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experimental values than are energies obtained from 3-21G level calculations. For the majority of hypervalent compounds the improvement is considerable, although deviations between calculated, 3-21G$^{(*)}$ level, and experimental hydrogenation energies are often large. Previous work has suggested the importance of electron correlation effects on calculated hydrogenation energies.

(4) Theoretical 3-21G$^{(*)}$ level electric dipole moments both for normal-valent and hypervalent compounds are consistently in better agreement with experimental values than are those obtained from the unsupplemented 3-21G basis set. Still, large discrepancies with experimental moments exist for some molecules.

(5) The 3-21G$^{(*)}$ basis set yields equilibrium structures and vibrational frequencies in close accord with those obtained from the 6-31G* basis set. Calculated hydrogenation energies and electric dipole moments differ is some systems by as much as 25%, although in these cases it is not always the larger 6-31G* basis set that is in better agreement with experiment.

The 3-21G$^{(*)}$ basis set is significantly less costly to apply than 6-31G*, the difference arising because of both a difference in number of Gaussian primitives employed and the lack of d-functions on first-row atoms. The exact cost differential varies widely, depending on the molecule (i.e., number of first-row elements) and on the particular task at hand (i.e., geometry optimization or frequency calculation, which are dominated by integral evaluation steps vs. single-point runs, which are often dominated by the SCF procedure); our own experience indicates a differential of between 4 and 6 times. Related to cost is range of application. Although 3-21G$^{(*)}$ and 6-31G* basis sets for hydrogen and for second-row atoms comprise the same number of atomic functions, they differ significantly in size for first-row elements (9 functions for 3-21G$^{(*)}$ vs. 15 for 6-31G*). Therefore, size (memory space) restrictions, while perhaps not influencing the selection of basis set for molecules comprising only hydrogen and second-row elements, are apt to be a more significant factor for molecules incorporating first-row atoms.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1; Ar, 7440-37-1.

Micellar Dediazoniation: Dramatic Directive Effects on the Course of Reaction

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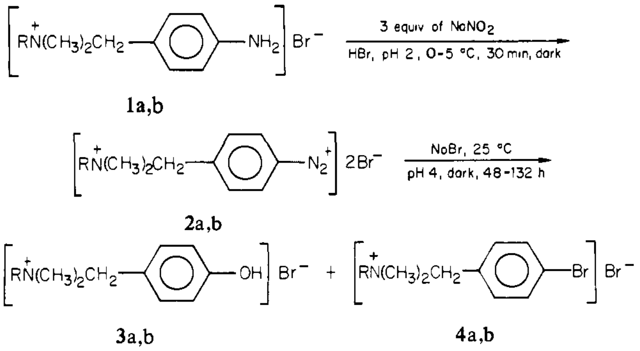
Abstract: Rate constants and products are reported for the dediazoniation reactions of nonmicellar (*p*-diazoniobenzyl)trimethylammonium dibromide and micellar (*p*-diazoniobenzyl)dimethyl-*n*-hexadecylammonium dibromide in aqueous solutions at pH 4, 23 °C, in the presence of various concentrations of bromide ion. Rate constants for the nonmicellar ($k \sim 6 \times 10^{-6}$ s^{-1}) and micellar ($k \sim 10^{-5}$ s^{-1}) dediazoniations were independent of bromide ions at concentrations ranging from 0.015 to 0.50 M, consistent with rate determining aryl cation formation in each case. However, product identity was strictly controlled by the reaction environment: in the concentration range $0.005 \leq [\mathrm{Br}^-] \leq 0.050$ M, micellar dediazoniation gave only (>95%) the corresponding aryl bromide whereas nonmicellar dediazoniation gave only (>95%) the corresponding phenol.

Swain and co-workers established that the dediazoniations of simple aryldiazonium ions proceeded via rate-determining formation of aryl cations, which selected between available nucleophiles in rapid subsequent reactions.[1,2] The availability of cationic surfactant aromatic diazonium ions[3] suggested that we examine *micellar* dediazoniation. Two questions could be addressed: (1) Forced to proceed in the positively charged Stern layer of a cationic micelle, and in the presence of approximated, nucleophilic bromide counterions, would the rate limiting step of the dediazoniation process remain the formation of an aryl cation? (2) Could the unusual microenvironment provided by the cationic micelles significantly alter the selectivity of product formation? The results provide affirmative answers to both questions and, in the second case, the outcome is striking.

Scheme I[a]



[a] Series a, R = n-$C_{16}H_{33}$; series b, R = CH_3.

Results and Discussion

The necessary starting materials, anilinosurfactants **1a** and **1b**, were prepared and diazotized (to **2a** and **2b**) by published procedures.[3] The reactions of interest are summarized in Scheme I.

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[1] Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783, et seq.

[2] Reviews: Bernasconi, C. F. *Chimia* **1980**, *34*, 1. Ambroz, H. B.; Kemp, T. J. *Chem. Soc. Rev.* **1979**, *8*, 353. Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141. Hegarty, A. F. In "The Chemistry of Diazonium and Diazo Groups", Part 2, Patai, S., Ed.; Wiley: New York, 1978; pp 511 f.

[3] Moss, R. A.; Rav-Acha, Ch. *J. Am. Chem. Soc.* **1980**, *102*, 5045.

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Table I. Rate Constants for Decay of Aryl Diazonium Ions[a]

	10^6k, s^{-1}	
total [Br^-], M	2a	2b
0.015	9.9	5.8
0.050	9.2	6.6
0.10	15	5.9
0.25	$9.5^{b,c}$	
0.50	9.7^c	4.9

[a] Conditions: [ArN_2^+] = 2.5×10^{-4} M, pH 4, 23 ± 2 °C. [b] $k = 9.7 \times 10^{-6}$ s^{-1} in the presence of 5.0×10^{-3} M added CTABr. [c] Rate constant determined by the infinity absorbance method.

Table II. Product Distributions (%) from Dediazoniation Reactions[a]

	from 2a		from 2b	
total [Br^-], M	3a	4a	3b	4b
0.005	<5	>95	$>95^b$	$<5^b$
0.015	<5	>95		
0.025	<5	>95		
0.050	<5	>95	>95	<5
0.10	<5	>95		
0.25			82	18
0.50	<5	>95	79	21

[a] Conditions are described in the text. The limits of NMR product detection were established as 5% by spiking experiments with pure products. [b] Reaction run for 72 h, 2.2 half-lives.

Surfactant **1a** and model compound **1b** were diazotized in aqueous HBr (pH 2) by using 3 equiv (excess) of $NaNO_2$.[3] The resulting solutions of the corresponding diazonium ions **2a** and **2b** were adjusted to pH 4 with NaOH, and dediazoniations were allowed to proceed (in the dark) at ~23 °C for 48–132 h (see below for reaction half-lives). Products were isolated by thorough extraction of the aqueous solutions with CH_2Cl_2 (**3a**, **4a**) or by lyophilization to dryness, followed by leaching with ethanol (**3b**, **4b**). Recovered products were stripped of solvent and identified by comparisons of their NMR spectra (Me_2SO-d_6) to those of authentic samples.[4] NMR spiking techniques were used to make definitive comparisons.

The kinetics of decay of 2.5×10^{-4} M solutions[6] of diazonium ions **2a** and **2b** at pH 4, 23 ± 2 °C, were followed spectrophotometrically at 255 or 260 nm, respectively, λ_{max} values for these ions in acidic solution. Monitoring of the darkened solutions was intermittent, to avoid inadvertent photolytic destruction of the diazonium ions. Rate constants were determined from absorbance data by the Guggenheim method, in which 12–15 data points were obtained at 15–30-min intervals, followed by a corresponding set of absorbances obtained 24–48 h later. The total bromide ion concentration was varied from 0.015 to 0.50 M. Good first-order kinetics ($r > 0.99$) were observed, and the resulting rate constants are displayed in Table I. From the "average" rate constant for reactions at all [Br^-], we estimate dediazoniation half-lives of ~18 and ~33 h for **2a** and **2b**, respectively.

For product studies, 5.0×10^{-3} M aqueous solutions of **1a** or **1b** were diazotized and dediazoniated (conditions above) for 48 (2.7 half-lives, 84% completion) or 132 h (4 half-lives, 94% completion), respectively. The reaction pH was monitored continually and maintained at 3.6–4.0 by appropriate additions of aqueous NaOH to correct for the observed slow, downward pH drift. Products were isolated as described above and quantitatively analyzed by NMR in Me_2SO-d_6.[7] Isolated yields were in the 50% range, but no other significant products were apparent in the NMR spectra. NMR product distributions appear in Table II as a function of [Br^-].

Various control experiments demonstrated that the product distributions accurately reflected the primary courses of the dediazoniation reactions. (a) addition of 0.5 equiv of **3a** to a fresh solution of **2a**, followed by dediazoniation ([Br^-] = 0.1 M) and analysis, revealed **3a**/**4a** ~ 1:1. Hence **3a** is not destroyed (e.g., by coupling to **2a**) under the reaction conditions. (b) Use of either 1.1 or 10.0 equiv of $NaNO_2$ during diazotization of **1a** (and decomposition of **2a**) did not alter the product distributions. (c) Synthetic product blends were quantitatively unchanged after submission to reaction and workup conditions. (d) Reactions of **2a** were extended to 5 and 6 half-lives with no change in product composition (i.e., no appearance of **3a**). (e) Product identities were verified by NMR spiking experiments, which also showed that 5% of **3a** could be readily detected in the product obtained from **2a** (apparently "pure" **4a**).

During the control studies, we observed that incompletely reacted solutions of **2a** or **2b** gave bromide-rich (**4a** or **4b**) product mixtures after workup; i.e., **2a** or **2b** in CH_2Cl_2 or EtOH, respectively, efficiently afford **4a** or **4b** as solvent was removed. For that reason, product distributions are based on reactions carried to at least 84% completion. We also noted that dediazoniation of **2a** carried out at pH 2.0 gave significant quantities of phenol **3a**, although the identical reactions at pH 3.6–4.0 (Table II) gave bromide **4a** and no detectable **3a**. Products were stable to pH 2.0 reaction conditions; moreover, neither IR studies of crude products nor the use of 10-fold excess $NaNO_2$ gave any indication for the involvement of aryl nitrite (**3a** with OH replaced by ONO) as a precursor to **3a**. Although we could speculate about the mechanistic origins of the **3a** observed in the low pH micellar dediazoniations, we prefer confining the present discussion to the pH 4 data presented in the tables.[8]

Examination of Table I reveals no correlation between k and [Br^-] for dediazoniations of either micellar **2a** or nonmicellar model compound **2b**. This is particularly apparent upon comparison of the 0.015 and 0.50 M bromide data, where a 33-fold increase in bromide concentration has little effect on k for either diazonium ion. These results are consonant with an aryl cation mechanism[1] for dediazoniation of either substrate, with no kinetic participation by bromide ion in either micellar or nonmicellar rate-limiting steps.[9] There does, however, appear to be a modest (~2-fold) rate enhancement of micellar over nonmicellar dediazoniations, perhaps attributable to net electrostatic destabilization of the cationic micellar **2a** ground state, relative to **2b**.

The most dramatic observation is the *complete product control* observed in micellar dediazoniations of **2a** (Table II). Thus, the exclusive phenol (**3b**) formation from nonmicellar **2b**, observed at bromide titers up to 0.05 M, is reversed to exclusive bromide (**4a**) formation from micellar **2a**. The results imply a product selectivity enhancement of at least 380 (95/5 ÷ 5/95). This striking turnabout must be attributed to the different reaction environments experienced by the nonmicellar aryl cations (from

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(4) The spectral properties of **3a** and **3b** have been fully described.[5] The NMR spectra of **4a** and **4b** are described here. (See the experimental section for syntheses.) **4a**: ($CDCl_3$) δ 0.88 (crude t, 3 H, $(CH_2)_{15}CH_3$), 1.27 (s, 28 H, $(CH_2)_{14}$), 3.30 and 3.77–3.30 (s + m, 8 H, $(CH_3)_2N^+CH_2(CH_2)_{14}$), 5.27 (s, 2 H, N^+CH_2Ar), 7.62 (s, 4 H, aryl). **4b**: (Me_2SO-d_6) δ 3.10 (s, 9 H, $(CH_3)_3N^+$), 4.67 (s, 2 H, N^+CH_2Ar), 7.83–7.47 ("q", 4 H, aryl).

(5) Moss, R. A.; Dix, F. M. *J. Org. Chem.* **1981**, *46*, 3029.

(6) The critical micelle concentrations of **2a**,[3] **3a**,[5] and (presumably) **4a** are ~2.5×10^{-4} M. That the kinetic studies of **2a** (Table I) pertain to micellar solutions is supported by the observations that the rate constant for dediazoniation of **2a** in 0.25 M NaBr solution was unchanged upon comicellization of **2a** with 5×10^{-3} M CTABr and that there is no apparent dependence of the rate constants on [Br^-].

(7) In Me_2SO-d_6, the benzylic singlets of **3a** and **4a** appear at δ 4.50 and 4.66, respectively, whereas the corresponding signals of **3b** and **4b** are found at δ 4.53 and 4.70.

(8) Further work is planned on dediazoniations at low pH, but we may note here that the observed effect is *not* specific to micellar reactions. Thus benzenediazonium ion was decomposed in 0.6 M aqueous NaBr solution at pH 4.5 and 1.5. The phenol/bromobenzene product ratio was significantly higher at the lower pH.

(9) Relative to benzenediazonium ion, **2a** and **2b** are perturbed by inductively withdrawing *p*-quaternary alkylammonium ion substituents. This should destabilize the corresponding aryl cations and is consistent with a rate constant for the dediazoniation of **2b** which lies between those of benzenediazonium and *p*-nitrobenzenediazonium ions.[1] However, because the latter ion follows the aryl cation dediazoniation mechanism,[1] it is not surprising that **2b** does also. On the other hand, the additional effects of the cationic micellar field and the high local bromide concentration (on **2a**, relative to **2b**) are also insufficient to bring about a mechanistic change (to S_NAr).

2b), which react mainly with their aqueous surroundings, vs. the micellar aryl cations (from **2a**), which strongly select in favor of the bromide ions concentrated in the micellar Stern layer. It is well-known that micellar catalysis of bimolecular reactions in water primarily depends upon concentration of the two reactants into a small volume.[10] Most frequently this phenomenon is expressed in an apparently enhanced reaction rate constant. In the present case, however, where the rate-determining and product-determining events are uncoupled, the micellar reactant concentration effect appears as a striking chemoselectivity. Further work is planned to identify the mechanistic factor(s) responsible for this remarkable enhancement. Micellar bromide approximation[10] is certain to be involved, but that this may not be the sole contributor is perhaps foreshadowed by the pH effect noted above.

While this work was under review, Sauer published a similar set of results concerning bromide and chloride ion selectivity, relative to water, for aliphatic (1-octyl, 2-octyl, or 1-hexyl) diazonium ions in micellar or nonmicellar environments.[11] In alkylammonium–alkyldiazonium ion micelles, the selectivities for the formation of alkyl bromides rather than alcohols, expressed as relative rate constants, were 3–4 times greater than in nonmicellar aqueous solutions.[11] Approximation of bromide counterions to the cationic alkylammonium–alkyldiazonium ion micelles must be a major source of these altered selectivities. Although Sauer's work[11] constitutes the closest analogy to our own investigations, there are other, if more distant, relatives. For example, the bimolecular aromatic substitution reactions of hydrazine or morpholine with 2,4-dinitrophenylsulfate occur with predominant nucleophilic attack at the aromatic carbon atom in water but completely by nucleophilic attack at sulfur in micellar CTABr.[12]

We are now designing experiments to more accurately determine the sources and quantitative limits of the micellar selectivity enhancements of aryl dediazoniation reactions.

Experimental Section[13]

Materials. The syntheses and properties of *n*-cetyldimethyl(*p*-aminobenzyl)ammonium bromide (**1a**),[3] trimethyl(*p*-aminobenzyl)ammonium bromide (**1b**),[3] *n*-cetyldimethyl(*p*-hydroxybenzyl)ammonium bromide (**3a**),[5] and trimethyl(*p*-hydroxybenzyl)ammonium bromide (**3b**)[5] have been fully described.

***n*-Cetyldimethyl(*p*-bromobenzyl)ammonium Bromide (4a).** In a 250-mL flask were placed 1.2 g (4.8 mmol) of *p*-bromobenzyl bromide and 25 mL of nitromethane. The mixture was stirred magnetically until a solution was obtained, and then an excess (2.5 g, 9.3 mmol) of dimethylcetylamine[14] was added. The solution was stirred overnight at room temperature, and the resulting precipitate was filtered and washed with cold nitromethane. Recrystallization of the crude solid from ethyl acetate afforded 1.7 g (3.3 mmol, 69%) of **4a**, mp 112–115 °C. The NMR spectrum has been described.[4]

Anal. Calcd for $C_{24}H_{45}NBr_2$: C, 57.8; H, 8.74. Found: C, 57.5; H, 8.43%.

Trimethyl(*p*-bromobenzyl)ammonium Bromide (4b). This compound was prepared from 1.5 g (6.0 mmol) of *p*-bromobenzyl bromide and 3.0 g (51 mmol) of trimethylamine (as a 1:2 solution in ethanol) in 25 mL of nitromethane as described above for **4a**. After the reaction mixture had been stirred overnight at room temperature, 50 mL of ether was added, and the solution was cooled. A white precipitate formed, was removed by filtration, and was recrystallized from 60:40 ethyl acetate/ethanol. We obtained 0.97 g (3.1 mmol, 52%) of **4b**, mp 223–224 °C. The NMR spectrum has been described.[4]

Anal. Calcd for $C_{10}H_{15}NBr_2$: C, 38.9; H, 4.90. Found: C, 38.7; H, 4.87%.

Diazotization Procedures.[3] All solutions were prepared by using N_2-purged distilled water; $NaNO_2$ solutions were used immediately upon preparation, and any excess NaBr needed to adjust the bromide titer (see tables) was added together with the $NaNO_2$. In general, substrates **1a** or **1b** were dissolved in waater at 0–5 °C, the $NaNO_2$/NaBr solution was added with magnetic stirring, and enough aqueous HBr was added to reduce the pH to 2.0. The final amine concentration was 2.5×10^{-4} M, and the $NaNO_2$ concentration was 7.5×10^{-4} M. The bromide titer was as specified in the tables. The diazotization was allowed to proceed at pH 2.0 for 30 min.[15] Then the pH was raised to 4.0 by the addition of dilute aqueous NaOH, the cooling bath was removed, and the dediazoniation reactions were permitted to proceed at 23 ± 2 °C for 48 (**2a**) or 132 h (**2b**). Departures from these conditions are noted to the text or tables. Product isolation and analysis methods are described above.

Acknowledgment. We are grateful to the National Science Foundation, the Busch Memorial Fund of Rutgers University, and the Research Corporation (L.R.) for financial support. We also thank Dr. K. W. Alwis, S. Ghosh, and W. Guo for experimental assistance.

Registry No. 1a, 74403-05-7; **1b**, 74403-06-8; **2a**, 74403-07-9; **2b**, 74403-08-0; **3a**, 77551-97-4; **3b**, 77551-99-6; **4a**, 82065-10-9; **4b**, 25251-62-1; *N*,*N*-dimethylcetylamine, 112-69-6; trimethylamine, 75-50-3; *p*-bromobenzyl bromide, 589-15-1.

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(10) Bunton, C. A.; Gau, L.-H.; Moffatt, J. R.; Romsted, L. S.; Savelli, G. *J. Phys. Chem.* **1981**, *85*, 4118 and references therein. The local counterion concentration has been estimated to be 3–5 M in the Stern layer of an Hartley model micelle: L. Romsted, Ph.D. Thesis, Indiana University, Bloomington, In, 1975.

(11) Singer, R.; Eibler, E.; Sauer, J. *Tetrahedron Lett.* **1982**, *23*, 1135.

(12) Fendler, J. H.; Fendler, E. J.; Smith, L. W. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 2097.

(13) NMR spectra were recorded on a Varian T-60 spectrometer and are reported relative to internal Me_4Si. Melting points are uncorrected. Microanalyses were performed by Robertson Laboratory, Florham Park, NJ. Reaction kinetics were monitored on a Gilford Model 250 spectrophotometer coupled to a Gilford Model 6051 recorder. Kinetic procedures and results are described in the results section and in Table I.

(14) Nahas, R. C. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 1978; pp 115–116.

(15) Our previous work[3] demonstrated that the diazotizations of **1a** and **1b** were essentially complete in ~15 min. under these conditions.