Arenediazonium Salts: New Probes of the Interfacial Compositions of Association Colloids. 1. Basic Approach, Methods, and Illustrative Applications

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Abstract: Product yields from the reactions of two different arenediazonium salts, $z\text{-ArN}_2^+BF_4^-$, bound to cetyltrimethylammonium halide ((CTA)X; X = Cl, Br) micelles and to aqueous three-component (CTA)X microemulsions containing an alcohol (R′OH), either 1-butanol (BuOH) or 1-hexanol (HexOH), are "snapshots" of the relative quantities of halide ion, water, and alcohol nucleophiles at the aggregates' interfaces. Yields of aryl ether, aryl halide, and phenol products measured simultaneously by HPLC are consistent with high concentrations of these nucleophiles in the immediate vicinity of the aggregates' interfaces. The interfacial concentration of each nucleophile is estimated from the yield of its respective product over wide ranges of (CTA)X and R′OH concentrations by assuming that the selectivities of the long-chain (hexadecyl), water-insoluble, aggregate-bound arenediazonium ions, 16-ArN_2^+, toward anionic or neutral nucleophiles compared to water are the same as the selectivities of the short-chain (methyl), water-soluble analogues, 1-ArN_2^+, toward the same nucleophiles in aqueous solutions. The suitability of dediazoniation reactions as interfacial probes and the basic assumptions used in our approach are described. The observed rate constants for dediazoniation of the arenediazonium salts are almost completely independent of the salt, (CTA)X, and R′OH concentrations, consistent with rate-determining loss of N_2 to give an aryl cation which reacts at diffusion-controlled rates with available nucleophiles. Salt-induced spectral shifts indicate formation of ion pairs in the ground state, and all our data are consistent with a heterolytic dediazoniation mechanism in which product distributions are determined by the equilibrium distribution of the ensemble of ground-state arenediazonium cation·anion and arenediazonium cation·molecule intimate pairs. Comparisons with previous results and potential applications are briefly discussed. The companion paper shows that ether product yields can also be used to estimate R′OH binding constants over a wide range of alcohol and surfactant concentrations.

Introduction

Surfactants, commonly known as soaps and detergents, are amphiphiles composed of nonpolar hydrocarbon tails attached to polar nonionic, zwitterionic, or ionic head groups.[1,2] Many surfactants and mixtures of surfactants in the presence and absence of oils, salts, and cosurfactants, such as medium-chain-length alcohols, form transparent, thermodynamically stable solutions of dynamic aggregates called association colloids,[1,3-6] which are one class of supramolecular aggregates and assemblies.[7,8] Some association colloids cosolubilize large quantities of oil and water:[9] a property with important commercial applications such as tertiary oil recovery,[10] the formulation of cleaning products,[11] and possible use in food chemistry for the solubilization and stabilization of flavors and oils.[12] Association colloids are also used as model systems for the compartmentalizing and organizing ability of biological membranes and the catalytic activity of enzymes,[1,13-16] and the relationships between aggregate structure and stability and the structure of surfactants and additives are important problems in solution chemistry.[5]

Association colloid structures depend upon both the concentrations and structures of the components in solution.[1,4-6,9,10] In dilute aqueous solutions above the critical micelle concentration, or cmc, single-chain ionic surfactants spontaneously form approximately spherical micelles with their hydrocarbon tails in the interior and their head groups and associated counterions at the surface (Figure 1). Large flexible rod-shaped aggregates are sometimes formed at higher surfactant concentrations. In nonpolar solvents, surfactants form reverse micelles with their head groups surrounding a small water pool. Three-component microemulsions, sometimes called alcohol-swollen micelles, are formed in aqueous solutions of a surfactant and a medium-chain-length alcohol. Some combinations of surfactant, alcohol, water, and oil form four-component microemulsions over a wide range of water to oil ratios with aggregate structures varying from oil-in-water droplets to water-in-oil droplets and in some cases

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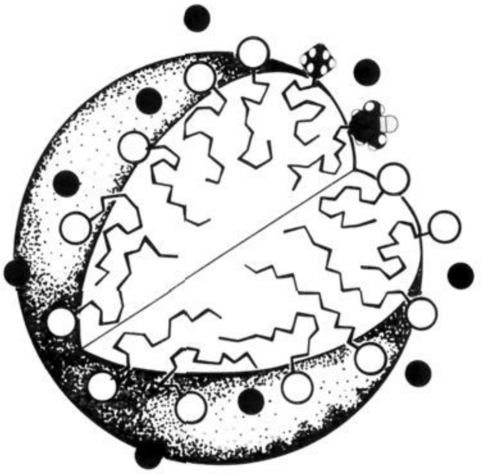

Figure 1. Drawing of a spherical cationic micelle adapted from ref 23. Faces of the empty section show the core filled by flexible tails of surfactant and substrate (**IIb**) having a radius approximately equal to the length of the extended surfactant chain and surrounded by the Stern layer containing substrate and surfactant head groups (open circles) and a fraction of the counterions (filled circles). Note that space-filling representations of the $-CH_2N(CH_3)_3^+$ group and the arenediazonium group were generated using the molecular mechanics program "Model" version 2.96 and scaled to the open circles.

bicontinuous regions at intermediate ratios.[9] What is unique about surfactant solutions is that spontaneous aggregation creates highly anisotropic interfacial regions which line the boundary formed by the highly polar aqueous and nonpolar oil regions and imparts new chemical and physical properties to the system. Interfacial regions are also formed by other supramolecular aggregates such as surfactant monolayers at air/water and oil/water interfaces, the endo and exo surfaces of bilayers formed by biological membranes, by ionic phospholipids or synthetic, twin-tailed surfactants, and by aqueous solutions of stretched and coiled polyelectrolytes and proteins.[1,3,5,7,8,14]

The structures and compositions of the internal regions of association colloids and other supramolecular aggregates are determined by a delicate balance of forces.[14] Aggregation is driven by the hydrophobic effect, i.e., the tendency of the hydrophobic portions of amphiphiles, additives, and polymer side chains to minimize their contact with water. Stability is maintained by the strong interactions of polar and ionic head groups of surfactants and additives with the adjacent aqueous phase, e.g., by hydration, electrostatic, ion–dipole, and hydrogen-bonding interactions. Determining the compositions of association colloid interfaces over a range of solution compositions provides important information regarding the contributions of these forces to aggregate structure and stability. However, interfacial compositions are difficult to determine experimentally because of wide variations in surfactant and additive structures, the dynamic nature of the aggregates, and the small fraction of the total solution occupied by the interfacial region. A number of experimental methods are currently used to estimate the distributions of ions and molecules between surfactant aggregates and the bulk phase, including solubility, conductivity, and potentiometry studies and NMR, UV/visible, and fluorescence spectroscopies.[6,14,17] Most of these methods monitor only one component at a time, and some are limited to narrow ranges of solution composition. For example, potentiometry and conductivity measurements, which monitor the ion concentration in the aqueous phase,[18] cannot be used in solutions with high counterion concentrations or in the presence of interfering ions; e.g., Br^- ion electrodes cannot be used in solutions containing Cl^-. Distributions of alcohols are also difficult to determine because they are transparent in much of the UV/visible region of the spectrum and water interferes in the IR. Alcohol distributions in three-component aqueous microemulsions are usually estimated by solubility,[19] vapor pressure,[20] and fluorescence quenching studies,[21] but these methods are limited primarily to medium-chain-length alcohols and may not be applicable to microemulsions containing substantial quantities of oil. All these methods provide estimates of fractions of ions or molecules bound to aggregates, but their interfacial concentrations can be estimated only by making assumptions about their distributions within aggregates and the interfacial volume.

Bimolecular chemical reactions can also be used to probe interfacial compositions of association colloids. Observed rate constants for reactions of aggregate-bound probes and their product distributions depend upon both the concentration of the second reactant and the rate constant for reaction within the aggregate.[22-24] A wide variety of chemical reactions have been studied in association colloids,[22,25] and several models, including the pseudophase ion-exchange (PIE)[22,24,25] and Poisson–Boltzmann equation (PBE)[26] models, have been developed for interpreting aggregate effects on reactivity. These models generally provide excellent qualitative and often good quantitative fits of surfactant and salt effects on the observed rates of bimolecular reactions, although they work less well at high salt concentrations and in the presence of high concentrations of hydrophilic counterions.[23] In both models, association colloids are treated as a separate phase, a pseudophase, distributed throughout the aqueous phase. In the PIE model, which provides the conceptual basis for exploring the use of dediazoniation reactions as interfacial probes, rate constants for reaction with an aggregate are assumed to be independent of the aggregate's size, shape, medium properties, and solution composition. Good fits of aggregate-induced changes in observed rate constants can often be obtained by using single values for the rate constants for reaction within the aggregate and by assuming that changes in observed rate constants are caused by aggregate- and salt-induced shifts in reactants' distributions among the aqueous, interfacial, and oil regions and their local concentrations within these regions.[23,25] Rate enhancements or inhibitions are typically 1–2 orders of magnitude and in some cases reach 3–6 orders of magnitude,[24] but estimated rate constants of reaction within the aggregate which give best fits to kinetic data are generally within an order of magnitude of their values in water. All current kinetic and spectrophotometric evidence is consistent with aggregate-bound, polar molecules (e.g., substrates) and ions (often the second reactant) being located (and reacting) in the water-rich interfacial region[1,6,17,23,24,26] (Figure 1). Thus, interfacial concentrations of ions and molecules can be estimated from product yields, provided that the rate constants or selectivities of reaction of the ions and molecules with the probe at the aggregate interface are known or are the same in the aggregate and in water.

We have developed a novel analytical method for estimating the relative quantities of weakly basic nucleophiles and their concentrations in interfacial regions of association colloids from

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thermal decomposition products of amphiphilic, aggregate-bound, arenediazonium salts.[27-32] Here we describe the characteristics of dediazoniation reactions which make them good probes of interfacial compositions, the methods for preparing the diazonium salts and reaction products, the analytical methods, and the kinetic, spectrophotometric, and competitive product distribution results which support our assumption that the selectivity of the dediazoniation reaction is the same in surfactant aggregates and in aqueous solution. On the basis of this assumption, product yields from the reactions of aggregate-bound diazonium salts are used to estimate interfacial counterion concentrations in cetyltrimethylammonium halide ((CTA)X; X = Br, Cl) micelles and interfacial concentrations of Br^-, H_2O, 1-butanol (BuOH), and 1-hexanol (HexOH) in aqueous three-component (CTA)Br microemulsions as a function of added BuOH and HexOH, respectively.[28,29] The companion paper (following in this issue) shows that ether product yields from reaction with BuOH and HexOH can be used to estimate their bound mole fractions and their mole fraction based partition and mass action binding constants in three-component aqueous (CTA)Br microemulsions. Papers 3 and 4 will describe the estimation of interfacial concentrations of Br^-, H_2O, BuOH, and HexOH over a wide range of (CTA)Br concentrations and the estimation of the binding constants of these alcohols in four-component reverse microemulsions of (CTA)Br, hexadecane, H_2O, and BuOH or HexOH.

Suitability of Arenediazonium Salts as Interfacial Probes

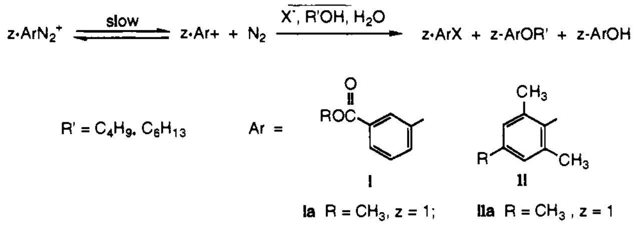
Dediazoniation reactions have a number of important characteristics that make them good probes of association colloid interfaces. In brief: (a) the dediazoniation reaction has been studied extensively and its basic characteristics are well understood; (b) dediazoniation rates are extraordinarily insensitive to medium effects so that competitive product distributions in micelles and water will depend primarily upon local nucleophile concentrations; (c) the selectivity of the reaction toward different charged or uncharged nucleophiles is very low, which ensures reasonable yields of products from competing reactions; and (d) the expected reaction products are stable. In addition, perturbation of aggregate structure by the probe should be minimal because long-chain arenediazonium salts are amphiphiles and are structurally similar to the surfactant, and because the dediazoniation products absorb strongly in the UV, they can be used in very low concentrations (see Discussion).

Arenediazonium salts have a rich, extensively explored, but still not completely understood chemistry.[33-38] They react both thermally and photochemically via heterolytic pathways that begin with rate-determining loss of N_2 and via radical pathways that begin with nucleophilic attack at the terminal nitrogen[37] or electrophilic addition to strong nucleophiles to give adducts or to aromatic rings to give azo dyes.[34] Swain[39-42] demonstrated that the heterolytic mechanism, first proposed by Waters,[43] best fits all available data for dediazoniation reactions of arenediazonium salts carried out in the dark, in aqueous acid containing O_2, and in the presence of weakly basic nucleophiles, and Zollinger showed that loss of N_2 is reversible.[35,36] Scheme I shows the heterolytic dediazoniation mechanism and products for reaction with Br^-, alcohol (R′OH), and H_2O for the two different hydrophobic substrates and their short-chain, water-soluble analogues used in our experiments. Substrates **Ia**, **Ib**, **IIa**, and **IIb** are respectively (3-(methyloxy)carbonyl)-, and (3-(hexadecyloxy)carbonyl)-, 2,4,6-trimethyl-, and 4-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborates. All our results (see below) are consistent with the heterolytic mechanism, i.e., reversible, rate-determining C–N bond cleavage to generate an aryl cation which reacts extremely rapidly with available nucleophiles. Homolytic pathways via radical intermediates[44] and reaction pathways with benzyne type intermediates[36] are excluded because, consistent with literature results, the reduction and isomerized products characteristic of these reactions are not observed.

Table I. Dediazoniation Rates for Benzenediazonium Tetrafluoroborate in Various Solvents at 25 °C

solvent	$10^5 k_{obs}$, s^{-1}	dielectric const	ref
dioxane	1.15	2.21	39
105% H_2SO_4	2.15	110.0	39
0.1% (0.01 M) H_2SO_4	4.59	80.1	39
CH_3COOH	2.26	8.2	39
CH_3COOH + 1 M LiCl	4.51		39
CH_2Cl_2	2.20	9.08	44
CH_3CN	3.30	37.5	44
DMSO	4.16	48.9	44
CH_3OH	9.1	32.7	44
CH_3CH_2OH	8.2	24.3	44

Scheme I



The single strongest piece of evidence for the heterolytic, unimolecular mechanism is the extraordinary insensitivity of dediazoniation rates to solvent polarity[39] (Table I). For example, despite obvious differences in expected products,[44] the observed rate constants, k_{obs}, for the dediazoniation of benzenediazonium tetrafluoroborate vary only 9-fold in nonpolar methylene chloride and dioxane, in dipolar, aprotic DMSO, in dipolar, protic alcohols, and in dilute, aqueous H_2SO_4 and 105% H_2SO_4, which differ in water activity by over a 1000-fold.[39] Even in acetic acid, which does not solvate ions well, k_{obs} increases by only 2-fold upon addition of 1 M Cl^-, and these rate constants are both close to the value in 0.1% aqueous H_2SO_4. In aqueous acid, observed rate constants for reactions of arenediazonium ions with nucleophiles that are conjugate bases of strong acids such as Cl^-, Br^-, H_2O, R′OH (R′ = alkyl), and SCN^- are virtually independent of their concentrations (±20% up to 5.0 M added nucleophile),[39,45] consistent with rate-determining loss of N_2.

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Table II. Effect of Added (CTA)X on k_{obs} for Dediazoniation of **Ib** in 0.1 M HX and **IIb** in 0.01 M HX at 40 ± 0.1 °C

Ib				**IIb**			
[(CTA)Br], M	$10^5 k_{obs}$, s^{-1}	[(CTA)Cl], M	$10^5 k_{obs}$, s^{-1}	[(CTA)Cl], M	$10^4 k_{obs}$, s^{-1}	[(CTA)Br], M	$10^4 k_{obs}$, s^{-1}
0.001		0.001	3.4	0.001	3.64	0.001	3.85
0.005	3.40	0.005	2.63	0.005	4.02	0.002	3.79
0.01	2.89	0.01	2.55	0.01	4.03	0.004	3.65
0.05	2.97	0.05	2.46	0.05	3.98	0.008	3.81
0.10	2.62	0.10	2.42	0.08	3.88	0.03	3.77
				0.10	3.47	0.05	3.74
				0.30	3.37	0.08	3.73
				0.35	3.35	0.10	3.70
				0.40	3.32	0.20	3.30
	2.97 ± 0.22 (±7.2%)[a]		2.5 ± 0.25 (±10%)[a]		3.67 ± 0.27 (±7.4%)[a]		3.70 ± 0.10 (±2.8%)[a]

[a] Average of values in the column above; includes average deviation and percent average deviation.

A variety of additional evidence is consistent with reversible, rate-determining, heterolytic C–N bond cleavage[39] including N_α–N_β exchange in unreacted starting material,[46] exchange with dissolved N_2 at 300 atm of nitrogen (about 3 M N_2 in trifluoroethanol),[36] inhibition of dediazoniation by high concentrations of dissolved N_2,[47] and a large entropy of activation, $\Delta S^{\ddagger} = 43 \pm 4.2$ J mol^{-1} K^{-1} at 298 K.[38] Dediazoniation rate constants for a wide variety of monosubstituted benzenediazonium salts are well fit by a linear free energy relationship based on resonance and field parameters developed for other reactions,[39] providing strong support for a single substituent-independent, dediazoniation mechanism in dilute aqueous acid in the dark.

Substantial evidence suggests that the the aryl cation intermediate must be extremely short-lived.[38,48] Scaiano and Kim-Thuan studied the transient UV spectra of a series of substituted benzenediazonium ions (H, *p*-Me, *p*-NEt_2, *p*-OMe, and *o*-Me) in water irradiated by nanosecond laser flash photolysis.[48] No absorbances different from those of the starting material and the expected hydrolysis products were found. They estimated the lifetime of the aryl cation to be less than 500 ps, assuming it was in the reaction path. Chateauneuf estimated the lifetime of the diphenylcarbenium ion to be only 750 ps by picosecond laser flash photolysis of diphenyldiazomethane in 2/1 MeCN/H_2O.[49] The diphenylcarbenium ion should be strongly resonance-stabilized and should have a much longer lifetime than the aryl cation which has the positive charge in an sp^2 orbital orthogonal to the π cloud of the benzene ring. Cacace showed that the β decay of para-ditritiated benzene gave a para-tritiated aryl cation that reacts with MeOH in the gas phase to give a mixture of ortho-, meta-, and para-substituted tritiated anisole products.[50] However, in liquid MeOH only para-substituted anisole was found, showing that the aryl cation lifetime in solution is less than the scrambling rate.

The selectivity of the benzenediazonium ion toward weakly basic anionic nucleophiles compared to water (55.5 M) is known to be very small and in the order Br^- and S (of SCN^-) > Cl^- and N (of SCN^-) > H_2O: 6 > 3 > 1.[39] These values are similar to ours (see below) but are orders of magnitude lower than selectivities typically observed for anionic nucleophiles competing with water in reactions with stabilized carbocations[39] or participating in bimolecular reactions at saturated carbon.[51] Such low selectivities by arenediazonium salts are consistent with a preassociation stepwise mechanism in which the aryl cation intermediate has a short but finite lifetime and reactant and catalyst form a complex before bond making and breaking occur.[52] For example, both 1- and 2-adamantyl chlorides form carbocations, which are probably more stable than the aryl cation, that are believed to react with both N_3^- and H_2O at the diffusion-controlled limit of N_3^- ($k_{diff} = 5 \times 10^9$ M^{-1} s^{-1}).[53] Recently, the selectivities of three different arenediazonium salts toward Br^- and Cl^- compared to solvent (H_2O/ethylene glycol and H_2O/glycerol mixtures) were found to be independent of solvent viscosity,[54] consistent with the aryl cation reacting with both anions and uncharged solvent molecules near the diffusion-controlled limit.

Results

Kinetics. All dediazoniation reactions were carried out at 40 °C for several reasons: to avoid precipitation of (CTA)Br, which forms metastable solutions at 25 °C, especially at high NaBr concentrations, because it has a Krafft point near room temperature[55] and to speed the reaction because the dediazoniation rates of both substrates, but particularly substrates **Ia** and **Ib**, are slow at room temperature. The kinetic results in Tables II–V show that, within an average deviation of ±20%, the observed first-order rate constants, k_{obs}, for the dediazoniation of substrates **Ia**, **IIa**, **Ib**, and **IIb** are almost independent of added surfactant (Table II), added salt (Tables III and IV), and, within limits, pH (Table V). Values of k_{obs} for **Ia** in aqueous solution and **Ib** in micelles are essentially the same (Tables II, IV, and V), but **IIa** reacts somewhat faster in aqueous solution than **IIb** in micelles (Tables III and V). This difference cannot be attributed to substituent effects because values of k_{obs} for dediazoniation of both **IIa** and **IIb** in 9/1 MeOH/H_2O (0.01 M HBr at 40 ± 0.1 °C) are similar and in opposite order: 4.14×10^{-4} s^{-1} (**IIa**) and 5.17×10^{-4} s^{-1} (**IIb**). Also, added BuOH has no effect on k_{obs}; between 0.44 and 0.87 M BuOH, $k_{obs} = 4.65 \times 10^{-4}$ s^{-1} ± 1.2% (four data points).[28]

Some trends are apparent in the data. Added salt reduces k_{obs}, but to a lesser extent in micelles than in aqueous solution (Tables III and IV). Small specific salt effects (see below) are apparent for the dediazoniation of **Ia** (Table IV). Added NaCl and NaBr slow the dediazoniation of **Ia**, but at constant ionic strength, increasing the concentration of these salts (columns 5 and 6) speeds the reaction from its lowest value in 5.0 M $NaClO_4$ (column 4). Rate constants for dediazoniation of **Ia** and **Ib** have not been measured previously, but they are consistent with the effects of other monosubstituents on dediazoniation rates.[30,56] Values of k_{obs} for **IIa** are, sensibly, about 3–4 times larger in aqueous solutions at 40 °C (Table III) than in various fluorinated solvents at 25 °C.[57] Table V shows that k_{obs} is independent of solution

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Table III. Effect of Added NaX on k_{obs} for Dediazoniation of **IIa** in 0.01 M HX and **IIb** in 0.01 M (CTA)X and 0.01 M HX

IIa[a]				**IIb**[b]			
[NaBr], M	10^4k_{obs}, s^{-1}	[NaCl], M	10^4k_{obs}, s^{-1}	[NaBr], M	10^4k_{obs}, s^{-1}	[NaCl], M	10^4k_{obs}, s^{-1}
0	5.52	0	5.0	0	3.69	0	3.57
0.5	5.78	0.52	5.54	0.25	3.78	0.25	3.27
1.0	5.81	1.04	5.51	0.5	3.7	0.5	3.17
1.5	5.48	1.56	5.32	1.0	3.62	1.0	3.09
2.0	5.07	2.08	5.15	1.5	3.61	1.5	2.97
2.5	4.54	2.6	5.00	2.0	3.53	2.0	2.94
3.0	4.19	3.12	4.87	2.5	3.68	2.5	2.94
3.5	3.98	4.16	3.92	3.0	3.84	3.0	2.89
4.0	3.74					3.5	2.85
						4.0	2.74
	4.9 ± 0.7 (±14.3%)[c]		5.11 ± 0.38 (±7.4%)[c]		3.68 ± 0.071 (±1.9%)[c]		3.04 ± 0.18 (±5.6%)[c]

[a] At 38.2 ± 0.1 °C. [b] At 40 ± 0.1 °C. (CTA)Br precipitates above 3.0 M NaBr. [c] Average of values in the column above; includes average deviation and percent average deviation.

Table IV. Effect of Added NaX on 10^5k_{obs} (s^{-1}) for Dediazoniation of **Ia** at Variable and Constant Ionic Strengths at 40 ± 0.1 °C

[NaX], M	NaBr	NaCl	$NaClO_4$	NaBr $\mu = 5.01$[a]	NaCl $\mu = 4.01$[b]
0	2.93	2.75			
0.5	2.68	2.59			1.66
1.0	2.72	2.63	2.73	1.56	1.70
1.5		2.71			1.76
2.0	2.43	2.45	2.52	1.56	1.9
3.0	2.59	2.33	2.09	1.86	2.11
4.0	2.42	2.06	1.86	1.87	2.20
5.0	2.22		1.33	2.20	
	2.57 ± 0.18 (±7.1%)[c]	2.50 ± 0.19 (±7.7%)[c]	2.11 ± 0.42 (±19.7%)[c]	1.76 ± 0.21 (±11.9%)[c]	1.89 ± 0.42 (±9.6%)[c]

[a] $[NaBr] + [NaClO_4] = 5.01$ M. [b] $[NaCl] + [NaClO_4] = 4.01$ M. [c] Average of values in the column above; includes average deviation and percent average deviation.

Table V. Effect of [HBr] and pH on k_{obs} for Dediazoniation of **I** and **II** at 40 ± 0.1 °C

[HBr], M or pH	10^5k_{obs}, s^{-1}		[HBr], M or pH	10^4k_{obs}, s^{-1}	
	Ia	**Ib**[a]		**IIa**	**IIb**[a]
0.62	2.63	2.30	0.1	6.34	3.31
0.12	2.59	2.29	0.01	6.32	3.69
0.061	2.60	2.39	0.001	6.41	3.52
0.012	2.64	3.17[b]	0.0001	6.15	3.94
3.6[c]	5.13		4.15[d]	6.3	2.85[b]
			5.03[d]	6.29	4.01[b]
			5.90[d]	6.21	
			6.07[e]	5.97	
			6.98[e]	6.45	
			7.87[e]	5.59	
			10.67[b,f]	8.9	

[a] In 0.01 M (CTA)Br. [b] Product mixture had a UV/visible spectrum markedly different from those at higher acidities. [c] Citrate buffer. [d] Sodium acetate/acetic acid buffer. [e] K_2HPO_4/KH_2PO_4 buffer. [f] In 0.001 M NaOH.

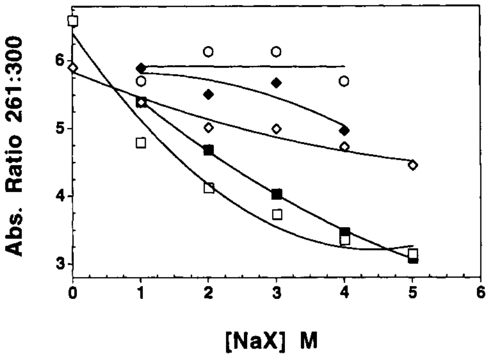

Figure 2. Salt effects on the ultraviolet absorbance ratio of **Ia** at 261 and 300 nm at 25 ± 0.1 °C in 0.01 M HX: (□) NaBr; (◇) NaCl; (○) $NaClO_4$; (■) HBr + NaBr + $NaClO_4$ (5.01 M); (◆) HCl + NaCl + $NaClO_4$ (5.01 M).

acidity above certain acid strengths. Below 0.01 M H^+ for **Ia** and 0.06 M H^+ for **Ib**, k_{obs} increases and the solutions turn pale yellow during the reaction instead of remaining colorless, indicating the formation of a new product or products. Diazonium salts **II** are more versatile. Values of k_{obs} for **IIa** are virtually constant up to pH 8, but only up to about pH 4 for **IIb** because the spectra of the products change above this pH, again indicating a change in the products formed. These pH effects are probably related to the lower acidity of cationic micelle surfaces, by about 1–2 pH units, compared to that of the surrounding bulk solution.[23,58] Cationic micelles may also speed azo dye formation between the phenol product and unreacted diazonium salt[30] or diazotate formation from reaction with HO^-.[37] To avoid complications caused by side reactions, we selected operational acidities within the plateau regions of the k_{obs}–pH profiles and confirmed that the UV spectra and the total yields are consistent with expected products. In sum, all our kinetic data in aqueous solutions containing O_2 and sufficient acid to suppress unwanted products are consistent with the well-established insensitivity of dediazoniation reactions to salt[45] and medium effects.[39]

Specific Salt Effects. Added NaX has significant effects on both the λ_{max} and absorbance of **Ia** at 25 °C.[30] Figure 2 shows the effect of added NaBr and NaCl at variable and constant ionic strengths ($[NaClO_4] + [NaX]$ = constant) on the absorbance ratio, 261/300 nm, of **Ia** (data in supplementary Tables S1 and S2). Both λ_{max} and the absorbance ratio are insensitive to added $NaClO_4$, but added NaBr significantly reduces both λ_{max} (not shown)[30] and the absorbance ratio even at constant ionic strength. The effect of added NaCl is more modest: the spectral shifts and the modest specific salt effects on the values of k_{obs} for **Ia** and **IIa** (Tables III and IV), especially at constant ionic strength, are consistent with ion-pair formation between arenediazonium salts and Br^- and to a lesser extent Cl^-.

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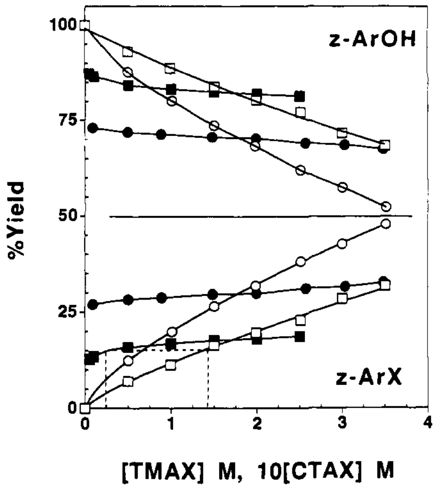

Figure 3. Dediazoniation product yields at 40 ± 0.1 °C from reaction of **IIa** in aqueous (TMA)X, 0.01 M HX (open symbols) and **IIb** in aqueous (CTA)X, 0.01 M HX with H_2O (upper curves), and halide ions (lower curves): (■, □) X = Cl; (●, ○) X = Br. Curves for (TMA)Cl and (TMA)Br are fitted, respectively, by the equations %1-ArBr = $19.95[\mathrm{TMABr}]^{0.695}$ and %1-ArCl = $11.75[\mathrm{TMAC}]^{0.771}$. Dashed line show that when %16-ArCl = %1-ArCl = 15%, Cl_m (in 0.025 M (CTA)Cl) = 1.4 M ([(TMA)Cl]) (see text).

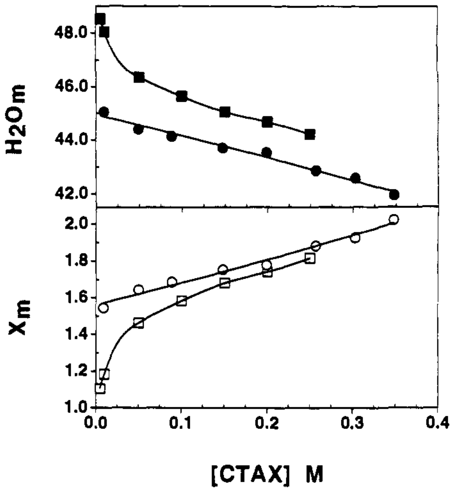

Figure 4. Effect of added (CTA)Cl (■, □) and (CTA)Br (●, ○) on interfacial concentrations of water, H_2O_m (upper curves), and their counterions, X_m (lower curves), estimated from product yields from dediazoniation of **IIb** (see text).

Table VI. (TMA)X (X = Br, Cl) and Water Concentrations, Normalized Product Yields, and Selectivities (S_w^X) for Dediazoniation of 1.24 × 10^{-4} M **IIa** in Aqueous 0.01 M HX at 40 ± 0.1 °C

[(TMA)Br], M	normalized yields		$[H_2O]$, M[a]	S_w^{Br}
	%1-ArBr	%1-ArOH		
0.000	0.00	100.0	55.5	
0.503	12.4	87.6	51.7	14.5
1.010	19.9	80.1	48.3	11.9
1.500	26.4	73.6	45.0	10.8
1.980	31.7	68.3	42.2	9.91
2.510	38.1	61.9	38.8	9.50
3.000	42.6	57.4	35.9	8.88
3.510	47.7	52.3	32.6	8.48

[(TMA)Cl], M	normalized yields		$[H_2O]$, M[a]	S_w^{Cl}
	%1-ArCl	%1-ArOH		
0.000	0.0	100.0	55.5	
0.500	7.0	93.0	51.8	7.77
0.993	11.3	88.7	49.4	6.32
1.500	16.3	83.7	46.1	5.97
1.990	19.7	80.3	43.4	5.34
2.510	22.9	77.1	40.0	4.72
3.000	28.4	71.6	36.7	4.82
3.500	31.7	68.3	34.4	4.56

[a] Calculated from the measured weight of H_2O in each solution.

Product Yields and Interfacial Concentrations. Figure 3 shows normalized yields of z-ArX and z-ArOH obtained from dediazoniation of **IIa** in aqueous solutions of (TMA)Cl and (TMA)Br with special provisions to prevent loss of 1-ArX products (see Experimental Section) and **IIb** in aqueous solutions of (CTA)Cl and (CTA)Br (data in supplementary Tables S3-S5). The results in Figure 3, where square brackets, [ ], here and elsewhere in the text indicate stoichiometric concentration in molarity, are consistent with the high interfacial counterion concentrations estimated for micelles.[25,59] At low [(CTA)X], but above the cmc, yields of 16-ArX in micelles are substantial, 27% 16-ArBr in 0.009 M (CTA)Br, 0.01 M HBr and 12.7% 16-ArCl in 0.005 M (CTA)Cl, 0.01 M HCl, whereas yields of 1-ArX in 0.01 M HX would be essentially zero at equivalent [(TMA)X]. The results are also consistent with the characteristic insensitivity of the degree of counterion binding, β, of Cl^- and Br^- to changes in micelle concentration[25,59,60] because yields of 16-ArX increase very slowly with added (CTA)X whereas yields of 1-ArX increase rapidly with added (TMA)X. Interfacial counterion concentrations, X_m, where subscript m indicates interfacial concentration in molarity, i.e., moles of nucleophile per liter of interfacial region sensed by the diazonium ion, were estimated from the results in Figure 3. The concentrations of X^- in water and in the interfacial region are assumed to be the same when yields of 1-ArX from dediazoniation of **IIa** in water and of 16-ArX from **IIb** in (CTA)X micelles are the same. For example, the interfacial concentration of Cl^- in 0.025 M (CTA)Cl is estimated to be 1.4 M because the yield of 16-ArCl is equal to that of 1-ArCl in 1.4 M (TMA)Cl (Figure 3, dashed lines). Figure 4 (data in supplementary Table S6) shows the interfacial Cl^- and Br^- concentrations calculated at each (CTA)X concentration from the fitted product yield curves in (TMA)Cl and (TMA)Br solutions in Figure 3.

Equation 1 defines the selectivity of the dediazoniation reaction toward halides ions compared to water, S_w^X, for reactions in

$$S_w^X = \frac{[H_2O](\%1\text{-ArX})}{[(TMA)X](\%1\text{-ArOH})} = \frac{H_2O_m(\%16\text{-ArX})}{X_m(\%16\text{-ArOH})} \qquad (1)$$

aqueous solution and at aggregate interfaces. Equation 1 was used to estimate the S_w^X for **IIa**, and the results are summarized in Table VI. Values of $[H_2O]$ were obtained from the weights of H_2O in each solution. Note the gradual decrease in S_w^X with added (TMA)X. The values of S_w^X at high (TMA)X concentrations are similar to literature values (see above). Estimates of H_2O_m (Figure 4) were obtained at each (CTA)X concentration by using eq 1 and by assuming that when the counterion concentrations in aqueous (TMA)X and (CTA)X are equal, the selectivities of the dediazoniation reaction of **IIa** in (TMA)X and **IIb** in (CTA)X are equal. Note the concomitant decrease in H_2O_m with increasing X_m.

Figure 5 shows the changes in interfacial concentrations of $R'OH_m$, Br_m, and H_2O_m estimated from dediazoniation product yields from **IIb** with added R'OH almost to the solubility limits of BuOH and HexOH in 0.01 M (CTA)Br, 0.01 M HBr (data in supplementary Tables S7-S10). Values of Br_m were estimated from the %1-ArBr–[(TMA)Br] data in Figure 3. Values of $BuOH_m$ were obtained by the same procedure from a plot of %1-ArOBu versus [BuOH] for dediazoniation of **IIa** in aqueous BuOH solutions up to the solubility limit of BuOH in water (ca. 1 M[61]) which was fitted by the linear equation %1-ArOBu =

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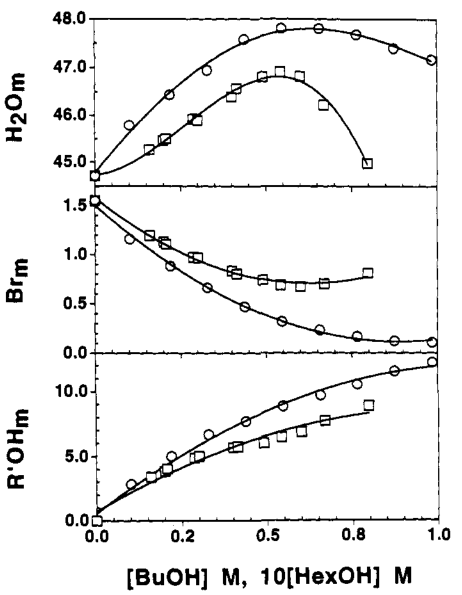

Figure 5. Effect of added BuOH (○) and HexOH (□) on the interfacial concentrations of water (H_2O_m), bromide ion (Br_m), and alcohol ($R'OH_m$) estimated from product yields from dediazoniation of **IIb** in 0.01 M (CTA)Br, 0.01 M HBr at 40 ± 0.1 °C. Note the scales change on the *y* axis and, for HexOH, on the *x* axis.

0.695[BuOH] - 0.0659 (five data points; cc = 0.990).[28] The solubility of HexOH in water, ca. 0.08 M,[61] is too low to give significant yields of 1-ArOHex, so we assumed that the selectivity of the dediazoniation reaction is the same toward BuOH and HexOH in water, and values of $HexOH_m$ were estimated from the %1-ArOBu-[BuOH] plot.

Equation 2 defines the selectivity of the dediazoniation reaction toward R'OH compared to water, S_w^A, for reactions in aqueous

$$S_w^A = \frac{[H_2O](\%1\text{-ArOR}')}{[R'OH](\%1\text{-ArOH})} = \frac{H_2O_m(\%16\text{-ArOR}')}{R'OH_m(\%16\text{-ArOH})} \qquad (2)$$

solution and at aggregates interfaces. Values of $[H_2O]$ were obtained from the weights of H_2O in each solution. Up to the solubility limit of BuOH in H_2O, $S_w^A = 0.31$, which is close to the value of $S_w^A = 0.28$ that we obtained for dediazoniation of 1-ArN_2^+ in a homogeneous solution of 9/1 $BuOH/H_2O$ containing 0.001 M HBr at 40 °C.[29] These two estimates show that S_w^A is virtually independent of solution composition. Values of H_2O_m were estimated from eq 4, which was obtained by combining eqs 1 and 2 with the mass balance equation (3).

$$\%z\text{-ArBr} + \%z\text{-ArOR}' + \%z\text{-ArOH} = 100 \qquad (3)$$

$$H_2O_m = \frac{\%16\text{-ArOH}(S_w^{Br}Br_m + S_w^A R'OH_m)}{100 - \%16\text{-ArOH}} \qquad (4)$$

Discussion

We assume that the cationic diazonio group is located in the same region of the micellar or microemulsion interface as the surfactant head groups (Figure 1) because 16-ArN_2^+ is an amphiphile and should have the same orientation in aggregates as the surfactant. Perturbation of aggregate structure should be minimal because 16-ArN_2^+ is structurally similar to (CTA)X, because the quaternary ammonium and arenediazonium groups are similar in size (Figure 1), and because the surfactant is always in large excess, i.e., $16\text{-ArN}_2^+/(CTA)X \geq 100/1$. The diazonium salt is insoluble in H_2O in the absence of (CTA)X and therefore should be virtually completely aggregate bound under our experimental conditions ([(CTA)X] ≥ 0.01 M). By comparison, *N*-1-hexadecyl-3-carbamoylpyridinium bromide, which is about as hydrophobic as 16-ArN_2^+, has a large binding constant ($K_s = 3.5 \times 10^3$ M^{-1}) in the case of (CTA)X micelles and is >97% bound in 0.01 M (CTA)X.[62]

The primary assumption used to estimate interfacial concentrations of Cl^-, Br^-, R'OH, and H_2O is that the yield from the reaction of 16-ArN_2^+ with a nucleophile in an aggregate will be the same as its yield from the reaction with 1-ArN_2^+ in aqueous solution when the concentrations of the nucleophile in the interfacial region and in aqueous solution are the same, i.e., that dediazoniation reactions in aqueous solution are good models for dediazoniation reactions at aggregate interfaces. On the basis of our results, we assume that S_w^A is constant at all solution compositions but that S_w^X depends on counterion concentration and type and we use the value of [(TMA)X] at which the yields of 1-ArX and 16-ArX are equal. Our approach to estimating interfacial concentrations depend not upon the reaction mechanism but only upon the assumption that selectivities of the dediazoniation reaction are the same in aggregates and in water. However, this assumption is supported by two important characteristics of the heterolytic dediazoniation mechanism: (a) the extraordinary insensitivity to medium effects which can be attributed to the similarity in structure, charge distribution, and probably solvation of the diazonium ion ground state and aryl cation intermediate (and transition states on each side of the intermediate) and (b) the extremely short lifetime of the aryl cation which limits the opportunity of ions and molecules in its immediate vicinity to relax to their equilibrium distributions. Thus, observed product distributions (and selectivities) should be determined by the equilibrium distribution of different nucleophiles in the immediate vicinities of the ensemble of diazonium ions in their ground states. Selectivity toward a halide ion over water is attributed to ground-state ion-pair formation (Figure 2), and selectivity toward water over an alcohol, to greater solvation of the diazonium ion by water in the ground state. This interpretation is consistent with Rys' detailed analysis of various factors that can contribute to chemical selectivity, in this case nonstoichiometric reactant distribution within the solvent cage of an encounter complex.[63] In the Appendix we show that competitive arenediazonium ion·anion pair and arenediazonium ion·molecule pair formation provides a good qualitative interpretation of the selectivities of dediazoniation reactions and their dependence on solution composition.

The higher interfacial concentrations of Br^- compared to those of Cl^-, $Br_m > Cl_m$ (Figure 4) are consistent with many observations of stronger binding to cationic micelles by Br^- than by Cl^-, as shown by experimental estimates of β and effects on chemical reactivity,[64] competitive ion exchange constants,[25] and Langmuir and Volmer specific interaction parameters.[26] The gradual increase in X_m and concomitant decrease in the interfacial water concentration, H_2O_m, with added (CTA)X are consistent with results obtained earlier using substrates **I** in (CTA)X solutions with added NaX.[31] Increases in X_m with added (CTA)X and NaX are consistent with the steady decrease in ^{79}Br[65] and ^{35}Cl[66] line widths and the increase in k_{obs} for the bimolecular reaction between micellar-bound methyl naphthalenesulfonate and Br^- or Cl^- with added (CTA)X and NaX.[65-67] This gradual increase in interfacial counterion concentration is in qualitative agreement with mass action,[68,69] Poisson–Boltzmann,[70] and electrolyte

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invasion[32] models for the distribution of counterions between micelles and water. However, it contradicts a simplifying assumption commonly used in the pseudophase ion-exchange model,[23] i.e., that interfacial counterion concentrations are constant because experimental estimates of β obtained by using ion-selective electrodes, conductivity, etc. are insensitive to added surfactant and salt. However, if the volume available to counterions at surfactant aggregate interfaces decreases with added surfactant and salt, e.g., by tighter head-group packing or by a decrease in the radial "thickness" (Figure 1) of the interfacial region, then X_m would increase even at constant β.

(TMA)X salts were used to estimate X_m and H_2O_m in the current experiments because the Me_4N^+ ion should be a better model than the Na^+ ion for the quaternary ammonium head group of (CTA)X at the micellar surface. Yields of 1-ArX are higher in the presence of (TMA)X (Figure 3) than in the presence of NaX salts,[28] and this may account for the somewhat lower values for X_m obtained here (a higher %1-ArX reduces X_m; Figure 3). Estimates of H_2O_m are also lower when (TMA)X solutions are used as the reference instead of NaX solutions because the TMA^+ ion is larger than the Na^+ ion[71] so that the $[H_2O]$ is lower in (TMA)X than in NaX solutions of equivalent concentration.

The results in Figure 5, obtained from simultaneous determinations of product yields from the reaction of micellar-bound **IIb** with Br^-, R′OH, and H_2O, show that added BuOH and HexOH reduce Br_m but not H_2O_m in the interfacial region of aqueous three-component (CTA)Br microemulsions. Estimates of interfacial concentrations can be obtained at any R′OH concentration from its solubility limit down to the sensitivity limit of the HPLC, ca. 1% yields. We found that mass action binding constants estimated from 16-ArOR′ yields from reactions with BuOH and HexOH are independent of the total [R′OH] (see the companion paper) and are in agreement with binding constants estimated from solubility data[61] when expressed in the same units. Estimates of $R'OH_m$ in units of moles per liter of *total* microemulsion volume (assuming the volumes of R′OH and (CTA)Br are additive and their densities are 0.81 and 1.0 g/mL, respectively) from values of K_a' at R′OH concentrations just below the solubility limit are $BuOH_m \approx 6.5$ M and $HexOH_m \approx 3.25$ M, approximately half the highest estimated $R'OH_m$ concentrations in Figure 5. This is a sensible result because the volume of the micellar interface has been estimated to be approximately half the total micellar volume.[25]

The decrease in Br_m with added R′OH (Figure 5) parallels the drop in the bound fraction of Br^- with added BuOH estimated from conductivities in (CTA)Br[72] and (MTA)Br (M = myristyl)[18] solutions. Values for H_2O_m with added R′OH exhibit a shallow maximum with a total change in H_2O_m of no more than 2–3 M, ca. 5–6%, which suggests that, even at high concentrations of bound R′OH, the hydroxyl group of R′OH retains its water of hydration upon binding to (CTA)Br aggregates and does not displace significant amounts of interfacial water. When NaX salts are used as reference solutions, H_2O_m is initially higher, ca. 50 M, and decreases at high [R′OH].[29]

Conclusions

Dediazoniation reactions of substrates **I** and **II** in cetyltrimethylammonium halide ((CTA)X) micelles and aqueous three-component (CTA)Br microemulsions containing BuOH or HexOH are consistent with the heterolytic mechanism, and product yields are consistent with the high concentrations of X^-, H_2O, and bound R′OH in the vicinity of the aggregates' interfaces. Product distributions from dediazoniation of $16\text{-}ArN_2^+$ bound to surfactant aggregates are "snapshots" of interfacial composition which can be used to estimate the interfacial nucleophile concentrations by using product yields and selectivities measured in aqueous solution. Our estimates of interfacial concentrations of counterions, Cl_m and Br_m, and water, H_2O_m, in (CTA)X micelles over a range of [(CTA)X] (Figure 4) and Br_m, H_2O_m, and interfacial concentrations of alcohols, $BuOH_m$ and $HexOH_m$, over a range of [R′OH] in three-component cationic microemulsions (Figure 5) are in agreement with values obtained by other methods. HPLC analysis of dediazoniation products easily distinguishes between chemically similar nucleophiles, e.g., between Cl^- and Br^- [31] and between H_2O and R′OH, over a wide range of solution composition, and this approach can be used with other weakly basic nucleophiles which react by the same mechanism, e.g., I^-, RCO_2^-, RSO_3^-, SO_4^{2-}, and SCN^-. Diazonium salts **I** were previously used to estimate Cl_m, Br_m, and their ion-exchange constants, K_{Cl}^{Br}, in (CTA)X micelles over a range of Br/Cl ratios and up to 4.0 M added NaX,[31] and the results were used to simulate counterion (X^-) effects on co-ion (H^+) distribution and k_{obs} for the acid-catalyzed hydrolysis of hydrophobic ketals bound to (CTA)X micelles.[32] In principle, interfacial concentrations and binding constants can also be estimated in anionic micelles, e.g., sodium dodecyl sulfate, in nonionic micelles having terminal –OH head groups, e.g., Brij and mono- and diglycerides, and in four-component oil-in-water, bicontinuous, and water-in-oil microemulsions.

Experimental Section

General Methods. Melting points were determined on Mel-Temp apparatus and are uncorrected. UV/visible spectra were taken on a Perkin-Elmer 559A spectrophotometer fitted with electronic temperature control, ^1H NMR spectra on a Varian XL 200, FTIR spectra on a Mattson Cygnus 100, and surface tensions on a Fisher Du-Nouy tensiometer. Product analyses were carried out on two different HPLC systems: (a) a Perkin-Elmer HPLC system composed of a Series 410 quaternary pump, an ISS 200LC autosampler fitted with a 20-μL loop, a LC-235 diode array detector, a PE-Nelson 900 series interface attached to an Ultra PC computer and Hewlett-Packard Laser Jet IIIp printer and (b) a Kratos HPLC system equipped with a 783 UV/visible variable-wavelength detector (sensitivity 0.001 au) and a Shimadzu CR3-A integrator.

Materials. Tetramethylammonium chloride ((TMA)Cl) and tetramethylammonium bromide ((TMA)Br) were recrystallized from EtOH and MeOH, respectively, and dried. Other salts, solvents, 2,4,6-trimethylphenol (1-ArOH), and 2,4,6-trimethylbromobenzene (1-ArBr) were reagent grade, and 2,4,6-trimethylchlorobenzene (1-ArCl) was a generous gift from Dr. John Lorand; all were used as received except where noted. (CTA)Br and (CTA)Cl were prepared previously and were without minima in their surface tension plots.[31] All aqueous solutions were prepared in distilled water which was passed over a carbon and deionizing resin and then redistilled. Conversions of diazonium salts **I** and **II** to expected products were at least 95% based on weights of added diazonium salts, and HPLC chromatograms were free of extraneous peaks.

4-*n*-Hexadecyl-2,6-dimethylbenzenediazonium Tetrafluoroborate (IIb). Using an anhydrous method,[73] about 15 mL of THF (distilled from Na and benzophenone) was injected into a two-neck 100-mL round-bottom flask fitted with septum caps and a magnetic stirrer, the system was cooled (10 min) to ca. −15 °C in an ice/MeOH bath, 1.7 mL (13.8 mmol) of $BF_3{\cdot}Et_2O$ (Aldrich, fresh) was added by syringe, and the mixture was stirred for 5 min. Then 3 g (8.7 mmol) of $16\text{-}ArNH_2$ (see below) dissolved in 15 mL of distilled THF was added via syringe, giving a clear solution, and 1.3 mL (11 mmol) of *tert*-butyl nitrite (Aldrich, fresh) in 15 mL of distilled THF was added via syringe over a 2-min period. After ca. 15 min of stirring, the temperature was increased to 0 °C and the solution was stirred for 6 h. A white precipitate began forming after about 20 min. The reaction mixture was transferred to a 500-mL beaker and 100 mL of cold pentane added; the off-white solid was collected on a Buchner funnel, recrystallized three times by dissolving it in CH_3CN (Fisher, HPLC grade) and forcing it from solution with cold anhydrous Et_2O, and

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(72) Bertoncini, C. R. A.; Nome, F.; Cerichelli, G.; Bunton, C. A. *J. Phys. Chem.* **1990**, *94*, 5875.

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then dried under vacuum ca. 1 h. Yield: 2.7 g (70%) of shiny white crystals which were stored in the freezer in the dark. This and other arenediazonium salts decompose slowly in the solid state, probably because of periodic exposure to light or moisture, and they must be recrystallized periodically. Dediazoniation of **IIb** gave quantitative conversion to expected products. Total recovery averaged 95% based on the weight of **IIb**, and HPLC chromatograms were free of unidentified peaks: IR (Nujol) ν_{max} (cm^{-1}) 2264 (ArN_2^+, m),[74] 1593 (Ar, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (3 H, t, RCH_3), 1.24 (26 H, br s, $-(CH_2)_{13}-$), 1.73 (2 H, br, $-CH_2-$), 2.72 (8 H, s with shoulder, *o*-$ArCH_3$ and *p*-$ArCH_2-$), 7.23 (2 H, s, Ar H). Substitution patterns on the aromatic rings of **IIb** and **IIa** are identical; both have single peaks for the aromatic protons and almost the same chemical shifts for the 2,6-methyl groups.

4-*n*-Hexadecyl-2,6-dimethylaniline (16-$ArNH_2$). Using a slightly modified form of the procedure of Wisniewski,[75] a mixture of 1-hexadecanol (70.31 g, 0.29 mol; Aldrich, recrystallized from MeOH), 2.6-dimethylaniline (100 g, 0.83 mol; Aldrich, freshly vacuum-distilled), and $ZnCl_2$ (57.24 g, 0.42 mol; Aldrich, fresh, anhydrous) was placed in a 1-L, three-neck round-bottom flask fitted with a heating mantle, stirrer, Dean–Stark trap, and thermometer and heated under dry N_2 at 260 °C for 21 h. On refluxing, the reaction mixture turned violet. It was then cooled to room temperature, transferred to a 2-L beaker in an ice bath, and acidified with excess 2.35 N H_2SO_4 to destroy the $ZnCl_2$·aniline complex, followed by careful neutralization with concentrated NH_4OH. A yellow-brown oil separated from the mixture, and the aqueous phase was extracted with Et_2O (three times); the combined oil and Et_2O extracts were dried over NaOH pellets. Excess Et_2O was removed on a rotary evaporator, and the excess 2,6-dimethylaniline was removed by vacuum distillation. Five successive treatments of the brown semisolid residue with Norit in hot MeOH followed by recrystallization from MeOH gave 18 g (18%) of white crystals (mp 58 °C): IR (KBr pellet) ν_{max} (cm^{-1}) 3433, 3340 ($ArNH_2$, w), 2918, 2848 (CH, s), 1634, 1491, 1464 (Ar, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (3 H, t, J = 6.4 Hz, RCH_3), 1.25 (26 H, br s, $-(CH_2)_{13}-$), 1.55 (2 H, m, $-CH_2-$), 2.16 (6 H, s, *o*-$ArCH_3$), 2.45 (2 H, t, J = 8.2 Hz, *p*-$ArCH_2-$), 3.47 (2 H, br s, $ArNH_2$), 6.77 (2 H, s, Ar H). Anal. Calcd for $C_{24}H_{43}N$: C, 83.41; H, 12.54; N, 4.18. Found: C, 83.70; H, 12.62; N, 4.18.

2,4,6-Trimethylbenzenediazonium Tetrafluoroborate (IIa). The procedure used to prepare **IIb** was also used to synthesize **IIa**. Freshly vacuum-distilled 2,4,6-trimethylaniline (Aldrich, 97%) gave an 83% yield of white crystals after three consecutive recrystallizations from CH_3CN/Et_2O. Dediazoniation of **IIa** gave quantitative conversion to expected products. Total recovery averaged 95% based on the weight of **IIa**, and HPLC chromatograms were free of unidentified peaks: IR (Nujol) ν_{max} (cm^{-1}) 2255 (ArN_2^+, m), 1584 (Ar, m); ^{1}H NMR (acetone-d_6) δ (ppm) 2.54 (3 H, s, *p*-$ArCH_3$), 2.79 (6 H, s, *o*-$ArCH_3$), 7.53 (2 H, s, Ar H).

4-*n*-Hexadecyl-2,6-dimethylphenol (16-ArOH) and 4-*n*-Hexadecyl-2,6-dimethylbromobenzene (16-ArBr). Both products were synthesized simultaneously by carrying out the dediazoniation reaction of **IIb** in aqueous (CTA)Br micelles and 0.1 M HBr with 4.0 M added NaBr to enhance the yield of the bromo product. A mixture of 205.8 g of NaBr (2 mol; 99+% ACS grade, Fisher), 18.22 g (0.05 mol) of (CTA)Br (freshly recrystallized), 50 mL of 1.0 M HBr, and 450 mL of water, which gave final molarities of 4.0, 0.1, and 0.1 M, respectively, was placed in a 1-L three-neck round-bottom flask and heated with stirring for about 1 h at 60 °C in a water bath to dissolve the reactants; 2.5 g of **IIb** was added, and cooled to room temperature, and 10.54 g (0.075 mol) of $NaClO_4 \cdot H_2O$ in 100 mL of H_2O was added; the heavy, white precipitate of $(CTA)ClO_4$ and other products were collected on a Buchner funnel, washed with H_2O several times, and air (2 h) and vacuum-dried (24 h). The precipitate was ground to a fine powder and extracted with about 250 mL of Et_2O with vigorous stirring (ca. 15 min), and the extract was filtered three times. Rotoevaporation of the combined extracts gave a white solid (1.9 g, 75%) which showed two spots by TLC (SiO_2, 90% hexane/10% EtOAc v/v; R_f = 0.23 and 0.74). The mixture was chromatographed on a 40 mm × 135 mm column containing silica gel (80 g; 70–230 mesh, Aldrich) and eluted first with pure hexane to remove 16-ArBr (R_f = 0.74) as a white low melting point solid (0.93 g, 40.4%; mp 39 °C) and then with 20% EtOAc/hexane (v/v) to remove 16-ArOH as a pale yellow solid (R_f = 0.23). Two consecutive Norit treatments of 16-ArOH in MeOH gave 0.25 g (12.8%) of white crystals, mp 76 °C. Analytical data for 16-ArBr: IR (KBr pellet) ν_{max} (cm^{-1}) 2914, 2849 (s, CH), 1473 (Ar, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (3 H, t, J = 6.4 Hz, RCH_3), 1.25 (26 H, br s, $-(CH_2)_{13}-$), 1.56 (2 H, m, $-CH_2-$), 2.37 (6 H, s, *o*-$ArCH_3$), 2.47 (2 H, t, J = 8.0 Hz, *p*-$ArCH_2-$), 6.88 (2 H, s, Ar H). Anal. Calcd for $C_{24}H_{41}Br$: C, 70.40; H, 10.09; Br, 19.51. Found: C, 70.72; H, 9.89; Br, 19.40. Analytical data for 16-ArOH: IR (KBr pellet) ν_{max} (cm^{-1}) 3450 (ArOH, br s), 2916, 2850 (CH, s), ≈1500 (Ar, three signals, w); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (3 H, t, J = 8.0 Hz, RCH_3), 1.25 (26 H, br s, $-(CH_2)_{13}-$), 1.57 (2 H, br, $-CH_2-$), 2.22 (6 H, s, *o*-$ArCH_3$), 2.45 (2 H, t, J = 8.0 Hz, *p*-$ArCH_2-$), 4.44 (1 H, s, br, ArOH), 6.79 (2 H, s, Ar H). Anal. Calcd for $C_{24}H_{42}O$: C, 83.17; H, 12.21; O, 4.62. Found: C, 83.34; H, 12.40; O, 4.93.

4-*n*-Hexadecyl-2,6-dimethylchlorobenzene (16-ArCl). 16-ArCl was synthesized using the same procedure as for 16-ArBr except (CTA)Cl, NaCl (99+% ACS grade, Fisher), and HCl were used instead of (CTA)Br, NaBr, and HBr, respectively. The crude yield of 16-ArOH and 16-ArCl together was 75%, and the yield of chromatographed 16-ArCl was 15% (white crystals, mp 43 °C): IR (KBr pellet) ν_{max} (cm^{-1}) 2917, 2849 (CH, s), 1463 (Ar, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.86 (3 H, t, J = 8.0 Hz, RCH_3), 1.25 (26 H, br s, $-(CH_2)_{13}-$), 1.53 (2 H, br, $-CH_2-$), 2.32 (6 H, s, *o*-$ArCH_3$), 2.45 (2 H, t, J = 8.0 Hz, *p*-$ArCH_2-$), 6.87 (2 H, s, Ar H). Anal. Calcd for $C_{24}H_{41}Cl$: C, 78.97; H, 11.32; Cl, 9.71. Found: C, 79.07; H, 11.46; Cl, 9.30.

***n*-Butyl 4-*n*-Hexadecyl-2,6-dimethylphenyl Ether (16-ArOBu).** According to the procedure of Miller et al.,[76] $Et_4NF \cdot xH_2O$ (0.17 g, 1.15 mmol; 98%, Aldrich) was dried under vacuum (1 Torr) for ca. 20 min in a 100-mL three-neck round-bottom flask; 16-ArOH (0.2 g, 0.58 mmol) dissolved in 10 mL of DMF was added and the mixture was vacuum-dried for ca. 15 min; *n*-BuI (0.21 g, 1.15 mmol; Aldrich, 99%) dissolved in 10 mL of DMF was added. The reaction mixture was stirred under a flow of dry N_2 for 24 h at 100 °C, cooled to room temperature, and transferred to a separatory funnel with several milliliters of Et_2O, and 100 mL of Et_2O and 50 mL of H_2O were added. The H_2O layer was extracted twice with Et_2O, and the combined Et_2O extracts were washed twice with H_2O, dried over $MgSO_4$, and rotoevaporated to give a yellow oil. Chromatography on basic alumina eluted with HPLC grade *n*-pentane gave white crystals of 16-ArOBu (0.15 g, 65%; mp 34 °C): IR (KBr pellet) ν_{max} (cm^{-1}) 2959 (CH, m), 2918, 2850 (CH, s), 1462 (Ar, m), 1245, 1151 (ArOR, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.86 (3 H, t, J = 8.0 Hz, RCH_3), 0.95 (3 H, t, $R'CH_3$, butyl), 1.25 (26 H, br s, $-(CH_2)_{13}-$), 1.55 (4 H, m, $-CH_2-$), 1.75 (2 H, m, $-CH_2-$), 2.23 (6 H, s, *o*-$ArCH_3$), 2.45 (2 H, t, J = 7.5 Hz, *p*-$ArCH_2-$), 3.71 (2 H, t, J = 7.5 Hz, $ArOCH_2-$), 6.79 (2 H, s, Ar H). Anal. Calcd for $C_{28}H_{50}O$: C, 83.51; H, 12.51; O, 3.97. Found: C, 83.16; H, 12.56; O, 4.01.

***n*-Hexyl 4-*n*-Hexadecyl-2,6-dimethylphenyl Ether (16-ArOHex).** 16-ArOH was combined with *n*-hexyl iodide (99%, Aldrich) using the same procedure described for 16-ArOBu. The purified product was a white crystalline (waxy) solid (60% yield; mp 41 °C): IR (KBr pellet) ν_{max} (cm^{-1}) 2914, 2849 (CH, s, 1463 (Ar, m), 1219, 1127 (ArOR, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (6 H, m RCH_3, $R'CH_3$), 1.24 (30 H, br s, $-CH_2-$), 1.54 (4 H, m, $-CH_2-$), 1.75 (2 H, m, $-CH_2-$), 2.22 (6 H, s, *o*-$ArCH_3$), 2.45 (t, J = 7.5 Hz, *p*-$ArCH_2-$), 3.71 (2 H, t, J = 7.5 Hz, $ArOCH_2-$), 6.78 (2 H, s, Ar H). Anal. Calcd for $C_{30}H_{54}O$: C, 83.65; H, 12.64; O, 3.71. Found: C, 83.32; H, 12.32; O, 3.56.

***n*-Butyl 2,4,6-Trimethylphenyl Ether (1-ArOBu).** 2,4,6-Trimethylphenol (99%, Aldrich) was combined with *n*-BuI using the same procedure described for 16-ArOBu. Chromatography yielded 65% of a colorless liquid: IR (neat) ν_{max} (cm^{-1}) 2959, 2929, 2872 (CH, s), 1497 (Ar, m), 1216, 1150 (ArOR, m); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.98 (3 H, t, $R'CH_3$), 1.60 (2 H, m, $-CH_2-$), 1.75 (2 H, m, $-CH_2-$), 2.23 (9 H, s, $ArCH_3$), 3.73 (2 H, t, J = 7.5 Hz, $ArOCH_2-$), 6.81 (2 H, s, Ar H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48; O, 8.32. Found: C, 81.35; H, 10.73; O, 8.09.

Kinetics. Dediazoniation reactions were monitored at 40 ± 0.1 °C, except where noted. Dediazoniations of substrates **II** were followed for at least 10 half-lives at the wavelength maxima of the diazonium salts: 280 nm (**IIa**) and 279 nm (**IIb**). Reaction was initiated by syringe injection of 30 μL of a freshly prepared 0.01–0.02 M solution of **IIa** or **IIb** in CH_3CN into 3.0 mL of reaction solution (final substrate concentration $(1–2) \times 10^{-4}$ M) containing all other reagents equilibrated at 40 °C for 10 min. Nucleophile concentrations were in large excess ensuring pseudo-first-order conditions and surfactant/diazonium salt ratios were ≥100, minimizing perturbation of micelle structure by the substrates. Plots of $\ln(A_\infty - A)$ vs t were linear for 3–4 $t_{1/2}$'s with cc ≥ 0.999. Half-lives were

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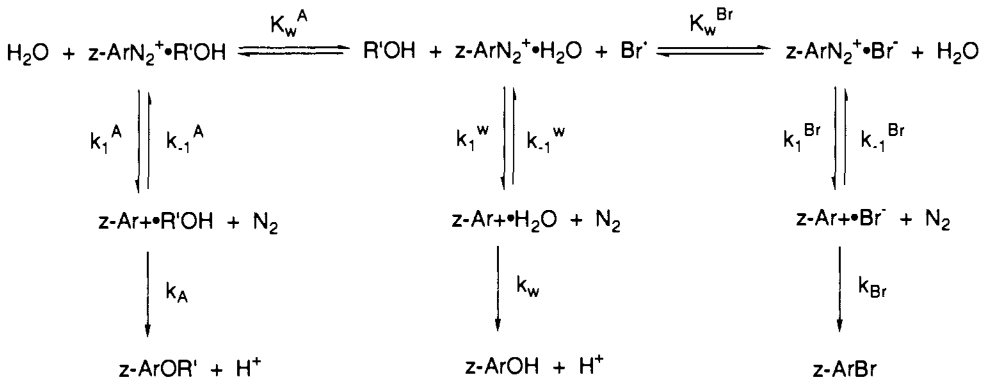
[74] Avram, M.; Mateescu, G. H. D. *Infrared Spectroscopy: Applications in Organic Chemistry*; Wiley-Interscience: New York, 1972.

[75] Wisniewski, M. *Pol. J. Chem.* **1983**, *57*, 593.

[76] Miller, J. M.; So, K. H.; Clark, J. H. *Can. J. Chem.* **1979**, *57*, 1887.

Scheme II



in the range of 30–40 min, and we assumed negligible reaction occurred during solution preparation (3–4 min) at ambient temperature.

Product Yields. Product yields were monitored by HPLC at shoulders of their main UV peaks ($\lambda_{max} \approx 205$ nm), and all peak areas, reported in microvolts (μV), are averages of triplicate injections which agreed within <1%. Normalized product yields were used in all calculations because measured product yields of duplicate or triplicate separate preparations were always >95%. Peaks were identified by spiking experiments, and chromatograms of independently prepared product solutions at four to five concentrations spanning the concentration range of interest were used to construct calibration lines (cc ≥ 0.99).

(a) Product Yields from IIa. A special procedure was developed for carrying out the dediazoniation of **IIa** in aqueous solution because yields of 1-ArX were variable and often 10–20% low from run to run. After much frustrating trial and error, this refactory problem was eventually attributed to phase separation and vaporization of 1-ArX in the head space of the volumetric flasks. The problem was finally solved relatively simply by layering cyclohexane over the solution to dissolve any 1-ArX that phase-separated and to prevent its loss by vaporization. Approximately 1.5-mL solutions of the needed concentrations of (TMA)X and HX were prepared by adding aliquots of standardized 1.0 M HX and water (weighed) to needed quantities of (TMA)X in 5-mL stoppered volumetric flasks, and the solutions were equilibrated at 40 ± 0.1 °C. To initiate reaction, 15-μL aliquots of an ice-cold stock solution of 1-ArN_2^+ in MeOH were injected into each (TMA)X solution, and the mixture was stirred on a Vortex mixer for a few seconds. Cyclohexane (50 μL) was layered via syringe on top of each reaction mixture, and the stoppered flasks were sealed with Parafilm. After 6 h (ca. 10 $t_{1/2}$'s), the flasks were removed from the constant-temperature bath, allowed to cool to room temperature, and filled to the mark with MeOH to give homogeneous solutions, which were analyzed immediately by HPLC to prevent loss of 1-ArX. Conditions for product separation on the Perkin-Elmer HPLC were the following: a Microsorb-MV C-18 (Rainin) reverse-phase column (4.6-mm i.d. × 25 cm; 5-μm particle size); a 20% H_2O/80% MeOH (v/v) mobile phase; flow rate = 0.8 mL/min; λ = 230 nm; injector loop volume = 20 mL; column pressure ≈ 2400 psi, run time ca. 30 min. Typical retention times: 1-ArOH, 5.9 min; 1-ArCl, 23.8 min; 1-ArBr, 27.0 min.

(b) Products Yields from IIb. HPLC conditions for product separation on the Kratos HPLC were the following: Varian reversed-phase C-18 column (4.0-mm i.d. × 15 cm; 5-μm particle size); 64% MeOH/36% *i*-PrOH (v/v) mobile phase; attenuation = 3.0; flow rate = 0.4 mL/min; typical column pressure = 57–79 bar; injector loop size = 100 μL; λ = 219 nm; AUFS = 0.300. Typical retention times: 16-ArOH, 7 min; 16-ArOBu, 15 min; 16-ArBr, 16.7 min.

Substrates and Products of Ia and Ib. Preparation and purification of these compounds, monitoring of their dediazoniation rates, and determination of product yields have been described.[30,31]

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Appendix

In 1978, Zollinger proposed the formation of tight and solvent-separated aryl cation·N_2 pairs to account for internal, N_α–N_β ^{15}N-label exchange and exchange with dissolved N_2 in unreacted diazonium salt.[35,36,47,57] The dediazoniation mechanism in Scheme II is a modification of Zollinger's approach, a preassociation stepwise route[52] which describes product distributions in terms of a diffusion-controlled equilibrium distribution of the ensemble of ground-state arenediazonium cation·anion and arenediazonium cation·molecule intimate pairs in three-component microemulsions and aqueous solutions containing H_2O, R'OH, and Br^-. This mechanism is consistent with the characteristic insensitivity of dediazoniation reaction rates to solvent polarity, their low selectivities toward different nucleophiles, the formation of ion pairs with halide ions, and Zollinger's ^{15}N-label exchange results. The equilibrium constants K_w^A and K_w^{Br} for exchange of H_2O with R'OH and Br^- between intimate ArN_2^+·molecule and ArN_2^+·ion pairs are defined by eqs A1 and A2, respectively, where subscripts

$$K_w^A = \frac{[z\text{-}ArN_2^+\cdot R'OH][H_2O]}{[z\text{-}ArN_2^+\cdot H_2O][R'OH]} \quad (A1)$$

$$K_w^{Br} = \frac{[z\text{-}ArN_2^+\cdot Br^-][H_2O]}{[z\text{-}ArN_2^+\cdot H_2O][Br^-]} \quad (A2)$$

and superscripts w, A, and Br stand for water, alcohol, and Br^-, respectively. The expression for exchange between Cl^- and H_2O (K_w^{Cl}) has the same form as that for Br^- and H_2O (eq A2). The exchange rates in these equilibria are assumed to be essentially diffusion-controlled and orders of magnitude faster than the rate of C–N bond cleavage to form the aryl cation·ion pair and ion·molecule intermediates, as expressed by k_1^A, k_1^w, and k_1^{Br} (Scheme II). We also assume that because the concentration of N_2 is extremely small compared to the concentrations of other nucleophiles present and because the lifetime of the aryl cation is very short, the rate of product formation from each aryl cation·molecule and aryl cation·anion pair is much faster than the rate of return to the ground state, i.e., $k_A \gg k_{-1}^A[N_2]$, $k_w \gg k_{-1}^w[N_2]$, and $k_{Br} \gg k_{-1}^{Br}[N_2]$ (Scheme II). On the basis of these assumptions, eqs A3 and A4 were derived for the competitive formation formation of *z*-ArBr and *z*-ArOR' compared to *z*-ArOH, by applying the steady-state assumption to the concentration of each aryl cation intermediate, i.e., $d[z\text{-}Ar+\cdot Br^-]/dt = d[z\text{-}Ar+\cdot R'OH]/dt = d[z\text{-}Ar+\cdot H_2O]/dt = 0$. Note that the

$$\frac{d[z\text{-ArBr}]/dt}{d[z\text{-ArOH}]/dt} = \frac{\%z\text{-ArBr}}{\%z\text{-ArOH}} = \frac{K_w^{Br} k_1^{Br}[Br^-]}{k_1^{w}[H_2O]} = S_w^{Br}\frac{[Br^-]}{[H_2O]} \qquad (A3)$$

$$\frac{d[z\text{-ArOR}']/dt}{d[z\text{-ArOH}]/dt} = \frac{\%z\text{-ArOR}'}{\%z\text{-ArOH}} = \frac{K_w^{A} k_1^{A}[R'OH]}{k_1^{w}[H_2O]} = S_w^{A}\frac{[R'OH]}{[H_2O]} \qquad (A4)$$

terms containing the rate and equilibrium constants in eqs A3 and A4 are equivalent to the selectivities of the reactions toward Br^- (S_w^{Br}) and R′OH (S_w^{A}) relative to water (see eqs 1 and 2). The equation defining the selectivity constant (S_w^{Cl}) for competition between Cl^- and H_2O has the same form as eq A3.

Values of S_w^{A} for homogeneous BuOH/H_2O solutions are essentially constant at low and high BuOH/H_2O ratios (see Results) suggesting that the rate and equilibrium constants in eq A4 are insensitive to solvent composition and polarity. Note that the activity coefficient ratios for cationic complexes and neutral molecules in eq A1 should be approximately 1 because the charge types in the numerator and denominator are identical and should have similar dependencies on solution composition at any salt concentration. Zollinger's results for the exchange of ^{15}N-labeled diazonio group with atmospheric N_2 in trifluoroethanol (TFE) and hexafluoro-2-propanol (HFIP) can also be interpreted as exchange between N_2 and solvent in intimate $z\text{-ArN}_2^+\cdot$molecule pairs. Zollinger found 6.33% and 16.5% exchange in TFE and HFIP, respectively, at 70% dediazoniation of **IIa** at 300 atm of N_2 at 25 °C.[44,47] Under these conditions, the concentrations of dissolved N_2, TFE, and HFIP are similar, approximately 3, 13.7, and 9.5 M, respectively, and the high percent exchange in these solvents can be attributed to relatively high concentrations of $z\text{-ArN}_2^+\cdot N_2$ complexes in the ground state.

The values for S_w^{Br} and S_w^{Cl} show a significant dependence on the concentrations of (TMA)Br and (TMA)Cl, respectively (Figure 3 and Table VI), which we attribute primarily to changes in K_w^{Br} and K_w^{Cl}. The activity coefficient ratios for the neutral molecules and ions in eq A2 should depend upon salt concentration because the charges are in a neutral ion pair and on free hydrated ions, and their activity coefficients and thus the activity coefficient ratios should change significantly over the wide range of salt concentrations used in these experiments (Table VI). This interpretation is consistent with modest specific salt effects on dediazoniation rates in the literature[45] and the specific salt effects on the absorbance ratios in Figure 2. The small, ca. 42%, decreases in S_w^{Br} and S_w^{Cl} with added (TMA)Br and (TMA)Cl up to 3.5 M (Table VI) are similar to the small, ca. 32% and 22%, decreases in k_{obs} with added NaBr and NaCl over the same concentration range (Table III), and the difference in the percentages can be attributed to specific salt effects of TMA^+ and Na^+ ions on activity coefficients.

Supplementary Material Available: Tables S1–S10, containing spectrophotometric data, peak areas, measured and normalized product yields, and numerical data for Figures 2–5 and Table VI (10 pages). Ordering information is given on any current masthead page.