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Butanolysis of 2-methylbenzenediazonium ions: product distribution, rate constants of product formation, and activation parameters

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We have determined the product distributions, the rate constants of product formation and substrate loss, and the activation parameters for the butanolysis of 2-methylbenzenediazonium, 2MBD, tetrafluoroborate in aqueous 1-Butanol (BuOH) solutions by combining UV–VIS spectroscopy, high performance liquid chromatography (HPLC), and a derivatization protocol that traps unreacted 2MBD as a stable azo dye. BuOH/H_2O solutions are miscible over a narrow composition range, but in reverse micelles composed of sodium dodecyl sulfate, SDS, BuOH, and water, are miscible between 45–80%. Two major and two minor dediazoniation products are observed, 2-cresol, ArOH, 2-butyl-tolyl-ether, ArOBu, and small amounts of 2-chlorobenzene, ArCl (from HCl added to control solution acidity) and toluene, ArH (a reduction product). Product yields depend on experimental conditions, but quantitative conversion to products is achieved over the entire composition ranges investigated. The observed rate constants, k_{obs}, obtained by monitoring 2MBD loss or by monitoring ArOH or ArOBu formation, are the same and they are only modestly affected by changes in the solution composition. The activation parameters obtained from the effect of temperature on k_{obs} show that the enthalpy of activation is relatively high compared to those found in bimolecular reactions and the entropy of activation is small but positive. The results suggest that 2MBD is mainly sampling in the BuOH-H_2O rich interfacial region of the reverse micelle and are consistent with 2MBD decomposing through a $D_N + A_N$ mechanism, i.e., a rate limiting formation of an aryl cation that reacts immediately with nucleophiles.

Keywords: kinetics; reverse micelles; solvolysis

INTRODUCTION

Kinetic and mechanistic studies in mixed solvents have an advantage in providing the opportunity to vary continuously the reaction conditions, in contrast to the more abrupt changes arising from studies of substituent effects.[1,2] Nevertheless, solubility problems may occur preventing systematic studies on individual substrates over the whole composition range. For example, short chain alkyl alcohols ($C_nH_{2n+1}OH$, $n < 3$) such as MeOH or EtOH are miscible with water at any proportion but the long chain ones ($n \geq 4$) do not because of their limited solubility in water. BuOH is partially soluble in water and only binary systems containing percentages of BuOH ranging 0–~10% and ~90–100% can be prepared, meanwhile pentanol is virtually insoluble in water at room temperature at any proportion. The solubility problem may be overcome; however, by using reverse micelles as reaction media, Scheme 1, which allows preparing reaction mixtures containing a wide range of percentages of alcohol ($n \geq 4$).[3–6]

The systems of "surfactant–water–organic solvent" type such as the reverse micelles, Scheme 1, find useful application in preparative chemistry including transformations of water-insoluble substances, nano-size particle, and in bioorganic synthesis.[7–10] They also can be considered as a model of biomembrane fragments and can be seen as an approach to better understanding the role of biomembrane environments in biocatalysis.[5,11,12]

Reverse micelles introduce new environments that may have large effects on the physical properties of the substrate such as stabilization of ground or excited states, acid-base, and redox equilibria, and so forth. The center of the reverse micelles, the so-called water pool, Scheme 1, provides a unique reaction site because of the "tailored" sizes that can be achieved with these systems.[13–16] The water in the water pool may have different properties depending on the ratio $w_o = [H_2O]/[SURF]$, and can be used in place of polar organic solvents to carry out chemical reactions.[7,17,18] Therefore, they may have significant effects on the location and reactivity of the substrates[5,19–22] and, as a consequence, the use of organized surfactant molecular assemblies such as micelles, reverse micelles, and micro and macroemulsions as reaction media is steadily increasing because their unique solubilization characteristics.[5,8,12–16,22–25]

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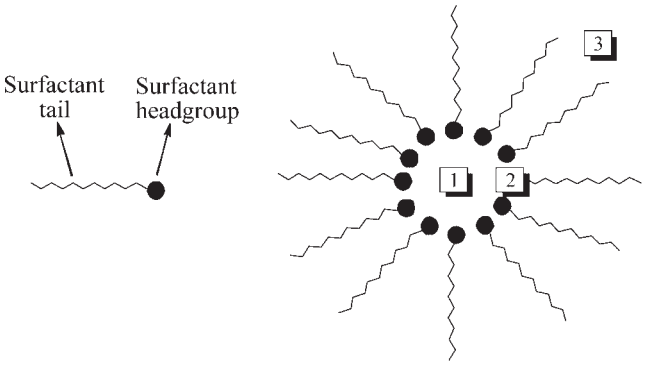
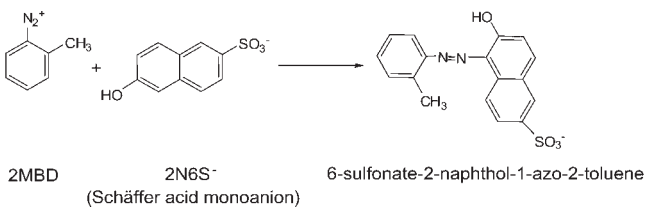


Scheme 1. Schematic representation of a surfactant molecule (left) showing the hydrophobic tail and the hydrophilic head group and of a reverse micelle (right) showing the different regions of the micellar solution: (1) water pool, (2) interface, (3) organic phase – in the present work, BuOH

Here we report an extension of our previous kinetic investigations on solvolytic dediazoniations in alcohol-water mixtures under acidic conditions.[26–31] To expand as much as possible the percentage of BuOH in the system, the solvolytic kinetic experiments were carried out both in binary BuOH/H_2O systems and in reverse micellar systems composed of BuOH, water, and sodium dodecyl sulfate, SDS, Scheme 1. The reverse micelles were prepared with $w_o = 28$, which allows changes in the percentage of BuOH in the system from 45% up to 99% BuOH, a range that cannot be otherwise attained. The ratio $w_o = 28$ was chosen because the size, shape, and some other structural characteristics of the reverse micellar aggregates formed are known.[32,33] 2-methylbenzenediazonium, 2MBD, and tetrafluoroborate were chosen as substrate because a substantial knowledge on their dediazoniation in a number of alcohol–water mixtures is available[26–28,34,35] and the effects of SDS micellar systems on its decomposition reaction are known.[31,36]

The kinetic study was carried out by employing UV–VIS spectroscopy and high performance liquid chromatography measurements in combination with a well-established protocol[37,38] that exploits the coupling reaction of 2MBD with 2-naphthol-6-sulfonic acid (2N6S, Schäffer acid), Scheme 2. The protocol is used to rapidly quench the solvolytic dediazoniation reaction at convenient times to determine the rate constants for product formation and the product distribution. Direct injection of ArN_2^+ ions into the chromatographic system is inadvisable because they spontaneously decompose and because of their extraordinary sensitivity to environmental changes,[39–42] i.e., they may react with any of the typical solvents employed in the mobile phase, including H_2O,[28,43] and the metallic parts of the chromatographic system, hence leading to erroneous product identification and concentration values.



Scheme 2. Basic representation of the coupling reaction between 2MBD and the Na salt of 2-Naphthol-6-sulphonic acid to yield a stable azo dye

RESULTS

Rate constants for product formation and for 2MBD loss in binary buOH/H_2O mixtures and in SDS/buOH/H_2O reverse micellar systems

Observed rate constants, k_{obs}, were obtained chromatographically and spectrometrically. Figure 1 shows illustrative kinetic profiles obtained chromatographically by monitoring the variation in the product formation with time in a BuOH/H_2O binary mixture and in a reverse micelle, which were obtained after application of the derivatization protocol described in the experimental section. Figure 1 shows that two main dediazoniation products are formed at any solvent composition, ArOH, and ArOBu. Other minor products such as ArCl and ArH were detected but the sum of their yields is less than 5% (see product distribution section below), and were not included in the kinetic plots for the sake of clarity.

The k_{obs} values obtained for product formation, Table 1, are the same regardless they are obtained by monitoring ArOH formation or ArOBu formation both in the binary mixture and in the reverse micelle. The obtained values are remarkably constant in spite of changing the percentage of BuOH in the system from 0% up to 90%, thus indicating that [BuOH] does not have a significant effect on k_{obs}.

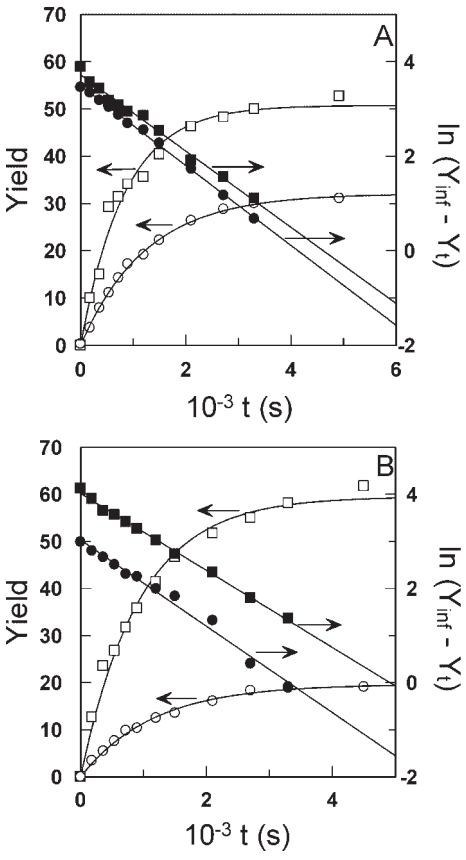


Figure 1. (A) Illustrative plots showing the formation of ArOH ([) and ArOBu (B) in (A) 90% BuOH/H_2O binary mixture, (B) reverse micelle composed of 27% H_2O, 10.4% SDS, 61.9% BuOH (w:w), and the corresponding linear plots according to Eqn (2) (α ArOH, β ArOBu). [OMBD] = 1.1×10^{-4} M, [HCl] = 0.01 M, T = 35 °C. The composition of the aqueous quenching solution was [2N6S] = 2 mM, [TRIS] = 98 mM

Table 1. Observed rate constants, k_{obs}, obtained in binary BuOH/H_2O systems and in reverse micelles by monitoring product formation (HPLC) and 2MBD loss spectrometrically

	$10^4 k_{obs}$[a] (s^{-1})	$10^4 k_{obs}$[b] (s^{-1})	$10^4 k_{obs}$[c] (s^{-1})
ArOH[d]	10.13	8.2 ± 0.3	7.3 ± 0.2
ArOBu[d]	—	8.1 ± 0.2	7.5 ± 0.4
ArH[d]	—	8.4 ± 0.4	—
Azo dye[e]	9.51	8.6 ± 0.5	7.7 ± 0.1
2MBD[f]	10.31	8.5 ± 0.4	7.9 ± 0.3

[a] 0% BuOH.
[b] 90% BuOH/H_2O (v/v).
[c] 73% BuOH (by volume with respect to the total reverse micelle volume).
[d] HPLC.
[e] Spectrophotometrically ($\lambda = 490$ nm).
[f] Spectrophotometrically ($\lambda = 316$ nm).[26] [2MBD] $\sim 2 \times 10^{-4}$ M, [HCl] $= 1.2 \times 10^{-2}$ M, T = 35 °C.

The protocol also allows determining the k_{obs} for 2MBD loss by monitoring spectrophotometrically the variation in the absorbance of the formed azo dye with time, Fig. 2. The obtained values, Table 1, are the same, within experimental error, as those for product formation, and the value at 0% BuOH is the same as that reported in the literature, $k_{obs} \sim 10.3 \times 10^{-4}\ s^{-1}$, obtained spectrophotometrically by monitoring 2MBD loss,[26] Table 1.

Activation parameters

Activation parameters for the reaction were determined by measuring the effect of temperature on k_{obs} and evaluated by means of the theory of absolute rates, Fig. 3. In all cases, values of $\Delta H^{\ddagger}$ are positive (average $\Delta H^{\ddagger} = 106\ kJ\ mol^{-1}$) and relatively high compared to those of bimolecular reactions, suggesting that the energy required to cleavage the C—N bond is not compensated by the energy released in the formation of new bonds, and the entropy is clearly positive (average $\Delta S^{\ddagger} = 34\ J\ mol^{-1}\ K^{-1}$). For comparison purposes, the enthalpy and entropy values for solvolytic dediazoniations of selected arenediazonium ions are given in Table 2.

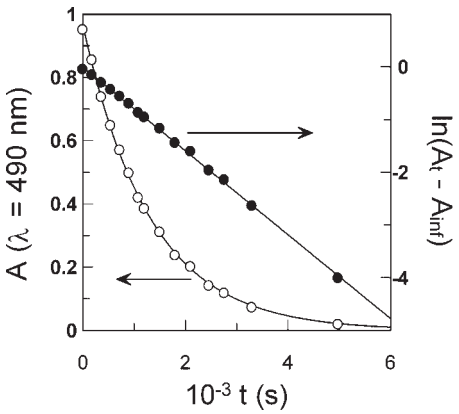


Figure 2. Illustrative plot showing the variation with time in the absorbance of the formed azo dye ($\lambda = 490$ nm) in a reverse micelle composed of 27% H_2O, 10.4% SDS, 61.9% BuOH (w:w) after 2MBD derivatization and first order plot. Experimental conditions as in Fig. 1

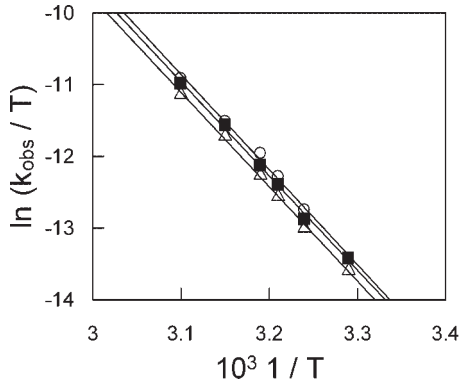


Figure 3. Effects of temperature on k_{obs} and representation according to the theory of absolute rates for the solvolytic dediazoniation of 2MBD in BuOH/H_2O binary mixtures and in reverse micellar systems. β 0%, X 60%, ∋ 99%. [OMBD] $\sim 1.0 \times 10^{-4}$ M, [HCl] = 0.01 M

Table 2. Activation parameters for representative arenediazonium ions in different solvents. Data from (a) Maskill *et al.*[44], (b) Crossley *et al.*[60], (c) Kuokkanen,[34,35] (d) Bravo-Díaz *et al.*[28] Solvents: (e) water, (f) MeOH g) EtOH, (h) TFE, (i) BuOH (this work). Typical temperature range investigated 20–60 °C

$XC_6H_4N_2^+BF_4^-$	$\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\ mol^{-1}\ K^{-1}$)
X = H	109[a,f]	37[a,b]
	112[c,h]	55[a,d]
X = 2-Me	111[b,e]	44[b,e]
	106[d,f]	40[d,f]
	103[d,g]	34[d,g]
	106[i]	34[i]
X = 3-Me	107[d,e]	43[d,e]
	106[d,f]	43[d,f]
	103[d,g]	34[d,g]
X = 4-Me	110[d,e]	22[d,e]
	109[d,f]	26[d,f]
	114[d,g]	41[d,g]
X = 3-MeO	99[a,e]	16[a,e]
	107[c,h]	54[c,h]
X = 3-Cl	111[a,e]	16[a,e]
	125[c,h]	69[c,h]

Product distribution

The product distribution was determined by HPLC analyses of the reaction mixtures once the reactions were completed (i.e., at infinite time) and the results are displayed in Table 3. In the binary mixtures, up to four dediazoniation products are detected. At low percentages of BuOH, the main dediazoniation product is ArOH, but upon increasing the percentage of BuOH in the system, the yields of ArH and ArOBu increase in detriment of that of ArOH, so that at 98% BuOH the main dediazoniation products are ArOBu and ArOH. The observed tendency is in keeping with previous results for alcoholysis of 2MBD and other toluenediazonium derivatives.[27,28] In the reverse micelles investigated, only three dediazoniation products were detected, ArOH, ArH, and ArOBu, and at any percentage of MeOH, the main dediazoniation products are ArOH and ArOBu. ArOH yield decreases upon

Table 3. Product distribution (expressed as percentage) in binary BuOH/H_2O and in reverse micellar systems. [OMBD] $\sim 1.0 \times 10^{-4}$ M, [hcl] = 0.01 M, T = 35 °C

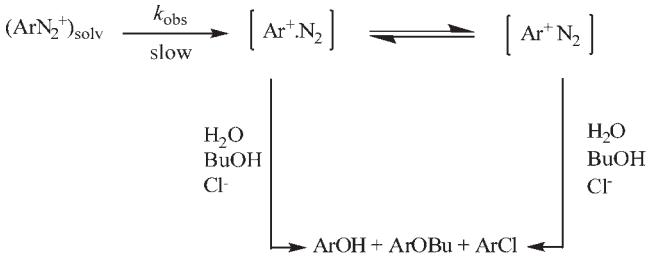
%BuOH	ArOH	ArCl	ArH	ArOBu	Total
BuOH/H_2O					
0.00	99.51	0.25	0.00	0.00	99.77
5.00	99.00	0.00	0.06	0.34	99.40
9.00	98.12	0.00	0.01	0.57	98.70
85.00	68.91	0.92	5.96	22.96	98.75
98.00	20.01	1.46	8.06	64.70	94.23
BuOH/SDS/H_2O					
54.14	69.87	—	2.07	18.76	90.70
65.70	67.41	—	2.52	20.84	90.76
70.40	66.75	—	1.67	23.38	91.79
75.15	63.90	—	3.27	25.20	92.37
80.62	61.74	—	3.02	29.11	93.86
89.26	58.41	—	2.95	33.22	94.57

increasing the percentage of BuOH and a concomitant increase in the percentage of the substitution product ArOBu is observed.

DISCUSSION

All runs obeyed first order kinetics for more than three half-lives at any solvent composition. Table 1 shows that k_{obs} for 2MBD loss is the same as that for product formation, and that k_{obs} values are essentially independent of nucleophile concentration. Product distribution analysis shows that the substitution products ArOH and ArOBu are obtained in significant yields and that quantitative conversion to products is achieved at any solvent composition, Table 3. A rate-limiting nucleophilic attack of BuOH would lead to a substantial change in k_{obs} upon changing the percentage of BuOH in the reaction mixture, which is not observed, Table 1. All kinetic and HPLC evidence is thus consistent with a mechanism in which the formation of a highly reactive aryl cation in the slow step is followed by further reaction with available nucleophiles in its solvation shell leading to formation of products, Scheme 3.

Table 3 shows that small amounts of the reduction product ArH were detected. It is presumably formed by homolytic decomposition of a transient diazo ether produced from reaction between 2MBD and BuOH, namely Ar-N=N-OBu.[29,30] The low yields obtained (<9%) and the fact that it is only detected at high



Scheme 3. Proposed reaction mechanism for solvolysis of ArN_2^+ in binary BuOH/H_2O mixtures showing the formation of a ion-molecule complex and a solvent separated ion-molecule pair[28,44]

[BuOH] suggest that this competitive mechanism is not the principal one under the experimental conditions employed, and for this reason the formation of this minor product was not further investigated.

The relatively high $\Delta H^{\ddagger}$ values found for the butanolysis of 2MBD suggest, as for other solvolytic dediazoniations carried out in pure water and in alcohol-water solutions of different ionizing power, Table 2,[28,29,42,44–46] a transition state that has undergone bond breaking with little compensating bond making as indicated in Scheme 3. Such values contrast with those typically 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.[47] Positive $\Delta S^{\ddagger}$ values as those found in this work, Table 2, suggest that the transition state has a greater structural freedom than reactants and contrast with those for bimolecular reactions such as S_N2 and cycloadditions,[48] which are largely negative and typically ranging between −40 and −160 J mol^{-1} deg^{-1}.

All results are thus consistent with the proposed stepwise mechanism shown in Scheme 3, in which the presumed aryl cation has a short but finite lifetime. Scheme 3 reflects that the formation of the aryl cation does not involve in separation of charge but its redistribution and consequently no significant reorganization of the coordination shell is expected upon formation of the corresponding aryl cation, which do not have time to diffuse away[49] because the rate constants for nucleophilic attack on carbocations have been reported to be close to the diffusion control limits.[50]

One might ask in what region of the reverse micelle, Scheme 1, the butanolysis of 2MBD is taking place. In principle, 2MBD may partition between the water pool, the interfacial region and the oil (BuOH) regions of the reverse micelle, Scheme 1, but the product distribution shown in Table 3 supports the hypothesis of 2MBD sampling in the interfacial region and not in the water pool or in the oil regions.

As indicated before, BuOH and water are miscible in a limited composition range (0–∼10% and ∼90–100% BuOH/H_2O v:v). If one assumes that the reaction is mainly taking place in the water pool, then as much as ∼10% of BuOH should be present in that region (maximum solubility of BuOH in water) and thus the product distribution should reflect that the ArOH derivative should be the main dediazoniation product and very low yields of the ArOBu derivative should be obtained as observed in the binary mixtures, Table 3.

However, the yield of ArOBu in the reverse micelle with the lowest percentage of BuOH, Table 3, is ∼19%, which is substantially higher than those found in binary systems, thus indicating that 2MBD is sampling in a BuOH rich region other than the water pool. On the other hand, if we assume that a substantial fraction of 2MBD can be solubilized in the oil region (here BuOH), one might expect a significant formation of ion-pairs with BF_4^- ions (counterion of ArN_2^+) and mainly with Cl^- (from HCl) thus leading to significant formation of the Ar-F and Ar-Cl derivatives,[42] which is not observed. In fact, no ArCl is detected the reverse micelles, Table 3.

As a consequence, the product distribution data in Table 3 suggest that OMBD ions are mainly located in the interfacial region and surrounded by BuOH, H_2O molecules and by the $—SO_4^-$ surfactant head groups, which may also act as nucleophiles in some dediazoniations.[51–53] The hypothesis of 2MBD ions mainly sampling in the interfacial region of the reverse

micelles is consistent with results in normal SDS micelles, where it has been shown by ^{1}H NMR experiments that the —N_2^+ group of 2MBD is located in the Stern layer.[36,54]

ArN_2^+ ions have been, and still are, employed to probe interfacial compositions of weakly basic nucleophiles in a number of surfactant assemblies and, in fact, Romsted and coworkers were able to measure local nucleophile concentrations in cationic reverse micelles by combining results from hydrophobic and hydrophilic arenediazonium ions.[55,56] Because 2MBD ions bear a positive charge and are somewhat hydrophobic, the data do not allow to completely discard that some reaction may be taking place in the water pool of the reverse micelle, and further investigations to determine the distribution constants as well as the effects of acidity and other nucleophile concentrations are in course and will be part of future reports.

In conclusion, we have been able to undertake a kinetic study of the butanolysis of 2MBD over a wide range of BuOH concentrations by employing nanostructured systems such as the reverse micelles. For the purpose, we employed a methodology that allows simultaneous determination of rate constants for product formation and arenediazonium ion loss and estimations of product yields. The obtained k_{obs} values for 2MBD loss and for product formation are the same and they remain remarkably constant upon changing nucleophile concentrations. The substitution products ArOH and ArOBu are the major dediazoniation products and quantitative conversion to products was achieved in all runs. Enthalpies of activation are high and entropies of activation are positive and their values are very similar to those found in pure water and in other water-alcohol solutions. Therefore, all evidence is consistent with a $D_N + A_N$ mechanism, i.e., a rate-determining formation of a highly unstable aryl cation that traps available nucleophiles in its solvation shell.

EXPERIMENTAL

Instrumentation

A Waters high performance liquid chromatographic system equipped with a quaternary model 600 pump, a model 717 automatic injector, a model 2487 dual λ absorbance detector and a computer for data storage was employed. Products were separated on a Microsorb-MV C-18 (Rainin) reverse phase column (25 cm length, 4.6 mm internal diameter, 100 Å, 5 μm particle size) using a gradient method with a mobile phase of ACN/H_2O containing 10^{-4} M HCl. The injection volume was 25 μL in all runs, the flow rate was 0.8 ml min^{-1} at room temperature and the UV detector was set at 210 nm.

pH was measured by using a previously calibrated Metrohm 713 pHmeter equipped with a temperature sensor. Auxiliary spectrophotometric experiments were performed on a Beckman DU 640 UV–VIS spectrophotometer equipped with a thermostated 6-cell device attached to a computer for data storage and manipulation.

Reagents and materials

Reagents were of the maximum purity available and were used without further purification. 2-cresol, ArOH, 2-butyl-tolyl-ether, ArOBu, 2-chlorotoluene, ArCl, toluene, ArH, and the surfactant sodium dodecyl sulfate, SDS, were purchased from Aldrich (USA) or Fluka (Switzerland). 2-Naphtol-6-sulfonic acid, sodium salt, (2N6S) was purchased from Pflatz & Bauer (USA). BuOH (HPLC grade, $\rho = 0.81$ g cm^{-3}) was from Fluka or Merck (Germany). Other materials employed were from Riedel de Häen (Germany) or Panreac (Spain). All solutions were prepared by using Milli-Q grade water system (Millipore, USA).

2-methylbenzenediazonium, 2MBD, tetrafluoroborate was prepared by employing a non-aqueous procedure as indicated elsewhere[38] and was purified by recristalization from acetonitrile/cold ether mixtures and stored in the dark at low temperature to minimize its decomposition. The UV–VIS spectrum of a 0.1 mM 2MBD aqueous acid (10 mM HCl) solution shows two broad bands, the main one centered at $\lambda = 258$ nm and a shoulder centered at 316 nm. The Beer's law plot (not shown) up to 10 mM 2MBD in 10 mM HCl is linear (correlation coefficient = 0.999) yielding $\varepsilon_{258} = 9660 \pm 54$ M^{-1} cm^{-1} and $\varepsilon_{316} = 1760 \pm 25$ M^{-1} cm^{-1} in agreement with literature values[57]. Spectrum of aqueous solutions of the potential dediazoniation products showed that an $\lambda = 210$ nm is an optimum wavelength to detect them by HPLC.

The HCl solutions were prepared from dilution from concentrated commercial HCl. The pH was determined potentiometrically from convenient diluted solutions. TRIS buffer (40 mM) was prepared by dissolving the solid commercial product according to standard procedures.[58]

HPLC mobile phase

The initial composition of the mobile phase was selected from literature data[38] and optimized by employing isocratic and gradient methods. We employed a gradient method because of the significant reduction of the analyses time achieved with respect to those obtained when employing isocratic methods while keeping an excellent sensitivity. Typical chromatograms and the corresponding chromatographic parameters are given as supplementary material.

The percentage of a given analyte was determined by employing the corresponding detector response factor obtained from calibration curves (data and figures available as supplementary material) obtained, Eqn (1). The initial 2MBD concentration was determined by weight,

$$\text{Yield} = 100\frac{[\text{Analyte}]}{[\text{2MBD}]} \quad (1)$$

Dediazoniation product distributions were determined at room temperature by analyzing in triplicate reaction mixtures once the dediazoniation reaction was finished, i.e., at infinite time. For the purpose, a number of reaction mixtures of the desired composition containing all reagents except 2MBD were prepared in volumetric flasks and thermostated at T = 35 °C for about 20 min. Then, aliquots of a freshly prepared 2MBD stock solution (typically ~ 20 μL) were added to the volumetric flasks and left to react for at least 5 h. After the reaction was completed, the solutions were cooled to room temperature and diluted with ACN up to the mark to ensure complete solubilization of dediazoniation products. Aliquots of these solutions were transferred to HPLC vials and analyzed in triplicate.

Methods

Derivatization protocol

The use of HPLC to determine observed rate constants for product formation is based on a derivatization protocol that

exploits the rapid reaction between ArN_2^+ ions and a suitable coupling agent (typically naphthols or naphthylamine derivatives) to give a stable azo dye. The method has been described in detail elsewhere[37,38] and here only the basic aspects will be indicated.

Dediazoniations were quenched at convenient time intervals by adding to the reaction mixture an aliquot of a stock quenching solution, prepared by dissolving the Na salt of 2-naphthol-6-sulfonic acid, 2N6S, in a TRIS buffer solution to yield final concentrations of 3 mM 2N6S. Addition of the quenching solution leads to the immediate formation of a stable azo dye, Scheme 2. The 2N6S coupling agent was chosen because their coupling reactions with a variety of arenediazonium ions may be very fast under appropriate experimental conditions and because both 2N6S and the derivatized azo dye bear a sulfonic group in their molecules making them to elute with other salts in the front peak minimizing interferences from these analytes in the chromatograms. It has been reported that micellar SDS solutions inhibit the azo coupling reaction when compared to that in absence of SDS.[59] Auxiliary UV–VIS experiments showed that both in binary $BuOH/H_2O$ mixtures and in reverse micellar systems, the azo coupling reaction is still much faster than that for the thermal decomposition of 2MBD, thus quenching effectively the dediazoniation reaction.

A complete, representative, experimental protocol is as follows. A number of volumetric flasks containing all reagents except 2MBD were prepared under identical experimental conditions and thermostated at $T = 35\ ^{\circ}C$. Dediazoniation was initiated by rapidly adding an aliquot of a freshly prepared aqueous acid stock solution of 2MBD to each volumetric flask so that final volume was 3 mL. At progressively longer intervals of time, 1 ml of the 2N6S quenching solution was added to the reaction mixture so that after addition the final 2N6S concentration was in about 10-fold excess over that of the arenediazonium salt and the final pH was ca 8.0. After dediazoniation was complete, the solutions were cooled to room temperature and transferred to 5 mL volumetric flasks and diluted with ACN up to the mark to ensure that all dediazoniation products were completely dissolved. Aliquots of these solutions were transferred to HPLC vials and analyzed in triplicate, giving a relative standard deviation of the peak areas lower than 2%.

Kinetic data

Spectrophotometic kinetic data were obtained by monitoring the variation with time of the absorbance of the azo dye formed after 2MBD derivatization (mentioned earlier) that for 2MBD loss at suitable wavelengths. The corresponding k_{obs} values were obtained by fitting the (absorbance, time) pairs of data to the integrated first order Eqn (2). HPLC kinetic data were determined by analyzing the variation in the yield of a particular product with time and by fitting the data to the integrated first order Eqn (2) using a commercial nonlinear least squares method,

$$\ln \frac{(M_\infty - M_t)}{(M_\infty - M_o)} = -k_{obs} t \qquad (2)$$

where k_{obs} stands for the observed rate constant and M_t, M_0 and M_∞ represent the measured magnitude (absorbance or yield of a particular dediazoniation product) at any time, at 0 time and at infinite time, respectively.

SUPPLEMENTARY MATERIAL

Typical chromatograms, chromatographic parameters evaluated from the chromatograms and HPLC calibration curves (3 pages) are provided upon request at any masthead.

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