Dediazoniation of 1-Naphthalenediazonium Tetrafluoroborate in Aqueous Acid and in Micellar Solutions

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> ABSTRACT: We have measured the rates and product yields of dediazoniation of 1naphthalenediazonium (1ND) tetrafluoroborate in the presence and absence of sodium dodecyl sulfate (SDS) micellar aggregates by employing a combination of UV–vis spectroscopy and high-performance liquid chromatography (HPLC) measurements. Kinetic data were obtained by a derivatization procedure with product yields were determined by HPLC. HPLC chromatograms show that in aqueous acid and in micellar solutions only one dediazoniation product is formed in significant quantities, 1-naphthol (NOH), and the observed rate constants (k_{obs}) are the same when 1ND loss is monitored spectrometrically and when NOH formation is monitored by HPLC. Activation parameters were obtained both in the presence and absence of SDS micellar aggregates. In both the systems, the enthalpies of activation are high and the entropies of activation are positive. The enthalpy of activation in the absence of SDS is very similar to that in the presence of SDS micelles, but the entropy of activation is lower by a factor of 4. As a consequence, SDS micelles speed up the thermal decomposition of 1ND and increase k_{obs} by a factor of 1.5 when [SDS] = 0.02 M. In contrast, results obtained in the presence of complexing systems such as crown ethers and polyethers show significant stabilization of the

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parent arenediazonium ions. Kinetic and HPLC data are consistent with the heterolytic $D_N + A_N$ mechanism that involves the rate-determining fragmentation of the arenediazonium ion into a very reactive phenyl cation that reacts competitively with available nucleophiles. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 301–309, 2008

INTRODUCTION

Arenediazonium ions are important intermediates widely used in synthetic and azo dye chemistry. Their peculiar redox characteristics and the variety of reactions that they may undergo also makes them very useful for other purposes, such as preparation of nano-tubes, [1,2], measurement of protease activities [3], and probing interfacial compositions of colloidal aggregates [4–6].

Reactions of arenediazonium ions may occur either at the arene nucleus (dediazoniation reactions; Scheme 1A) or at the terminal nitrogen of the diazonium group (nucleophilic additions; Scheme 1B), which constitute a classical route to obtain azo dyes and pigments [7]. In principle, all aromatic and heteroaromatic diazonium salts can be used as electrophilic reagents. Their electrophilicity depends on substituents: electronwithdrawing substituents increase their electrophilicity, meanwhile electron-donating substituents decrease it. Therefore, the coupling components must be substances that possess structures with very high electron densities at one or more carbon atoms. This requirement is usually achieved by the presence of hydroxy or amino groups, which increase the C-nucleophilicity of the coupling component [8].

Dediazoniations of aromatic diazonium ions may proceed by a number of mechanisms leading to a wide range of products [7–9]. In the absence of catalysts, in aqueous acid and in the dark, dediazoniations are believed to proceed through a heterolytic $D_N + A_N$



Scheme 1 (A) Two-step $D_N + A_N$ dediazoniation mechanism. Rate-limiting formation of an aryl cation that is trapped by available nucleophiles. (B) Nucleophilic addition to the electrophilic β -nitrogen of the diazonium group.

mechanism [7–9] via the rate-determining loss of N_2 , generating a highly reactive phenyl cation that reacts rapidly and with very low selectivity with available nucleophiles [7–9]. In alcohol–water mixtures and some nonaqueous solvents, products associated with free radicals may be observed, especially under experimental conditions where formation of diazoethers is favored (low acidities and high-alcohol concentrations) [10,11]. Formation of diazoethers also seems to be favored when electron-withdrawing groups are present on the arenediazonium ion [7–9,11].

Several groups investigated (and still they do) the effects of micellar and macromolecular systems on dediazoniations, and two major lines of research are evident. On the one hand, the basic physical organic aspects of the reactions have been explored [12–15]. Alternatively, new methods to estimate interfacial compositions of weak nucleophiles in colloidal interfaces were developed based on the unique characteristics of dediazoniation reactions [4–6]. To date, literature reports indicate that micellar systems change dediazoniation product distribution but do not modify substantially dediazoniation rate constants [4,16,17], but macromolecular systems such as crown ethers alter the rate constants significantly but not the product distribution [7,18].

Micelles are dynamic aggregates of amphiphilic molecules that create highly anisotropic interfacial regions, lining the boundary formed by the highly polar aqueous and nonpolar hydrocarbon regions. Because of the formation of the interfacial region imparts new chemical and physical properties to the system [4,19–23], the micelle acts as a microreactor concentrating, separating, or diluting reactants, and micelles often have substantial effects on the chemical reactivity [21,22,24]. Because of their unique characteristics, micelles have been exploited as of heterogeneous environments and microenvironments on a large variety of reactions, providing relatively simple reference systems for understanding processes that are important for grasping the complex behavior encountered in biological assemblies [25-29].

Here we report the effects of sodium dodecyl sulfate (SDS) micellar aggregates on the spontaneous dediazoniation of 1-naphthyldiazonium ions (1ND). Dediazoniation rates were monitored both spectrometrically and by employing a derivatization method that allows

simultaneous determination of the rate constants for the formation of dediazoniation products and their yields [30]. Although thermal decomposition of benzenediazonium ions has been extensively studied under different conditions [7,8], very few references to the reactions of arenediazonium ions containing fused rings can be found in the literature and none in the presence of micellar aggregates. For instance, Kuokkanen et al. studied the decomposition of naphthalenediazonium ions in the presence of complexing molecules such as crown ethers and acyclic polyethers in the gas phase and in 1,2-dichloroethane, concluding that the naphthalenediazonium ions are stabilized by forming a nonreactive complex with the $-N_2^+$ group inserted into the crown cavity; the largest stability achieved when using 21-crown-7 and its derivatives rather than with the nonspecific adduct formed with 15-crown-5 [31,32]. For example, the observed rate constant decreases by a factor of ~ 223 when [21-crown-7] = 4 $\times 10^{-4}$ M compared to that in its absence. In contrast, our results here show that SDS micelles enhance the spontaneous rate of dediazoniation by a factor of ~ 1.5 when [SDS] > 0.01.

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 high-performance liquid chromatography (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, Woburn, MA, USA) reverse phase column (25-cm length, 4.6mm 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 210 nm. pH was measured using a previously calibrated Metrohm 713 pH meter.

Materials

Reagents were of the maximum purity available and were used as received. 1-Naphthol (NOH), naphthalene (NH), and the reagents used in the preparation of 1ND (as tetrafluoroborate salt) were purchased from Aldrich, Milwaukee, WI, USA. Other materials employed were from Riedel de Häen, Seelze, Germany. All solutions were prepared by using Milli-Q grade water. 1ND was synthesized by following an anhydrous method [33] and was stored in the dark at low temperature to minimize its decomposition. Its purity was checked by UV–vis and ¹H NMR spectroscopy. 1ND stock solutions were prepared by dissolving the appropriate amount of the diazonium salt in aqueous HCl to minimize diazotate formation [7] 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 120 min with storage in an ice bath to minimize decomposition.

Methods

Kinetic data were obtained both spectrometrically and chromatographically. Spectrophotometric kinetic data were obtained by monitoring the disappearance of diazonium ion at 365 nm. The Beer's law plot (Fig. 1) for aqueous 1ND solutions up to 20×10^{-5} M is linear (cc. = 0.999), yielding $\varepsilon_{365} = 6100 \pm 120$ M⁻¹ cm⁻¹ in keeping with literature data [31].

Chromatographic kinetic data were obtained following a procedure developed in this laboratory [30] based on the derivatization of 1ND with the Bratton–Marshall reagent *N*-(1-naphthyl)ethylenediamine (NED) that reacts rapidly with arenediazonium ions in the acidic solution [34] yielding an stable purple dye. Dediazoniation was quenched at convenient times by adding to the reaction mixture an aliquot of a stock quenching solution prepared by dissolving NED, with an approximately 20-fold excess after mixing with respect to that of 1ND, in an aqueous acid ([HC1] = 0.001 M) solution. The reaction mixtures were analyzed by HPLC at room temperature within 4–5 h after dediazoniation was quenched.

The use of a coupling reaction to stop the dediazoniation reaction requires its rate to be faster than the dediazoniation rate. Auxiliary experiments carried out by following azo dye formation spectrometrically shows that under our experimental conditions the coupling



Figure 1 Variation of the absorbance of 1ND ($\lambda = 365$ nm) with the concentration [HCl] = 0.01 M, $T = 25^{\circ}$ C.

reaction is essentially over in the time of mixing reagents. The micellar effects on azo dye formation were previously studied [34], and the experimental conditions employed were chosen to ensure that azo dye formation is much faster than dediazoniation. All samples were analyzed by HPLC in duplicate or triplicate, and the relative standard deviation of the peak areas was less than 2%.

Preliminary HPLC experiments in the absence and presence of SDS ([SDS] = 0.1 M) showed that the main decomposition product is NOH, and only traces of the reduction product NH were detected. Calibration curves for converting HPLC peak areas into concentrations were obtained simultaneously for the dediazoniation products NOH and NH 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 = 8.4 × 10⁹ [NOH] $(t_r = 3.9)$; area = 1.06×10^{10} [NH] $(t_r = 8.5)$. Yields of dediazoniation products (Y) were determined as a percentage from the ratio of the dediazoniation product concentration, [analyte], and the initial diazonium salt concentration, $[1ND_0]$, estimated by weight (Eq. (1)).

$$Y = 100 \frac{[\text{Analyte}]}{[1\text{ND}_0]} \tag{1}$$

Observed rate constants were obtained by fitting the absorbance-time or yield-time data to the integrated first order (Eq. (2)), using a nonlinear least-squares method provided by a commercial computer program (GraFit 5.0), where M is the measured magnitude, either absorbance or yields. All runs were done at $T = 55 \pm 0.1^{\circ}$ C, except when investigating the influence of temperature or otherwise indicated.

$$\ln \frac{M_t - M_\infty}{M_0 - M_\infty} = -k_{\rm obs}t \tag{2}$$

RESULTS

Dediazoniation of 1ND in the Absence of SDS

Effects of Acidity and Temperature. The effects of HCl on k_{obs} were determined by monitoring the decrease in the absorbance of 1ND with time at different HCl concentrations at $T = 55^{\circ}$ C and by fitting the kinetic data to Eq. (2). In all runs, the first-order kinetics was obtained for more than $3t_{1/2}$. Results are displayed in Table I, showing that k_{obs} is not affected

Table I Effect of Acidity on k_{obs} for the Spontaneous Dediazoniation of 1ND. (1ND) $\sim 1 \times 10^{-4}$ M, T = 55°C

[HCl] (M)	$10^5 k_{\rm obs} \ ({\rm s}^{-1})$		
1.0	7.21 ± 0.05		
10^{-1}	7.12 ± 0.04		
10^{-2}	7.30 ± 0.04		
10^{-3}	7.15 ± 0.05		
10^{-5}	7.30 ± 0.06		

by changing the acidity of the medium in the concentration ranges employed, yielding average values of $k_{obs} = (7.20 \pm 0.05) \times 10^{-5} \text{ s}^{-1}$. This value is in good agreement with the reported literature values obtained by employing different techniques [31]. The effects of NaCl ([NaCl] = 0–1 M) on k_{obs} were also investigated, and no significant changes in k_{obs} were found (data not shown).

HPLC chromatograms show that NOH is the main dediazoniation product and, as indicated before, k_{obs} for NOH formation was determined at different acidities and temperatures by monitoring the variation of its yield as a function of time. Figure 2 is a representative and shows that product formation follows a first-order kinetics, with $k_{obs} = (7.1 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$, a value equal to that determined by monitoring 1ND loss spectrometrically at the same temperature (Table I). Figure 2 also shows that final NOH yield is more than 90%, that is, quantitative conversion of 1ND to NOH is achieved.

Activation parameters were determined by measuring k_{obs} at different temperatures according to the theory of absolute rates by means of Eq. (3), where k_B and *h* are the Boltzmann and Planck constants, respectively. Figure 3 shows the corresponding linear plot, and the determined activation parameters are indicated



Figure 2 Representative example of the determination of $k_{\rm obs}$ for product formation and log plot. Yields calculated by employing Eq. (2). [1ND] $\sim 2 \times 10^{-4}$, [HCl] = 0.01 M, $T = 55^{\circ}$ C.



Figure 3 Effects of temperature on k_{obs} according to Eq. (3). [1ND] $\sim 1 \times 10^{-4}$ M, [HCl] = 0.01 M.

in Table II; the values of ΔH^{\ddagger} are relatively high compared with those for bimolecular reactions [35-37], and the entropic term is clearly positive. For the sake of comparisons, we have included in Table II the activation parameters obtained for some representative benzenediazonium ions.

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

SDS Micellar Effects on Dediazoniation of 1ND. The effects of SDS on k_{obs} were obtained by running the reaction at different [SDS]. Figure 4A shows that, upon increasing [SDS], k_{obs} increases following a saturation kinetics pattern, reaching a plateau region at [SDS] > 0.01 M with $k_{obs} = 9.0 \times 10^{-4} \text{s}^{-1}$, approximately 1.5 times its value in the absence of SDS. Although



Figure 4 (A) Effects of SDS on k_{obs} . D_n is the micellized surfactant, defined as $D_n = [SDS] - CMC$. The solid line was calculated by employing Eq. (5) with CMC = 0.002 M. $[1ND] = 2 \times 10^{-4} \text{ M}, [HCI] = 0.01 \text{ M}, T = 55^{\circ}\text{C}. (B)$ Variation in the percentage of NOH formed with time and log plot according to Eq. (1) in the presence of SDS micellar aggregates. $[1ND] = 1 \times 10^{-4} \text{ M}, [SDS] = 0.01 \text{ M}, [HCl] =$ 0.01 M, and $T = 55^{\circ}$ C.

 154 ± 8

9.5

Sake of Comparisons, Activation Data for Selected Benzenediazonium Salts Are Also Included				
$XC_6H_4N_2^+BF_4^-$	E_a (kJ/mol)	ΔH^{\ddagger} (kJ/mol)	ΔS^{\ddagger} (J/mol)	$10^5 k_{25^{\circ}C} (s^{-1})$
$X = H^a$	113	109	37	5.30
X = 3-MeO ^a	_	99	16	24.0
$X = 3-Cl^a$	_	111	16	0.18
$X = Me^a$	108.2	106	40.4	23.2
$X = 2 - Me^a$	109.5	107	43.0	18.3
$X = 3 - Me^a$	112.4	110	21.6	3.45
$1ND^{b}$	116 ± 2	113 ± 2	38 ± 6	7.20
1ND ^c	118	116	50	7.33
$1ND^{d,e}$	115 ± 1	118 ± 1	153 ± 13	9.3

 119 ± 1

 Table II
 Activation Parameters in Aqueous and in Micellar Systems for the Thermal Decomposition of 1ND. For the

^a Data from Crossley et al. [55] and Maskill et al. [54].

 116 ± 0.4

^b This work, in the absence of SDS.

^c Data estimated from that reported by Kuokkanen et al. [31] at $T = 25^{\circ}$ C taking into consideration the activation energy.

^d This work, in SDS micellar systems.

e [HCl] = 0.01 M.

 $1ND^{d,f}$

f [HCl] = 0.1 M.

the increase in k_{obs} is modest, the results contrast with those obtained for dediazoniations in the presence of crown ethers and acyclic polyethers, where a significant stabilization of the parent diazonium ion is observed [7,31,32].

Figure 4B shows that NOH formation follows a first-order kinetics with $k_{obs} = (1.01 \pm 0.05) \times 10^{-3}$ s⁻¹, a value equal to that obtained spectrometrically by monitoring 1ND loss at the same [SDS] (Fig. 4A). Activation parameters were determined in the presence of SDS by measuring k_{obs} at different temperatures by means of Eq. (3). Table II lists the determined activation parameters.

DISCUSSION

HPLC data in the absence of SDS show that 1ND is transformed quantitatively to NOH (Fig. 2). In the presence of SDS (Fig. 4B), NOH is again the main dediazoniation product but conversion to NOH is less than quantitative. This phenomenon has already been observed in dediazoniations taking place in SDS micellar systems [38,39] and is attributed to a competing reaction between the arenediazonium ions and the sulfate head groups of the surfactant, yielding the corresponding aryl alkyl sulfate, which is unstable and further hydrolyzes leading to the formation of aryl sulfates $(ArOSO_3^-)$, which are not detected by reversed-phase HPLC because of its ionic nature [12]. Because no other peaks that might be attributed to radical pathways, i.e., NH, were observed in the chromatograms, we assumed, as Cuccovia et al. [38] and Bravo et al. [39] did in the past, that the formation of the unknown product is a competitive reaction with an unidentified component, which leads to a reduction in the total observed yields, which are calculated on the basis of the initial PNBD concentration.

HPLC and spectrophotometric kinetic data (Table I and Figs. 2 and 4) show that k_{obs} for 1ND loss is the same as that for NOH formation in the presence or in the absence of SDS micelles. The determined k_{obs} values are independent of acidity (Table I) and of the nucleophile (Cl⁻) concentration. All kinetic and HPLC evidence are consistent with a mechanism in which the formation of an intermediate in the slow step is followed by further reaction with nucleophiles leading to formation of products [40], that is, consistent with 1ND undergoing decomposition through a rate-limiting formation of a highly reactive aryl cation that further reacts with any nucleophile available in its solvation shell, i.e., the commonly accepted heterolytic $D_N + A_N$ mechanism (Scheme 2A).



Scheme 2 Proposed stepwise dediazoniation mechanism showing the formation of a ion–molecule complex and a solvent separated ion–molecule pair [53,54].

The obtained values for the activation parameters (Table II) are consistent with the proposed preassociation stepwise mechanism like the one shown in Scheme 2, in which the aryl cation has a short but finite lifetime, and that has been employed to describe product distribution in terms of ion-molecule or ionnucleophile pairs [41,42]. Nucleophilic attack may occur on "free" carbocations, contact ion-molecule pairs or contact ion-solvent pairs. Rate constants for nucleophilic attack on carbocations have been reported to be close to the diffusion control limits, $\sim 10^9$ to 10^{13} M⁻¹ s⁻¹[43]. With lifetimes in the nanosecond order of magnitude, aryl cations do not have time to diffuse away and a hypothetical preassociation of the nucleophile with the precursor would not account for much of the trapping, in a similar fashion than other extremely short-lived carbocations behave [44]. Thus, in the absence of specific interactions, arenediazonium ions will decompose mainly through the solvated aryl cations, i.e., upon unimolecular removal of N2, one nucleophile molecule of the first coordination shell will form the corresponding dediazoniation product. Consistent with this interpretation, Scheme 2 reflects that the formation of the aryl cation does not involve the separation of charge, but its redistribution and consequently no significant reorganization of the coordination shell is expected upon formation of the corresponding aryl cation.

The relatively high ΔH^{\ddagger} values found suggest a transition state that has undergone bond breaking with little compensating bond making as indicated in Scheme 2; the enthalpy of activation is as high as in many unimolecular reactions of alicyclic and aliphatic compounds [36,37], in clear contrast with typical values usually 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 [36].

Solvolytic unimolecular reactions can show positive or negative ΔS^{\ddagger} values. Positive ΔS^{\ddagger} values as those found in this work (Table II) suggest that the transition state has a greater structural freedom than reactants, in line with the reported positive volumes of activation, ΔV^{\ddagger} , for a number on dediazoniations in different solvents [45–48], and contrast with those for bimolecular reactions such as S_N2 and cycloadditions [49], which are largely negative and typically ranging between -40 and -160 J mol⁻¹ deg⁻¹. Because the parent arenediazonium ion and the aryl cation polarize their neighboring solvent molecules to a similar extent (Scheme 2), the gain of 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.

In the presence of micelles, ΔH^{\ddagger} is about the same than in its absence but ΔS^{\ddagger} is about 3–4 times higher. This could be because 1ND may be partially solvated in the transition state by the surfactant molecules, and because the micellar Stern layer has a lower polarity than the bulk water [22]. The increase in the ΔS^{\ddagger} value compared to that in the absence of SDS decreases ΔG^{\ddagger} , making 1ND dediazoniation to proceed faster than in pure water. As a consequence, Fig. 4A shows that in the presence of SDS micelles, the rate constant for the thermal decomposition of 1ND increases modestly. Such a micellar effect can be interpreted quantitatively in terms of the pseudophase model [19,22,50] (Scheme 2), which assumes that the micelles are uniformly distributed in the aqueous phase and act as a separate phase, the so-called pseudophase in which the reaction takes place.

Micellar aggregates can modify chemical reactivity essentially in two ways, namely (I) by governing the concentrations of reactants within the micellar pseudophase and (II) by governing the polarity of their immediate vicinity [22,23]. Since 1ND ions are cations with a hydrophobic part, they are distributed between the aqueous and micellar pseudophases (Scheme 3). Assuming that the micellized surfactant is at thermal equilibrium with solutes throughout the reaction, the rate of the reaction will be the sum of the rates in each pseudophase (Eq. (4)).

$$v = k_{\rm w}[1\rm{ND}_{\rm w}] + k_{\rm m}[1\rm{ND}_{\rm m}]$$
(4)



Scheme 3 Proposed reaction mechanism in the presence of SDS micellar aggregates.

where the subscripts w and m stand for the water and micellar pseudophases, respectively. By considering the corresponding mass balances, Eq. (5) can be derived, where K_s stands for the association constant of 1ND to the micellar aggregate and D_n represents, as indicated before, the concentration of micellized surfactant, which is defined as $D_n = [SDS_T] - CMC$ (where CMC is the critical micelle concentration) [19,22].

$$k_{\rm obs} = \frac{k_{\rm w} + k_{\rm m} K_{\rm s} \mathbf{D}_n}{1 + K_{\rm s} \mathbf{D}_n} \tag{5}$$

The solid line in Fig. 4A was drawn by fitting the $(k_{\rm obs}, D_n)$ pairs of data to Eq. (5). Values of $K_{\rm s} = 290 \pm 30 \, {\rm M}^{-1}$ and $k_{\rm m} = (9.0 \pm 0.1) \times 10^{-4} {\rm s}^{-1}$ were obtained.

The K_s value is very similar to that obtained for the association of some benzenediazonium ions, for instance, $K_s = 250 \text{ M}^{-1}$ and $K_s = 300 \text{ M}^{-1}$ for 2-methylbenzenediazonium [17] and 4-nitrobenzenediazonium ions [39], respectively. Such a value indicates that even at low-surfactant concentrations (above the CMC), a substantial fraction of 1ND ions is incorporated into the micellar aggregate, for instance, when [SDS] = 0.05 M, more than 90% of the total 1NBD is incorporated into the micellar aggregate. The obtained k_m value is about 1.5 times higher than k_w , and the increase is a consequence of the increasing entropy of activation (Table II).

CONCLUSIONS

The present kinetic study suggests that, in aqueous acid solution, the thermal decomposition of 1naphthalenediazonium salts in the absence or presence of SDS micellar aggregates occurs by an S_N 1-like reaction mechanism, with the formation of a highly reactive 1-naphthyl cation in the slow rate-determining step of the heterolytic decomposition of the uncomplexed ion or the complex. Subsequent fast product-determining reactions with nucleophiles (counterion, solvent, SDS, etc.) give the products. Activation parameters provide further support for such a mechanism because of the relatively high enthalpy and entropy values found.

HPLC data show that in aqueous acid the only significant reaction is that with water to give NOH. In the presence of SDS micelles, 1ND is incorporated into the micellar aggregates and a value of $K_s = 290 \text{ M}^{-1}$ for the association constant was estimated showing that a significant fraction of 1ND is incorporated into the micellar pseudophase at low-surfactant concentrations, where it undergoes thermal decomposition in the Stern layer with a k_{obs} value approximately 1.5 times higher than that in aqueous acid solution. HPLC data show that NOH is the major dediazoniation product, in keeping with the current view of micelles as water-permeated structures. The SDS micellar induced an increase in k_{obs} in contrast with that observed for methylbenzene-diazonium ions in anionic micellar systems [17] but confirm that micellar effects on the rate of spontaneous dediazoniations are modest.

In cationic micelles such as cetyltrimethylammonium halides (CTAX), k_{obs} should not be affected by increasing [CTAX] because hydrophilic ArN_2^+ ions such as the methyl derivatives are likely to be excluded from the Stern layer [51,52]; however, the hydrophobic ones such as 16-hexadecylbenzenediazonium ions are completely associated with CTAX micelles [4,12,38], but they are not water soluble and thus no comparisons between k_{obs} values in the absence and in the presence of surfactant can be made.

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