $k_{obs} = 7.80 \times 10^{-4} s^{-1}$ (MMBD), equal, within experimental error (<5%), to those obtained spectrophotometrically.

Observed rate constants for loss of arenediazonium ions were also obtained from the variation of the absorbance of the azo dye with time. We chose as representatives the results shown in Figure 3, obtained at different temperatures for OMBD (A) and MMBD (B). k_{obs} values are the same, within experimental error, to those following diazonium salt loss spectrophotometrically (Table I and Fig. 4) and ArOH formation chromatographically (Fig. 2).

Effect of Added Electrolytes on Product Distribution

The effects of HCl, NaCl, and CuCl₂ on product yields was determined by analyzing conveniently prepared samples at infinite time, i.e., after dediazoniation was over. Table II shows that conversion to products is essentially quantitative. Only two products are formed—ArOH and ArCl—ArOH being the major product. As shown, changes in electrolyte concentration have no significant influence on product yields in the range of concentrations employed.

Run	10 ⁴ [OMBD]/M	[HCl]/M	[NaCl]/M	10 ³ [CuCl ₂]/M	$10^4 k_o / s^{-1}$
1	2.11	0			10.19
2	2.11	0.1	_	_	9.90
3	2.11	0.5	—	_	9.50
4	2.11	0.7	_	_	10.42
5	2.11	1.0	_	_	10.41
6	2.11	0.02	0.1	_	10.71
7	2.11	0.02	0.3		11.30
8	2.11	0.02	0.5	—	10.56
9	2.11	0.02	0.7	_	10.23
10	2.31	0.02	1.0		10.86
11	2.31	0.02	1.0	2.02	9.47
12	2.31	0.02	1.0	4.04	10.71
13	2.31	0.02	1.0	6.06	11.35
14	2.31	0.02	1.0	8.08	9.40
15	2.31	0.02	1.0	10.00	10.33
Run	10 ⁴ [MMBD]/M	[HCl]/M	[NaCl]/M	10 ³ [CuCl ₂]/M	$10^4 k_o/s^{-1}$
1	1.00	0			7.94
2	1.00	0.01		_	7.97
3	1.00	0.4			8.10
4	1.00	0.6		_	8.08
5	1.00	0.8	_		8.11
6	1.00	1.0	_		8.17
7	1.00	_	0.2	_	8.12
8	1.00	_	0.4	_	8.05
9	1.00	_	0.6	_	7.92
10	1.00	_	0.8	_	7.88
11	1.00	_	1.0		7.81
12	1.00	0.01	1.0		8.00
13	1.00	0.01	1.0	0.10	7.99
14	1.00	0.01	1.0	0.50	8.08
15	1.00	0.01	1.0	1.00	8.02
16	1.00	0.01	1.0	5.00	7.96
17	1.00	0.01	1.0	10.00	7.92
18	1.00	0.01	1.0	50.00	8.30

Table I Effects of Added HCl, NaCl, and CuCl₂ on k_{obs} for Dediazoniation of OMBD and MMBD at T = 35°C

Influence of Temperature on k_{obs} : Activation Parameters

Experimental activation parameters were determined by measuring k_{obs} at different temperatures. To compare values, we have also obtained activation parameters for *p*-methylbenzenediazonium ion, PMBD. Figure 4 shows the corresponding Arrhenius plots. 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.

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

Table III shows the activation energy and the activation parameters obtained; values of $\Delta H^{\#}$ are relatively high compared with those for bimolecular reactions, [26,27] and the entropic term is substantially positive. For the sake of comparison, we have included $k_{\rm obs}$ values at one fixed temperature ($T = 35^{\circ}$ C).

DISCUSSION

HPLC data (Table II and Figs. 2 and 3) show that quantitative conversion to products is achieved, and only two dediazoniation products are formed: ArOH and ArCl. No other peaks that might be attributed to



Figure 2 Variation of *o*- and *m*-cresol yields (\bigcirc) with time obtained from quenching experiments and ln plots (\bigcirc). Experimental conditions: [OMBD] = 3.11×10^{-4} M, [HCl] = 0.01 M, [NaCl] = 1.0 M, *T* = 35° C; [MMBD] = 1.0×10^{-4} M, [HCl] = 0.01 M, [NaCl] = 1.0 M, *T* = 35° C.

radical pathways, i.e., Ar-Ar, Ar-N = N-Ar, Ar-H, were detected. The absence of reduction or isomerized products is consistent with the heterolytic mechanism (Scheme 2A). Yields of dediazoniation products (Table II) remain essentially constant on changing electrolyte concentrations within the concentration range employed, suggesting a very low selectivity. The selectivity of arenediazonium ions towards nucleophiles like H_2O and Cl^- can be defined as

$$S_W^{\rm Cl} = \frac{(Y_{\rm ArCl})[\rm H_2O]}{(Y_{\rm ArOH})[\rm Cl^-]}$$
(4)

For OMBD and MMBD, using $[H_2O] = 54.5$ M in 1.0 M NaCl [28] selectivity values are $S_W^{Cl} = 2.7(1.0 \text{ M NaCl})$ and $S_W^{Cl} = 2.6(1.0 \text{ M NaCl})$, respectively. These values are very similar to the ones in the

literature for other arenediazonium ions like benzenediazonium [29], $S_W^{Cl} = 3$, *p*-methylbenzene diazonium [14], $S_W^{Cl} = 1.7-3.4$, or 2,4,6- trimethylbenzene diazonium [2], $S_W^{Cl} = 4$. These rather constant selectivity values support the heterolytic mechanism.

Spectrophotometric kinetic data (Table I) indicate that dediazoniation rate is not affected by added electrolytes like HCl, NaCl, or CuCl₂, as found for *p*-methylbenzenediazonium ion [14]. HPLC kinetic data (Figs. 2 and 3), indicate that the rate of formation of ArOH is the same as that of disappearance of diazonium salt. All these results are consistent with a $D_N + A_N$ mechanism being the slow step the formation of a highly reactive aryl cation intermediate, which shows a very low selectivity towards different nucleophiles (Scheme 2A).

Analysis of activation parameters indicate that enthalpies of activation are as high as in many unimolecular reactions of alicyclic and aliphatic compounds [27,30]. These values contrast with those usually



Figure 3 Typical plots of the variation of absorbance (\bigcirc) for formation of the azo dye (quenching experiments) vs. time and ln plots (\bigcirc). Experimental conditions: [OMBD] = 3.11 × 10⁻⁴ M, [HCI] = 0.01 M, [NaCI] = 1.0 M, *T* = 35°C; [MMBD] = 1.0 × 10⁻⁴ M, [HCI] = 0.01 M, [NaCI] = 1.0 M, *T* = 30°C.



Figure 4 Arrhenius plot for dediazoniations of OMBD (\bigcirc) , MMBD (\bullet) , and PMBD (\Box) .

found for bimolecular reactions, which 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, [27] thus, $\Delta H^{\#}$ values suggest a transition state that has undergone bond breaking with little compensating bond making.

Entropies of activation are positive as in some unimolecular $S_N 1$ reactions and contrast with those for bimolecular reactions such as $S_N 2$ and cycloadditions [31], which are largely negative, typically ranging between -40 and -160 J mol⁻¹ deg⁻¹. In a number of solvolytic unimolecular reactions [30,32], a neutral molecule dissociates to give an ion- pair; thus, the transition state shows a significant charge separation that significantly polarizes the solvent molecules compared with the parent substrate. Molecular vibrations of the substrate are lost, i.e., the system gains entropy, which is compensated by the loss of entropy due to restricted motion of the solvating molecules; therefore, in the overall process the entropy term does not contribute significantly to $\Delta G^{\#}$. Solvation is energy releasing; consequently, $\Delta H^{\#}$ values for those unimolecular reactions are not usually high, and they are particularly solvent dependent. Dediazoniation, as described in Scheme 2A, suggest that formation of the aryl cation does not involve separation of charge but its redistribution; thus, the parent arenediazonium ion and the aryl cation polarizes the solvent to a similar extent; therefore, the gain of entropy is not compensated and dediazoniations show relatively high $\Delta H^{\#}$ values, showing lower solvent dependence [12] than those unimolecular reactions: in 19 solvents [33] the rates of heterolytic dediazoniation vary by a factor of only 9.

Solvolytic unimolecular reactions can exhibit both positive and negative $\Delta S^{\#}$ values [31,34]. Positive $\Delta S^{\#}$ values, as we have found, suggest that the transition state has a greater structural freedom than reactants, in line with the reported positive volumes of activation, $\Delta V^{\#}$, for a number of dediazoniations in different solvents [18,35–37], providing support for the D_n + A_n mechanism. On the other hand, because $\Delta S^{\#}$ values are positive, they compensate the large enthalpy term, making dediazoniations proceed at considerable rate compared with other unimolecular reactions, as found for a number of dediazoniations [12,17–19].

Substituents in the aromatic ring have marked effects on the stability of arenediazonium ions [11,12]. Substituent effects are not understandable on the basis of the Hammett equation, [12,29,38] because most *para* and *meta* substituents, including electronwith-drawing (like $p = NO_2$) and electron-donating groups (like $-N(CH_3)_2, -CH_3$) show a marked stabilizing effect, but they fit the Swain-Lupton [39] equation, which separates the resonance and inductive effects [9,12,40]. As shown in Table III, the effects of the methyl groups on dediazoniation rates are surprising, though modest. In the *ortho* and *meta* position it is rate retarding compared with the value for benzenediazonium ion.

Electronic substituent effects [9] can be classified into those associated with their polarity (inductive, field) and those associated with their ability to transfer charge (resonance). The methyl group behaves as an 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 [27,30], an effect that decreases with distance. On the other hand, if the methyl group is conjugated to an electron-deficient site through an aromatic system, then the electron-deficient site can attract charge from the carbon-hydrogen bonds of the methyl group through the π system [31] (hyperconjugation). Direct

10 ⁴ [OMBD]/M	[HCl]/M	[NaCl]/M	10^2 [CuCl ₂]/M	Y _{омв-он}	Y _{OMB-Cl}
3.3	0.02	0.3		95.67	2.8
3.3	0.02	0.5		92.41	3.6
3.3	0.02	0.7		90.93	2.4
3.3	0.02	1.0		90.41	4.4
3.3	0.30	_		98.62	
3.3	0.50			96.44	2.5
3.3	0.70			95.80	3.2
3.3	1.00			90.67	4.1
3.3	0.02	1.0	4.0	93.42	4.1
3.3	0.02	1.0	6.0	94.93	3.9
3.3	0.02	1.0	8.0	95.00	3.9
3.3	0.02	1.0	10.0	95.22	4.0

 Table II
 Effects of Added HCl, NaCl, and CuCl₂ on Dediazoniation Product Yields

10 ⁴ [MMBD]/M	[HCl]/M	[NaCl]/M	10 ³ [CuCl ₂]/M	$Y_{\text{MMB-OH}}$	Y _{MMB-Cl}
1.0	0.01	0.2		94.83	_
1.0	0.01	0.4	_	94.01	2.2
1.0	0.01	0.6	_	91.08	2.7
1.0	0.01	0.8	_	89.90	3.5
1.0	0.01	1.0	_	88.90	4.3
1.0	0.01	_	_	95.30	
1.0	0.04	_	_	96.40	
1.0	0.06	_	_	97.90	
1.0	0.08	_	_	96.34	
1.0	0.01	1.0	7.0	92.60	4.9
1.0	0.01	1.0	9.0	90.50	6.2
1.0	0.01	1.0	10.0	92.47	4.3
1.0	0.01	1.0	30.0	93.05	4.5

resonance interaction with the reaction site takes place only in the *para* position [31]; thus, high negative σ^+ values are reported for the *para*-methyl group ($\sigma^+ =$ -0.25 [41] or $\sigma^+ = -0.31$ [31]) compared with those for *meta*-methyl group ($\sigma^+ = -0.06$ [31]). Therefore, *para*-methyl stabilizes more the substrate (*p*-methylbenzenediazonium ion) than the intermediate aryl cation, meanwhile the *ortho* and *meta* methyl groups stabilize more the corresponding aryl cation than the parent methylbenzenediazonium ion (Scheme 2A). These arguments are consistent with the observed kinetic behavior of other *para* or *meta*-substituted arenediazonium ions with π -donating capability like —OH ($\sigma^+ = -1.25$ [41]) or —OCH₃ ($\sigma^+ = -0.61$ [41]): experimental rate constant values for dediazoniations with *para* —OH or —OCH₃ substituents are lower than those obtained when substituents are placed in the *meta* position [15,35]. These results

Table III Activation Parameters for Benzenediazonium Ion and Its Three Methyl Derivatives and Rate Constants at a Fixed Temperature ($T = 35^{\circ}C$)

1^{-1} $\Lambda H^{\#/k}$ I mol ⁻¹ $\Lambda S^{\#/l}$ mol ⁻¹ K ⁻¹
3)
$106 \pm 6 \qquad 40.4 \pm 10$
$107 \pm 5 \qquad 43.0 \pm 13$
4) 110 ± 4 21.6 ± 8

^a BD stands for benzenediazonium. Values for BD and those in parentheses are taken from ref. 15.

are also in agreement with a recent theoretical electron-density analyses [9] that indicates that a *para* $-NH_2$ group ($\sigma^+ = -1.61$ [41]) enhances the C-N bonding.

CONCLUSIONS

Rates of solvolysis of two diazonium ions have been measured in water over a range of temperatures. Our results show that dediazoniation of OMBD and MMBD proceed heterolyticly, because only two products are formed, ArOH and ArCl, and because of the absence of products associated with the radical pathway. Observed rate constants for product formation are the same as the rate constants for the decomposition of diazonium salt. Both product yields and rate constants are essentially independent of acidity (up to 1.0 M) and nucleophile concentration (up to $[Cl^-] = 1.0 \text{ M}$) in agreement with literature values determined for other diazonium ions. The low selectivity of the reaction toward Cl⁻ vs. H₂O is consistent with the formation of a highly reactive aryl cation intermediate.

The effects of methyl groups are different: *p*-methyl decrease the rate of dediazoniation meanwhile *o*- and *m*-methyl enhances it compared with the value for benzenediazonium ion. Enthalpies of activation are high, and entropies of activation are positive, making dediazoniations proceed at a considerable rate compared with typical unimolecular reactions.

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