PERKIN 2

Revisiting the reactions of nucleophiles with arenediazonium ions: dediazoniation of arenediazonium salts in aqueous and micellar solutions containing alkyl sulfates and alkanesulfonates and an *ab initio* analysis of the reaction pathway

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Dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate, 1-ArN_2BF_4 (for the *z*-Ar compounds described in this paper, *z* refers to the length of the carbon chain of the substituent at C4 of the benzene ring), in aqueous solutions containing sodium methyl sulfate, $NaMeSO_4$, or sodium methanesulfonate, $NaMeSO_3$, yields 2,4,6-trimethylphenol, 1-ArOH, 2,4,6-trimethylphenyl methyl sulfate, 1-$ArOSO_3Me$ and 2,4,6-trimethylphenyl methanesulfonate, 1-ArO_3SMe, respectively. The relative yields of 1-ArO_3SMe or 1-$ArOSO_3Me$ and 1-ArOH depend on the $NaMeSO_4$ or $NaMeSO_3$ concentrations. 4-*n*-Hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate, 16-ArN_2BF_4, was used to determine the local head group concentration in sodium dodecyl sulfate and sodium dodecanesulfonate micelles by chemical trapping comparing the relative product yields with those obtained in water using the short chain analogs.

Ab initio calculations of the spontaneous dediazoniation of phenyldiazonium ion in the gas phase, as well as in aqueous solution with, or without, added $MeSO_3^-$, yield potential energy surfaces for the reaction. For this model the calculated and experimental values of the spontaneous dediazoniation rate constants in aqueous solution, as well as the product composition, were similar to those obtained with 1-ArN_2^+. These results suggest that in aqueous solution nucleophiles can only compete with water if a diazonium ion·nucleophile complex is formed prior to N_2 loss. Calculations show that the addition of nucleophiles to the arenediazonium ion occurs without a saddle point in the potential energy surface, suggesting that the free phenyl cation is not an obligatory intermediate in aqueous solutions.

Introduction

Arenediazonium salts are currently being used to probe interfacial compositions of micelles, microemulsions, reverse micelles and cyclodextrins.[1–4] The basis of the method is the determination of the products resulting from the reaction of the arenediazonium ion with nucleophiles under conditions where the site of dediazoniation of particular probes can be estimated with confidence.[1]

The central assumption of the method is that the selectivity of 4-*n*-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate, 16-ArN_2BF_4, towards two different nucleophiles, *e.g.* X and H_2O, in micelles is the same as the selectivity of its short-chain analog 2,4,6-trimethylbenzenediazonium tetrafluoroborate, 1-ArN_2BF_4, towards the same nucleophiles in bulk solution and in the absence of micelles. The local X concentration, $[X]_b$, at the interface is deduced from the product ratios, *e.g.* 16-ArX/(16-ArX + 16-ArOH), measured after spontaneous decomposition of the interfacially incorporated diazonium cation, 16-ArN_2^+. These ratios are compared with standard curves of product yield of the same nucleophile, X, with 1-ArN_2^+, *versus* X concentration, [X], in aqueous solution and $[X]_b$, at the interface, is obtained.[1] The experimental and theoretical basis for the method and its assumptions have been extensively discussed (see reference 1 and references therein).

Using this method, which has been referred to as chemical trapping, we determined interfacial halide ion concentrations in anionic micelles of sodium dodecyl sulfate, SDS.[5] Upon spontaneous dediazoniation of 16-ArN_2^+ in SDS containing NaCl a product loss of *ca.* 20% was observed, in addition to the expected phenol and chloro-derivatives.[5] This finding led us to suppose that 16-ArN_2^+ could be reacting with the surfactant, a very weak nucleophile, *i.e.* dodecyl sulfate monoester.

Studies of the kinetics and product distribution resulting from the dediazoniation of benzenediazonium ion in the aqueous phase have shown that reacting nucleophiles exhibit a discrete selectivity. This selectivity, compared to water, is small and in the order Br^- and S (of SCN^-) > Cl^- and N (of SCN^-) > SO_4^- > water: 6 > 3 > 1.4 > 1.[6–8] Even sulfate, a very reluctant nucleophile, has been indirectly shown to form phenyl sulfate upon dediazoniation of phenyldiazonium ion in aqueous solution, although the product was not isolated at the time.[8b] This selectivity is orders of magnitude lower than that observed for other reactions of the same series at stabilized carbonium ions or saturated carbon.[9]

The spontaneous dediazoniation of substituted phenyldiazonium salts has been extensively investigated.[10] A variety of studies, including substituent effects,[7] solvent and nucleophile effects,[6–8] N_2 incorporation and rearrangement,[11,12] have led to a widely accepted mechanism involving rate limiting loss of N_2 and formation of an extremely reactive aryl cation intermediate, *z*-Ar^+, that reacts with surrounding nucleophiles in a time scale faster than that required for cation diffusion.[10] A modification of this description, a pre-association stepwise route, has been used to describe product distribution in terms of a diffusion-controlled distribution of the ensemble of ground state arenediazonium cation·anion and arenediazonium cation·molecule intimate pairs.[1,13]

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The formation of ion pairs between the ground state arenediazonium cation and a sulfate monoester could therefore account for the formation of a reaction product between SDS and 16-ArN_2BF_4 used to measure the local concentration of co-ions in SDS micelles.

Here we demonstrate the formation of substituted phenyl alkyl sulfates (and phenyl alkanesulfonates) upon dediazoniation of *z*-ArN_2^+ both in bulk aqueous solution of sodium methyl sulfate, $NaMeSO_4$, and sodium methanesulfonate, $NaMeSO_3$, and in micelles of SDS and sodium dodecanesulfonate, SDSu. The experimental results can be accommodated by the accepted unimolecular formation of an aryl cation by invoking the formation of a ground state ion pair between the diazonium ion and the weakly nucleophilic sulfate monoester. However, theoretical calculations suggest that in aqueous solution nucleophiles other than water will only react if they form a tight ion pair with the diazonium ion. Moreover, the calculations show that dediazoniation from this ion pair is induced by the nucleophile, suggesting that the free phenyl cation is not an obligatory intermediate in the dediazoniation reaction.

Materials and methods

General purification methods

Hexadecyltrimethylammonium bromide, CTAB, (Merck) was recrystallized from methanol–acetone. Sodium dodecyl sulfate, SDS, (BDH) and dodecanesulfonate, SDSu, (Sigma) were recrystallized from hot methanol, washed with acetone, and dried under vacuum. 4-*n*-Hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate, 16-ArN_2BF_4, and 2,4,6-trimethylbenzenediazonium tetrafluoroborate, 1-ArN_2BF_4, were prepared as described.[1] 4-*n*-Hexadecyl-2,6-dimethylphenol, 16-ArOH, and 4-*n*-hexadecyl-2,6-dimethylaniline were kindly provided by Dr L. S. Romsted (Rutgers University). 2,4,6-Trimethylphenol, 1-ArOH, and 2,4,6-trimethylaniline were purchased from Aldrich. Sodium methanesulfonate (Sigma), $NaMeSO_3$, was recrystallized from methanol–water and dried under vacuum over P_2O_5. Sodium methyl sulfate, $NaMeSO_4$, was obtained from partial alkaline hydrolysis of dimethyl sulfate (Riedel) followed by solvent evaporation and recrystallization from methanol.[14] All other reagents were of analytical grade. Distilled water was passed through a MilliQ System (Pharmacia) and was used in the preparation of all solutions.

Syntheses

Preparation of hexadecyltrimethylammonium methanesulfonate, $CTAMeSO_3$, and hexadecyltrimethylammonium methyl sulfate, $CTAMeSO_4$. Amberlyst A-26 (Merck), in the Cl^- form (2.7 g), was eluted with an aqueous solution of $NaMeSO_4$ or $NaMeSO_3$ (1.0 M), until no Cl^- was detected in the eluate.[15] The resin was eluted with water and then extensively washed with methanol. A methanolic solution of CTAB (0.75 g) was passed through the column, the eluent was collected and the solvent evaporated. The products thus obtained, *e.g.* $CTAMeSO_4$ or $CTAMeSO_3$, contained no Br^-.[15]

Preparation of tetraethylammonium dodecyl sulfate, TEADS, and tetraethylammonium dodecanesulfonate, TEADSu. 20 g of Dowex-50 W-X4, H^+ form, (Bio Rad, cation exchange resin, 100–200 mesh) was treated with a solution of (20%) tetraethylammonium hydroxide (Sigma) until the pH of the eluate was *ca.* 9.0. The column was eluted with water until neutrality and then with methanol. Approximately 0.3 g of SDS or SDSu, in methanol, was applied to 6 mL of the resin and eluted with methanol. The solvent was removed (rotary evaporator) and the resulting TEADS (or TEADSu) was dried under vacuum.

Synthesis of 2,4,6-trimethylphenyl methyl sulfate, 1-$ArOSO_3$-Me. 1-$ArOSO_3Me$ was prepared by two different methods:

(a) To 0.38 g of $CTAMeSO_4$ dissolved in 3 mL of dried $CHCl_3$ was added 0.024 g of 1-ArN_2BF_4. After 24 h the solution was passed through a silica column (1 g), eluted with hexane–$CHCl_3$ (95 : 5) (200 mL) and $CHCl_3$–methanol 90 : 10 (10 mL). 1-$ArOSO_3Me$ was eluted with the latter solvent in 25% yield. The purity of the sample was checked by HPLC (see conditions below). NMR and mass spectra were identical to those obtained with material from the synthesis below.

(b) 1-$ArOSO_3Me$ was also prepared from 1-ArN_2BF_4 and dimethyl sulfate as described for a similar compound.[16] To 0.1 g of 1-ArN_2BF_4 was added 0.7 g of dimethyl sulfate (Riedel). The solution was stirred, at room temperature, for 48 h and then extracted with hexane–$CHCl_3$ (95 : 5) several times. After solvent evaporation the product was purified on a silica column (3 g) using hexane–$CHCl_3$ (95 : 5 and 50 : 50) as solvent, in 72% yield. Anal. Calcd. for $C_{10}H_{14}O_4S$: C, 52.16; H, 6.13; O, 27.79; S, 13.92. Found: C, 52.55; H, 5.93%. ^1H NMR ($CDCl_3$) δ: 2.26 (3H, s, *p*-$ArCH_3$), 2.34 (6H, s, *o*-$ArCH_3$), 4.15 (3H, s, O-CH_3) and 6.88 (2H, s, ArH). Electrospray MS: $[M + H]^+$ at *m*/*z* 231, $[M + Na]^+$ at *m*/*z* 253.

Synthesis of 2,4,6-trimethylphenyl methanesulfonate, 1-ArO_3-SMe. To 0.072 g of $CTAMeSO_3$ dissolved in 2 mL of dried $CHCl_3$ was added 0.017 g of 1-ArN_2BF_4. After 24 h the solution was passed through a silica column (1.0 g), eluted with hexane–$CHCl_3$ 95 : 5 (100 mL) and $CHCl_3$–methanol 90 : 10 (100 mL). 1-ArO_3SMe was eluted with the latter solvent in 37% yield. The purity of the sample was checked by HPLC using the solvents described below.

Isolation of 1-ArO_3SMe from reaction in aqueous phase. In 10 mL of HCl (2×10^{-4} M) was dissolved 0.1 g of 1-ArN_2BF_4 and 3.5 g of $NaMeSO_3$. Cyclohexane (0.5 mL) was layered over the solution. After 24 h at 30 °C the solution was extracted with $CHCl_3$ (3×20 mL) until no product was detected in the aqueous layer by HPLC. The solvent was evaporated and the product was purified on 2.0 g of silica, using hexane–$CHCl_3$ (95 : 5) (300 mL), (90 : 10) (300 mL) and $CHCl_3$–methanol (90 : 10) (10 mL). The product was eluted with the last solvent in 20% yield. Anal. Calcd. for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59; O, 22.41; S, 14.96. Found: C, 56.30; H, 6.35; S, 14.21%. ^1H NMR ($CDCl_3$) δ: 2.26 (3H, s, *p*-$ArCH_3$), 2.34 (6H, s, *o*-$ArCH_3$), 3.28 (3H, s, S-CH_3) and 6.88 (2H, s, ArH). Electrospray MS: $[M + H]^+$ at *m*/*z* 215.0, $[M + Na]^+$ at *m*/*z* 237, $[M + MeOH]^+$ at *m*/*z* 247.

Synthesis of 4-*n*-hexadecyl-2,6-dimethylphenyl *n*-dodecyl sulfate, 16-$ArOSO_3Do$. 16-$ArOSO_3Do$ was synthesized by adding 0.15 g of tetraethylammonium *n*-dodecyl sulfate, dissolved in 10 mL of dried THF, to 0.021 g of 16-ArN_2BF_4. After 6 h at 30 °C the solvent was evaporated and the product was extracted with hexane–$CHCl_3$ (50 : 50) and then purified on a silica column (1.0 g) using hexane–$CHCl_3$ (50 : 50) in 24% yield. Anal. Calcd. for $C_{36}H_{66}O_4S$: C, 72.67; H, 11.18; O, 10.76; S, 5.39. Found: C, 72.67; H, 11.18%. ^1H NMR ($CDCl_3$) δ: 0.88 (6H, m, RCH_3, $R'CH_3$), 1.26 (44 H, br s, -$(CH_2)_n$-), 1.56 (2H, m, *p*-Ar-CH_2-CH_2), 1.82 (2H, m, -CH_2-CH_2-O-), 2.35 (6H, s, *o*-$ArCH_3$), 2.50 (2H, m, *p*-$ArCH_2$-), 4.46 (2H, m, -CH_2O-) and 6.86 (2H, s, ArH). Electrospray MS: $[M + H]^+$ at *m*/*z* 595.35, $[M + H + MeOH]^+$ at *m*/*z* 627.4.

Isolation of 16-$ArOSO_3Do$ from reaction in SDS in aqueous phase. 20 mg of 16-ArN_2BF_4, dissolved in 1 mL of methanol was added to 50 mL of SDS (0.04 M) in HCl (2×10^{-4} M) and the mixture was mantained at 35 °C. Aliquots of the solution were injected into the HPLC at intervals. The area of the peak with the retention time of 16-$ArOSO_3Do$ increased with time, reaching a maximum between 2–4 h and decreasing thereafter. At the time when the peak area reached the maximum value the product was extracted with $\mathrm{CHCl_3}$ (3 × 30 mL). The extracts were evaporated and the sample, diluted in methanol, was applied to the HPLC. The fractions with the retention time of 16-$\mathrm{ArOSO_3Do}$ were collected, concentrated and re-applied to HPLC. The isolated product has ^{1}H NMR and mass spectra identical to those of the synthesized product.

Synthesis of 4-*n*-hexadecyl-2,6-dimethylphenyl *n*-dodecanesulfonate, 16-$\mathbf{ArO_3SDo}$. 16-$\mathrm{ArO_3SDo}$ was synthesized by adding 0.15 g of tetraethylammonium *n*-dodecanesulfonate, dissolved in 1 mL of dry THF, to 0.02 g of 16-$\mathrm{ArN_2BF_4}$. After 12 h at 60 °C, 1 mL of a 1.2 M solution of $\mathrm{CaCl_2}$ was added to the solvent. The detergent precipitated and the mixture was filtered. The precipitate was washed several times with $\mathrm{CHCl_3}$. The aqueous phase of the filtrate was separated and extracted with $\mathrm{CHCl_3}$. The $\mathrm{CHCl_3}$ extracts were combined, the solvent was evaporated and the product was purified on a silica column (1 g), using hexane–$\mathrm{CHCl_3}$ (90 : 10) and (80 : 20) in 50% yield. Anal. Calcd. for $\mathrm{C_{36}H_{66}O_3S}$: C, 74.68; H, 11.49; O, 8.29; S, 5.54. Found: C, 74.15; H, 11.20%. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.88 (6H, m, $\mathrm{RCH_3}$, $\mathrm{R'CH_3}$), 1.26 (44 H, br s, -$\mathrm{(CH_2)}_n$-), 1.56 (2H, m, *p*-Ar-$\mathrm{CH_2}$-CH_2-), 2.05 (2H, m, C$H_2$$\mathrm{CH_2S}$), 2.34 (6H, s, *o*-$\mathrm{ArCH_3}$), 2.50 (2H, m, *p*-$\mathrm{ArCH_2}$), 3.36 (2H, m, -$\mathrm{CH_2S}$-) and 6.86 (2H, s, ArH). Electrospray MS: $[\mathrm{M + H}]^+$ at *m*/*z* 579.24, $[\mathrm{M + H + MeOH}]^+$ at *m*/*z* 601.26.

Isolation of 16-$\mathbf{ArO_3SDo}$ from reaction in SDSu micelles. This was performed as for 16-$\mathrm{ArOSO_3Do}$, but after a reaction time of 24 h. The NMR and ES-MS spectra of both 16-$\mathrm{ArOSO_3Do}$ and 16-$\mathrm{ArO_3SDo}$ were identical to those of synthesized products.

General spectroscopy details

^{1}H NMR spectra were recorded on a Bruker, AC 200 (200 MHz) or Varian, Inova (300 MHz) spectrometer. Samples were dissolved in $\mathrm{CDCl_3}$ and chemical shifts referenced to $\mathrm{CHCl_3}$ (δ 7.27) and TMS (δ 0.00) as internal standards. Mass spectra were recorded with a MICROMASS, PLATT FORM II spectrometer, by electrospray ionization, in the positive mode. The sample was injected by infusion, at 70 °C. Elemental analysis was determined in the Central Analítica of Instituto de Química da Universidade de São Paulo. Product yields were determined on a Shimadzu HPLC equipped with a SPD- 10A UV/Visible detector, C-R6A integrator, lC-6 AD pump, 20 µl sample loop, and a Microsorb C18 (Rainin) reverse phase column (4.6 mm id × 25 cm; 5 mm particle size).

Dediazoniation reactions

Aqueous solutions (1.0 mL) of HCl, SDS, and SDSu at several concentrations were prepared by adding stock solutions of each component into teflon-stoppered amber vials. An aliquot (0.02 mL) of a freshly prepared methanolic solution of 16-$\mathrm{ArN_2BF_4}$ (0.01 M) was added to the temperature equilibrated solutions. All reaction mixtures were 2×10^{-4} M HCl and 2×10^{-4} M 16-$\mathrm{ArN_2BF_4}$. After 24 h, 1 mL of *n*-propanol (HPLC grade) was added to all vials and the solutions were mantained at 5 °C until product analysis.

The reaction products were eluted with methanol–propan-2-ol (80 : 20 (v/v)) (1.0 mL min^{-1}, pressure = 67 kgf cm^{-2} (64.9 atm)) and detected at 225 nm. Typical retention times for 16-ArOH, 16-$\mathrm{ArO_3SDo}$ and 16-$\mathrm{ArOSO_3Do}$ are 5.6, 10.3 and 11.1 min, respectively. The concentrations of 16-ArOH and 16-$\mathrm{ArO_3SDo}$ are given by: [16-ArOH] = area of 16-ArOH peak (µV × s) × 5.99×10^{-11} (µV^{-1} × s^{-1} × M), [16-$\mathrm{ArO_3SDo}$] = area of 16-$\mathrm{ArO_3SDo}$ peak (µV × s) × 6.37×10^{-11} (µV^{-1} × s^{-1} × M). Volts refer to the calibrated detector response. The conversion factors were obtained by injecting known amounts of the pure compound and relating the amounts to the peak area.

The standard curve of percent yield of 1-$\mathrm{ArO_3SMe}$ *vs.* [$\mathrm{NaMeSO_3}$] was obtained by using 1-$\mathrm{ArN_2BF_4}$ (2×10^{-4} M) and $\mathrm{NaMeSO_3}$ (0.05–3 M). Typically 0.02 mL of an aqueous solution of 0.01 M 1-$\mathrm{ArN_2BF_4}$ was added to 1.0 mL of solutions containing $\mathrm{NaMeSO_3}$ and HCl (2×10^{-4} M). Cyclohexane (0.05 mL) was added to all vials. After 48 h at 30 °C, 1.5 mL of methanol–*n*-propanol (1:1) solution was added and the samples were mantained at 5 °C until HPLC analysis.

The products of dediazoniation of 1-$\mathrm{ArN_2}^+$ in water were analyzed by HPLC using the same column described above employing, as eluent, methanol–water (63 : 37 (v/v)), (0.7 mL min^{-1}, pressure = 155 kgf cm^{-2} (150.1 atm)). The retention times for 1-ArOH, 1-$\mathrm{ArO_3SMe}$ and 1-$\mathrm{ArOSO_3Me}$ are 12.5, 14.0 and 22.4 min respectively. The concentration of each product was calculated as follows: [1-ArOH] = area of 1-ArOH peak (µV × s) × 4.40×10^{-11} (µV^{-1} × s^{-1} × M), [1-$\mathrm{ArO_3SMe}$] = area of 1-$\mathrm{ArO_3SMe}$ peak (µV × s) × 5.43×10^{-11} (µV^{-1} × s^{-1} × M).

Kinetics

A methanolic solution of 16-$\mathrm{ArN_2}^+$ (0.01 M) (0.2 mL) was added to samples containing 0.04 M SDS (or SDSu) (10 mL) in HCl (2×10^{-4} M) and mantained at 35 °C (SDS) or 40 °C (SDSu). At intervals, aliquots of 0.25 mL were withdrawn, diluted with 0.25 mL of *n*-propanol and analyzed by HPLC. After 48 h, 0.075 mL of 6 M HCl was added to 4.5 mL of both mixtures, giving a final HCl concentration of 0.1 M, and the reaction was followed by HPLC as described above.

Dediazoniation rates were also monitored spectrophotometrically at 280 nm as described previously.[1]

Hydrolysis of 1-$\mathbf{ArOSO_3Me}$ and 16-$\mathbf{ArOSO_3Do}$. This was performed by adding an aliquot of the diester, dissolved in dry acetonitrile, to a solution containing the desired mixtures of solvents and/or detergent. Aliquots of 0.1 mL were injected into the HPLC and the decrease in the area of the diester was followed.

Hydrolysis of 16-$\mathbf{ArOSO_3}^-$. Samples containing 16-$\mathrm{ArOSO_3}$-Do were hydrolyzed in SDS (0.04 M) and HCl (2×10^{-4} M) and the kinetics were followed by HPLC monitoring of the disappearance of the substrate. At the end of the reaction, an aliquot of HCl (12.5 M) was added to the solution giving a final [HCl] of 0.1 M and the appearance of 16-ArOH was followed.

Results

Experimental investigation of the reaction of dediazoniation of *z*-$\mathbf{ArN_2}^+$ (*z* = 1 or 16) in aqueous solution containing alkanesulfonates and alkyl sulfates

The values of the first order rate constant for 1-$\mathrm{ArN_2}^+$ dediazoniation, k_φ, (30 °C, 2×10^{-4} M HCl) in the absence of salt, with 3.0 M $\mathrm{NaMeSO_3}$ and 3.0 M $\mathrm{NaMeSO_4}$, were 1.87×10^{-4}, 1.2×10^{-4} and 1.3×10^{-4} s^{-1} respectively (Table 1). The k_φ for 16-$\mathrm{ArN_2}^+$ dediazoniation was determined in the presence of SDS, SDSu and CTAB (0.04 M in 2×10^{-4} M HCl, 40 °C) in order to analyze the effects of micellar charge on the rate limiting $\mathrm{N_2}$ loss (Table 1). The value of k_φ in CTAB was 3.6×10^{-4} s^{-1}, very close to that obtained by Romsted and co-workers (Table 1).[1] In SDS and SDSu micelles the values of k_φ were 1.9×10^{-4} and 1.6×10^{-4} s^{-1}, respectively, half of those in positively charged micelles (Table 1).

The dediazoniation of 16-$\mathrm{ArN_2BF_4}$, in aqueous SDS (35 °C), was followed by measuring the increase in the area of the 16-ArOH peak. From the analytical HPLC data and the initial concentration of 16-$\mathrm{ArN_2BF_4}$, the final yield of 16-ArOH was estimated to be 80% after 10 half-lives. The area of a new

Table 1 Rate constants for z-ArN_2^+ dediazoniation

[Substrate]/M	T/°C	Conditions	$10^4\ k_\varphi/s^{-1}$
$1\text{-}ArN_2^{+\,a}$	30	HCl (2×10^{-4} M)	1.87 ± 0.04
$1\text{-}ArN_2^{+\,a}$	30	HCl (2×10^{-4} M) $NaMeSO_4$ (3 M)	1.20 ± 0.03
$1\text{-}ArN_2^{+\,a}$	30	HCl (2×10^{-4} M) $NaMeSO_3$ (3 M)	1.30 ± 0.04
$1\text{-}ArN_2^{+\,b}$	40	HCl (1×10^{-2} M)	6.32
$1\text{-}ArN_2^{+\,b}$	40	HCl (1×10^{-2} M) TMABr (3 M)	4.19
$1\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M)	5.40 ± 0.04
$1\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M) $MeSO_3Na$ (3 M)	3.80 ± 0.04
$1\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M) $MeSO_4Na$ (3 M)	3.50 ± 0.05
$16\text{-}ArN_2^{+\,b}$	40	HCl (2×10^{-4} M) CTAB (0.01 M)	3.57
$16\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M) CTAB (0.04 M)	3.50 ± 0.1
$16\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M) SDS (0.04 M)	1.93 ± 0.05
$16\text{-}ArN_2^{+\,a}$	40	HCl (2×10^{-4} M) SDSu (0.04 M)	1.64 ± 0.03

[a] This work, k_φ determined spectrophotometrically, $[1\text{-}ArN_2^+] = 2.5 \times 10^{-4}$ M; $[16\text{-}ArN_2^+] = 1.5 \times 10^{-4}$ M. [b] Data from reference 1(*b*).

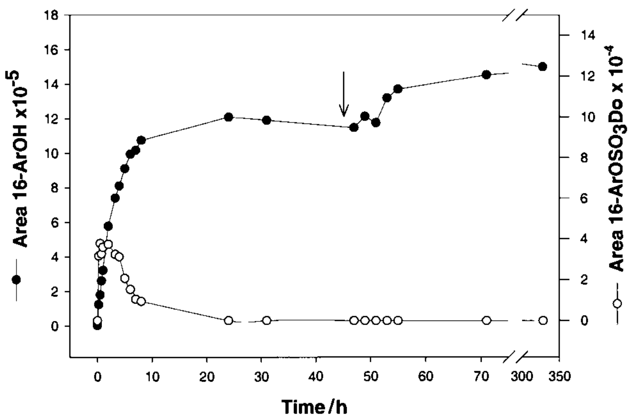


Fig. 1 Dediazoniation of $16\text{-}ARN_2^+$. Area peak of $16\text{-}ArOSO_3Do$ (○) and 16-ArOH (●) *vs.* time. The reaction was performed in HCl (2×10^{-4} M), SDS (0.04 M), $[16\text{-}ArN_2^+] = 1.5 \times 10^{-4}$ M and 35 °C. The arrow indicates addition of HCl to a final concentration of 0.09 M.

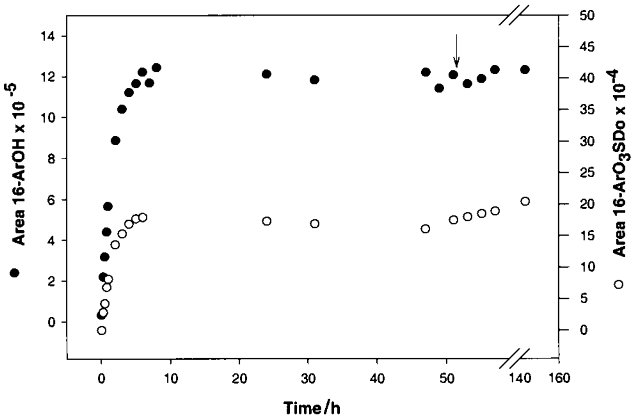


Fig. 2 Dediazoniation of $16\text{-}ArN_2^+$. Area peak of $16\text{-}ArO_3SDo$ (○) and 16-ArOH (●) *vs.* time. The reaction was performed in HCl (2×10^{-4} M), SDSu (0.04 M), $[16\text{-}ArN_2^+] = 1.5 \times 10^{-4}$ M and 40 °C. The arrow indicates the addition of HCl to a final concentration of 0.09 M.

compound increased during reaction, reaching a maximum, and then decreased to undetectable levels (Fig. 1). A quantitative yield of 16-ArOH (100% yield on the basis of initial $16\text{-}ArN_2BF_4$ concentration) was obtained upon addition, after 48 h of reaction, of HCl (final concentration 0.1 M) (Fig. 1). The compound produced transiently (Fig. 1), isolated from the HPLC, was identical to authentic $16\text{-}ArOSO_3Do$ (see Experimental section).

The dediazoniation of $16\text{-}ArN_2^+$ in SDSu (at 40 °C) was also followed by HPLC and, besides 16-ArOH, another peak was noticeable (Fig. 2). This product does not hydrolyze at a detectable rate upon addition of HCl (0.1 M). The product isolated from the reaction had HPLC retention time, NMR and mass spectra identical to authentic $16\text{-}ArO_3SDo$ (see Experimental section). Dediazoniation of $16\text{-}ArN_2^+$ in SDS and SDSu micelles, therefore, produces the compounds expected for alkyl sulfate or alkanesulfonate ion attack on the corresponding aryl cation.

Direct evidence that very weak nucleophiles, such as alkyl sulfates or alkanesulfonates, react in water with phenyldiazonium salts was obtained by studying the dediazoniation of $1\text{-}ArN_2^+$ with added $NaMeSO_3$ or $NaMeSO_4$.

The spontaneous dediazoniation of $1\text{-}ArN_2^+$ in aqueous $NaMeSO_4$ produced, besides the expected 1-ArOH, a transient HPLC peak (not shown). This compound had an HPLC retention time identical to authentic $1\text{-}ArOSO_3Me$. The kinetics of the change in $[1\text{-}ArOSO_3Me]$ with time were similar to the data shown in Fig. 1 for the dediazoniation of $16\text{-}ArN_2^+$ in micelles.

Dediazoniation of $1\text{-}ArN_2^+$ in aqueous $NaMeSO_3$ yielded $1\text{-}ArO_3SMe$, which, as expected, is stable under the reaction conditions.[17] The compound isolated from the aqueous reaction mixture was identical to authentic $1\text{-}ArO_3SMe$ (see Experimental section).

Having demonstrated that sulfate and sulfonate products are obtained both in aqueous solution and in micelles of SDS and SDSu, it is possible to relate the relative yields of the products obtained in water to the local concentrations of the nucleophiles in the micellar interface.[1]

The percent yield of $1\text{-}ArO_3SMe$ ($\%1\text{-}ArO_3SMe$) was calculated from eqn. (1):

$$\%1\text{-}ArO_3SMe = 100 \times [1\text{-}ArO_3SMe]/([1\text{-}ArOH] + [1\text{-}ArO_3SMe]) \quad (1)$$

The standard curve relating the % yield of $1\text{-}ArO_3SMe$ *vs.* $[NaMeSO_3]$ was linear up to 3.0 M salt (Fig. 3) with a slope of $7\%\ M^{-1}$.

The standard curve relating the % yield of $1\text{-}ArOSO_3Me$ with $[NaMeSO_4]$ was obtained indirectly, because the dediazoniation of $1\text{-}ArN_2^+$ in aqueous $NaMeSO_4$ produces exclusively 1-ArOH and $1\text{-}ArOSO_3Me$ and the latter product is hydrolyzed during the course of the dediazoniation reaction. The concentration of $1\text{-}ArOSO_3Me$ was obtained by subtracting the [1-ArOH] formed at each $[NaMeSO_4]$ from the initial diazonium concentration ($[1\text{-}ArN_2^+]_o$) (eqn. (2)).The yield of $1\text{-}ArOSO_3Me$ ($\%1\text{-}ArOSO_3Me$) is given by eqn. (3). The

$$[1\text{-}ArOSO_3Me] = ([1\text{-}ArN_2^+]_o - [1\text{-}ArOH]) \quad (2)$$

$$\%1\text{-}ArOSO_3Me = 100 \times ([1\text{-}ArN_2^+]_o - [1\text{-}ArOH])/[1\text{-}ArN_2^+]_o \quad (3)$$

calculated $\%1\text{-}ArOSO_3Me$ was a linear function of $[NaMeSO_4]$ with a slope of $9\%\ M^{-1}$ (Fig. 3).

Table 2 Rate constants for hydrolysis of sulfate esters

Substrate	T/(°C)	Conditions	$10^4\ k_\psi$/s^{-1}
Me(p-MPS)[a]	25	MeOH–H_2O (30:70 (v/v))	8.0
1-$ArSO_4Me$[b]	30	MeOH–H_2O (30:70 (v/v)) HCl (2×10^{-4} M)	6.1
1-$ArSO_4Me$[b]	30	SDS (0.04 M) HCl (2×10^{-4} M)	1.5
16-$ArSO_4Do$[b]	35	SDS (0.1 M) HCl (2×10^{-4} M) CH_3CN (6.7%)	1.4
16-$ArSO_4Do$[b]	35	SDS (0.1 M) HCl (0.01 M) CH_3CN (6.7%)	1.9
16-$ArSO_4Do$[b]	35	SDS (0.1 M) HCl (0.1 M) CH_3CN (6.7%)	0.27
Phenyl SO_4^-[c]	40	HCl (1 M)	0.32

[a] Data from reference 19. [b] This work, k_ψ determined by HPLC: [1-$ArSO_4Me$] = 1.1×10^{-4} M; [16-$ArSO_4Do$] = 6.1×10^{-6} M. The average error for these rate constants is 5%. [c] Data from reference 21.

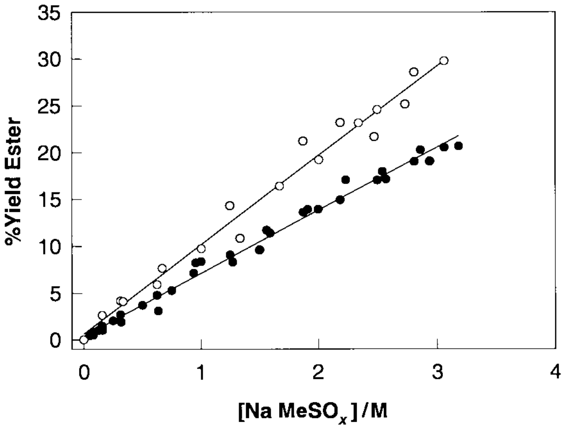


Fig. 3 Effect of $NaMeSO_3$ (●) and $NaMeSO_4$ (○) on the % yield of esters in HCl (2×10^{-4} M), [1-ArN_2^+] = 2.5×10^{-4} M, 30 °C.

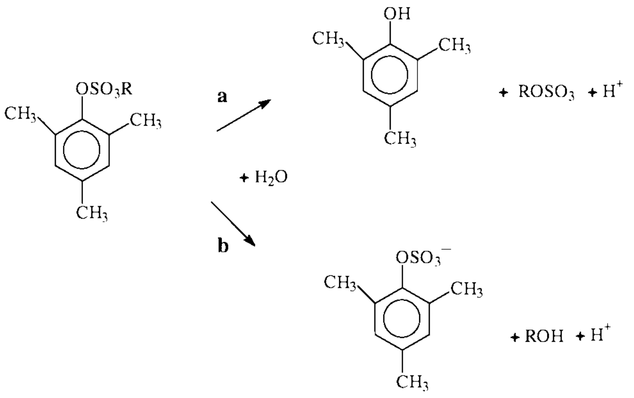
From the standard curves obtained with the reaction of 1-ArN_2^+ with $MeSO_3Na$ and $MeSO_4Na$, the local concentrations of alkyl sulfate and alkanesulfonate anions at the interfaces of SDS and SDSu micelles were determined.

The dediazoniation of 16-ArN_2^+ was carried out in 0.04 M SDS or SDSu containing HCl (2×10^{-4} M) at 30 °C. The % yields of 16-ArO_3SDo and 16-$ArOSO_3Do$, calculated from eqns. (1) and (3) for the Do analogs, respectively, were 20.5% for 16-$ArOSO_3Do$ and 15.0% for 16-ArO_3SDo. From these % yields, and the appropriate standard curves (Fig. 3), the calculated values of the local concentrations of alkyl sulfate and alkanesulfonate anions at the surface of SDS and SDSu were 2.27 M and 2.14 M respectively. These values are in excellent agreement with previous estimates of local head group concentrations obtained by a large variety of both experimental and theoretical methods for micelles of the same surfactants.[18]

In the calculation of the % yield of sulfate diesters (eqn. (2)), we assumed that the products of diester hydrolysis are the corresponding aryl sulfates and that these compounds are stable and not detected by our HPLC conditions. This hypothesis was confirmed studying the kinetics and product composition of diester hydrolysis (Scheme 1, pathway b).

The rate of hydrolysis of 1-$ArOSO_3Me$ and 16-$ArOSO_3Do$ was determined under several conditions (Table 2) by HPLC. In methanol and methanol–water (30% (v/v)) (35 °C) the value of the first order rate constant, k_ψ, for 1-$ArOSO_3Me$ solvolysis was comparable to that obtained for a similar compound, p-methylphenyl methyl sulfate, Me(p-PMS), in the same solvent mixture (Table 2).[19]

The hydrolysis of 16-$ArOSO_3Do$ was studied by using several substrate, acetonitrile, HCl and SDS concentrations. The reaction exhibited first order kinetics only at low [substrate], high [SDS] and large volumes of acetonitrile (~7% (v/v)), indicating, as observed previously for other hydrophobic substrates, extensive aggregation even at low substrate concentration.[20] The values of k_ψ for 16-$ArOSO_3Do$ hydrolysis in Table 2 are those obtained by using the experimental conditions for first order kinetics.



Scheme 1

The value of k_ψ for 16-$ArOSO_3Do$ hydrolysis was similar to that determined for the hydrolysis of 1-$ArOSO_3Me$ in SDS (Table 2) and is compatible with the kinetics of formation and decomposition of 16-$ArOSO_3Do$ shown in Fig. 1. The k_ψ for 16-$ArOSO_3Do$ hydrolysis is independent of pH in the range studied (Table 2) and, between 2×10^{-4} M and 0.01 M HCl, the only product of hydrolysis is 4-hexadecyl-2,6-dimethylphenyl sulfate, 16-$ArOSO_3^-$, (Scheme 2). Under these conditions, no phenol was detected, by HPLC, in the hydrolysis of either 16-$ArOSO_3Do$ or 1-$ArOSO_3Me$, even after 10 half lives.

The value of k_ψ for the acid-catalyzed hydrolysis of 16-$ArOSO_3^-$, in SDS, 0.1 M HCl, at 35 °C, is of the same magnitude as that for sodium phenyl sulfate at 40 °C and 1 M HCl (Table 2).[21] Micellization of long chain monoalkyl sulfates increases the rate of acid-catalyzed hydrolysis.[14] The similarity of the values of k_ψ for hydrolysis of 16-$ArOSO_3^-$ in SDS in 0.1 M HCl (35 °C) and phenyl sulfate in 1.0 M HCl (40 °C) (Table 2) can be attributed to catalysis by SDS. Hence, because the hydrolysis of 16-$ArOSO_3^-$ is acid dependent we can assume that, in 2×10^{-4} M HCl, k_ψ is of the order of 5.4×10^{-8} s^{-1}. Hydrolysis of 16-$ArOSO_3Do$, yielding only 16-$ArOSO_3^-$, can be obtained by properly selecting the acid concentration, minimizing the hydrolysis of 16-$ArOSO_3^-$ to 16-ArOH. At low [HCl] and temperature, eqn. (2) can therefore be used with confidence.

Theoretical study of the dediazoniation of 1-ArN_2^+ in the presence of methanesulfonate

Details of the *ab initio* calculations. The reaction pathways for dediazoniation of arenediazonium were explored, taking benzenediazonium and methanesulfonate as a model, using *ab initio* quantum chemistry methods. Full geometry optimizations were done at the Hartree–Fock (HF) level of theory using the standard 6-31+G* basis set. Electron correlation was included by single-point calculation at second-order Møller–Plesset perturbation theory (MP2) level, also using the 6-31+G* basis set. In order to determine the nature of the stationary points and to obtain the thermodynamic properties the vibrational harmonic frequencies at the HF/6-31+G* level

Table 3 Solvation Gibbs energies (in kcal mol^{-1}) (aqueous solution)[a]

Species	ΔG_{solv}
N_2	−0.4
H_2O	−6.1
$CH_3SO_3^-$	−58.6
$C_6H_5N_2^+$	−50.5
$C_6H_5^+$	−52.8
MS2	−6.2
MS3	−66.7
MS4	−21.1
TS5	−20.0
MS5	−47.7
TS7a	−48.4
TS5b	−50.4

[a] Values obtained by the IPCM model using the MP2/6-31+G* wave function.

were calculated. The effect of solvent (aqueous solution) was evaluated using the isodensity surface polarizable continuum model (IPCM)[22] and the MP2/6-31+G* wave function by performing single-point calculations on gas phase optimized structures (Table 3). The relative permittivities and isodensity values used were 78.0 and 0.0004, respectively. The *ab initio* data were used to calculate the thermodynamic properties employing statistical mechanics and the rate constants were obtained using transition state theory. We have adopted the standard state of 1 mol L^{-1} and 298.15 K for reporting the reaction and activation thermodynamic data.[23] All calculations were done with the GAUSSIAN 94 program system.[24]

Reaction pathways. The study of the potential energy surface for arenediazonium cation interacting with water and methanesulfonate led us to the reaction steps presented in Scheme 2.

$$C_6H_5N_2^+ \xrightarrow{1} \underset{(MS1)}{C_6H_5^+} + N_2$$

$$C_6H_5{}^{\circ C+} + CH_3SO_3^- \xrightarrow{2} \underset{(MS2)}{C_6H_5\text{–}O\text{–}SO_2CH_3}$$

$$C_6H_5^+ + H_2O \xrightarrow{3} \underset{(MS3)}{C_6H_5\text{–}OH_2^+}$$

$$C_6H_5N_2^+ + CH_3SO_3^- \xrightarrow{4} \underset{(MS4)}{C_6H_5N_2^+\cdots{}^-O_3SCH_3} \xrightarrow{5} C_6H_5\text{–}O\text{–}SO_2CH_3 + N_2$$

$$C_6H_5N_2^+ + H_2O \xrightarrow{6} \underset{(MS5)}{C_6H_5N_2^+\cdots OH_2} \xrightarrow{7} C_6H_5\text{–}OH_2^+ + N_2$$

Scheme 2

The optimized structures are shown in Figs. 4 and 5, the Gibbs energy profile in the gas phase and aqueous solution, respectively, are in Figs. 6 and 7. Tables 4 and 5 present the calculated activation and reaction properties.

In reaction 1 (Scheme 2) the unimolecular elimination of nitrogen from the arenediazonium ion proceeds without a saddle point on the potential energy surface. The calculated reaction enthalpy and the Gibbs energy for this step are 32.1 kcal mol^{-1} and 23.5 kcal mol^{-1}, respectively (Table 5). The solvent has a small but significant effect on this step, stabilizing the products by 2.7 kcal mol^{-1}. Thus, in aqueous solution the Gibbs energy of reaction is 20.8 kcal mol^{-1}. For the calculation of activation properties, an approximate method was used, since this pathway has no saddle point. In our model, it was assumed that the generalized transition state occurs at a center of mass distance of 6.0 Å, and the phenyl cation and the nitrogen molecule are considered as free rotors with no interaction between them.[25,26] Based on this model, the activation enthalpy, $\Delta H_g^\ddagger$, and Gibbs energy, $\Delta G_g^\ddagger$, in the gas phase were estimated.

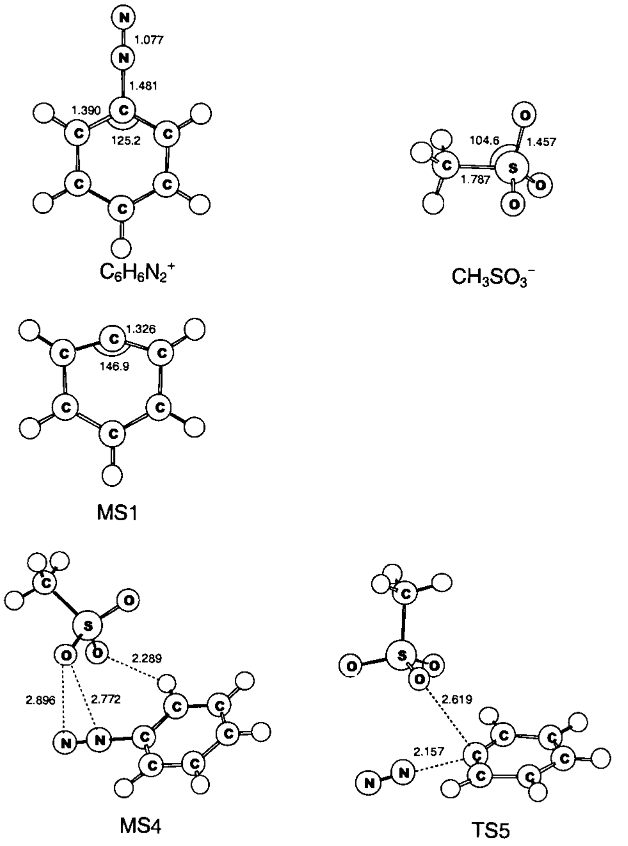


Fig. 4 Minimum and transition state structures located on the potential energy surface for the $C_6H_5N_2^+ + CH_3SO_3^-$ system. The dotted lines define distances between neighboring atoms.

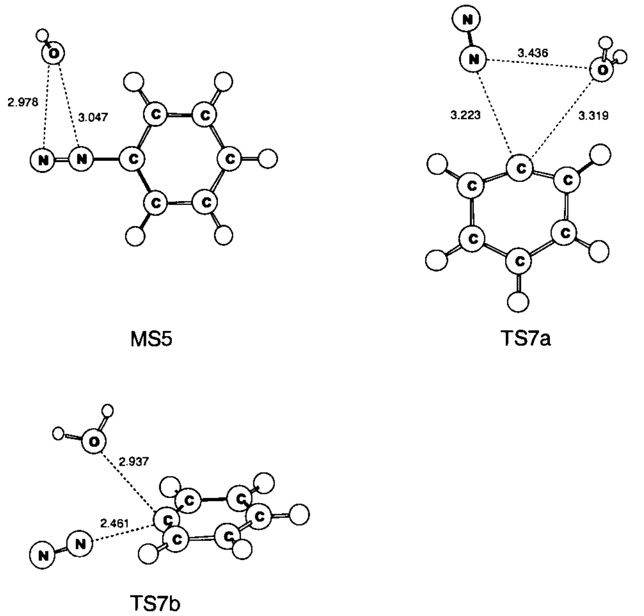


Fig. 5 Minimum and transition state structures located on the potential energy surface for the $C_6H_5N_2^+ + H_2O$ system. The dotted lines define distances between neighboring atoms.

For reaction 1 (Scheme 2), *i.e.* the elimination of N_2 from benzenediazonium ion, we can write eqn. (4), where $\Delta G_g^\ddagger(-1)$

$$\Delta G_g^\ddagger(1) = \Delta G_g(1) + \Delta G_g^\ddagger(-1) \qquad (4)$$

is the activation Gibbs energy for the inverse reaction. Using canonical flexible transition state theory (CFTST) and assuming that the interaction term (potential of mean force) is small,[26] we have eqn. (5), where *h* is the Planck constant, *d* is the

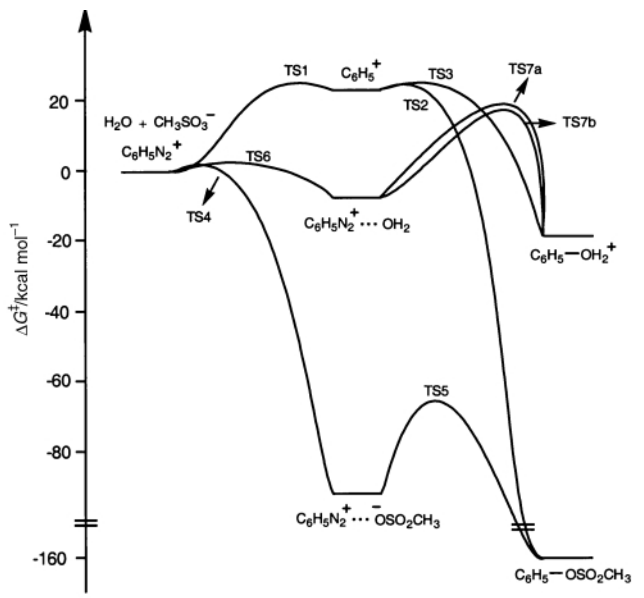


Fig. 6 Gibbs energy profile for the $C_6H_5N_2^+ + H_2O + CH_3SO_3^-$ system in the gas phase. Units of kcal mol^{-1}.

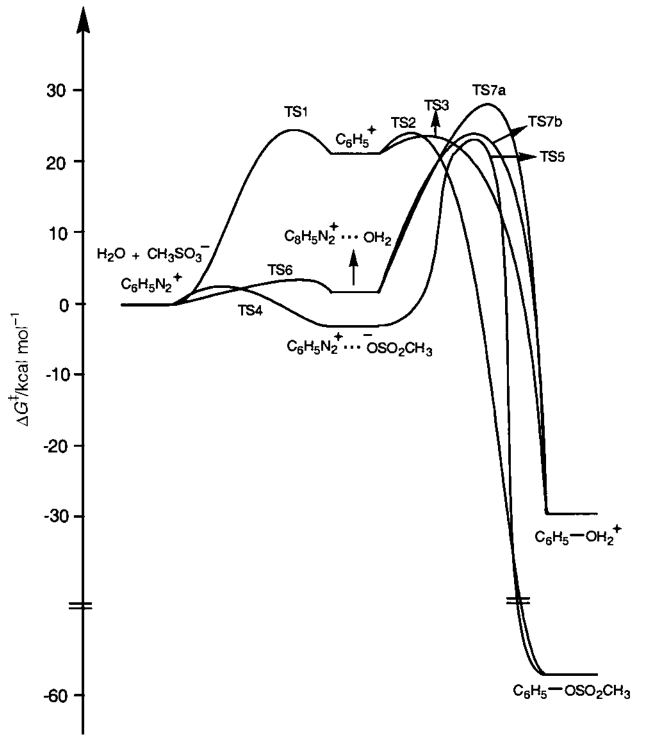


Fig. 7 Gibbs energy profile for the $C_6H_5N_2^+ + H_2O + CH_3SO_3^-$ system in the aqueous solution. Units of kcal mol^{-1}.

$$\Delta G_{\mathrm{g}}^{\ddagger}(-1) = -RT\ln\left[hd^2\left(\frac{8\pi}{\mu k_{\mathrm{b}}T}\right)^{1/2}\right] \qquad (5)$$

collision distance (assumed to be 6.0 Å), μ is the reduced mass and k_{b} is the Boltzmann constant. Our calculation of this property led to $\Delta G_{\mathrm{g}}^{\ddagger}(-1) = 1.7$ kcal mol^{-1}, which is the value used in eqn. (6).

$$\Delta G_{\mathrm{g}}^{\ddagger}(1) = \Delta G_{\mathrm{g}}(1) + 1.7 \text{ kcal mol}^{-1} \qquad (6)$$

Using a similar approach we can write that the activation enthalpy for step 1 (Scheme 2) is given by eqn. (7), and the

$$\Delta H_{\mathrm{g}}^{\ddagger}(1) = \Delta H(1) + \Delta H_{\mathrm{g}}^{\ddagger}(-1) \qquad (7)$$

activation enthalpy was obtained by the thermodynamic relation, eqn. (8), which leads to eqn. (9), yielding the activation enthalpy for step 1, eqn. (10).

Table 4 Activation properties and rate constants for the gas phase and aqueous solution processes shown in Figs. 6 and 7 and Scheme 2[a]

	1	5	7a	7b
$\Delta E^{\ddagger}$	—	29.8	34.0	31.8
ΔZPE‡	—	−3.4	−4.6	−4.3
$\Delta E^{\ddagger}$ + ΔZPE‡	—	26.4	29.4	2.75
$\Delta H_{\mathrm{g}}^{\ddagger}$	31.8[b]	26.9	30.5	28.5
$\Delta S_{\mathrm{g}}^{\ddagger}$	22.1[b]	5.7	13.4	11.7
$\Delta G_{\mathrm{g}}^{\ddagger}$	25.2[b]	25.2	26.5	25.0
$\Delta\Delta G_{\mathrm{solv}}$	—	1.1	−0.7	−2.7
$\Delta H_{\mathrm{sol}}^{\ddagger}$[c]	29.1[b]	28.0	29.8	25.8
$\Delta S_{\mathrm{sol}}^{\ddagger}$[c]	15.1[b]	5.7	13.4	11.7
$\Delta G_{\mathrm{sol}}^{\ddagger}$	24.6[b]	26.3	25.8	22.3
$k(T)$[d]	5.8×10^{-6}	3.3×10^{-7}	7.6×10^{-7}	2.8×10^{-4}

[a] Activation energies ($\Delta E^{\ddagger}$), differences in zero point energies between the transition state and the reagents (ΔZPE‡) and thermodynamic properties obtained by *ab initio* calculations at the MP2/6-31+G*//HF/6-31+G* level of theory. Energies, enthalpies and Gibbs energies in kcal mol^{-1} and entropies in cal mol^{-1} K^{-1}. Standard state is chosen as 1 mol L^{-1} at 298.15 K. [b] Estimated values (see text). [c] Values estimated by the approximation $\Delta H_{\mathrm{sol}}^{\ddagger} \approx \Delta H_{\mathrm{g}}^{\ddagger} + \Delta\Delta G_{\mathrm{solv}}$ and $\Delta S_{\mathrm{sol}}^{\ddagger} \approx \Delta S_{\mathrm{g}}^{\ddagger}$. [d] Rate constants in units of s^{-1}.

$$\Delta H_{\mathrm{g}}^{\ddagger}(-1) = -T^2\frac{\partial}{\partial T}\left(\frac{\Delta G_{\mathrm{g}}^{\ddagger}(-1)}{T}\right) \qquad (8)$$

$$\Delta H_{\mathrm{g}}^{\ddagger}(-1) = -\tfrac{1}{2}RT \qquad (9)$$

$$\Delta H_{\mathrm{g}}^{\ddagger}(1) = \Delta H_{\mathrm{g}}(1) - \tfrac{1}{2}RT \qquad (10)$$

In aqueous solution, the activation properties were estimated by eqns. (11) and (12), where $\Delta G_{\mathrm{sol}}^{\ddagger}(-1)$, the activation free

$$\Delta H_{\mathrm{sol}}^{\ddagger}(1) \approx \Delta H_{\mathrm{g}}^{\ddagger}(1) + \Delta\Delta G_{\mathrm{solv}}(1) \qquad (11)$$

$$\Delta G_{\mathrm{sol}}^{\ddagger}(1) \approx \Delta G_{\mathrm{sol}}(1) + \Delta G_{\mathrm{sol}}^{\ddagger}(-1) \qquad (12)$$

energy for the phenyl cation–nitrogen reaction, was taken as being diffusion controlled ($k_{-1} = 10^{10}$ L mol^{-1} s^{-1}). These equations lead to an activation free energy in aqueous solution of 24.6 kcal mol^{-1}, resulting in a rate constant of 5.8×10^{-6} s^{-1} (Table 4). The activation enthalpy is estimated as 29.1 kcal mol^{-1} and the activation entropy as 15.1 cal mol^{-1} K^{-1}. This positive entropy reflects the loose nature of the transition state relative to the reagent.

The phenyl cation could react with water or methanesulfonate without an activation barrier (reactions 2 and 3, Scheme 2), through a thermodynamically favorable pathway.

The following reaction pathway involves the formation of a benzenediazonium–methanesulfonate ion pair (reaction 4, Scheme 2). The structure of MS4 shown in Fig. 4 indicates that the oxygens of the sulfonate interact with the nitrogens of the diazonium cation and a hydrogen of the aromatic ring. This species should be very stable in the gas phase, with a formation Gibbs energy of −91.1 kcal mol^{-1}. In aqueous solution, the Gibbs energy increases to −3.1 kcal mol^{-1}, as a result of the very strong stabilizing effect of the aqueous solvent on the ionic fragments. The tight ionic pair can react through the transition state TS5 (Fig. 4), corresponding to a nucleophilic attack of the sulfonate on the carbon of the aromatic ring. The barrier for this step is solvent insensitive, since in the gas phase the Gibbs energy barrier is 25.2 kcal mol^{-1} and

Table 5 Thermodynamic properties and equilibrium constants for the gas phase and aqueous solution reactions shown in Scheme 2[a]

	1	2	3	4	5	6	7
ΔE	36.6	−196.8	−56.6	−99.8	−60.4	−14.0	−6.0
ΔZPE	−5.1	4.7	6.4	1.1	−1.5	1.7	−0.5
$\Delta E + \Delta$ZPE	31.5	−192.1	−50.2	−98.7	−61.9	−12.3	−6.5
ΔH_g	32.1	−191.9	−51.2	−97.6	−62.2	−11.8	−7.3
ΔS_g	28.8	−29.2	−28.5	−21.8	−21.5	−16.1	16.4
ΔG_g	23.5	−183.2	−42.7	−91.1	−68.6	−7.0	−12.2
$\Delta\Delta G_{solv}$	−2.7	105.2	−7.8	88.0	14.5	8.9	−19.4
ΔG_{sol}	20.8	−78.0	−50.5	−3.1	−54.1	1.9	−31.6
K_{eq}[b]	5.7×10^{-16}	5.7×10^{57}	1.0×10^{37}	1.9×10^{2}	4.5×10^{39}	4.1×10^{-2}	1.5×10^{23}

[a] Reaction energies (ΔE), differences in zero point energies between products and reagents (ΔZPE) and thermodynamic properties obtained by *ab initio* calculations at the MP2/6-31+G*//HF/6-31+G* level of theory. Energies, enthalpies and Gibbs energies in kcal mol^{-1} and entropies in cal mol^{-1} K^{-1}. Standard state is chosen as 1 mol L^{-1} at 298.15 K. [b] Equilibrium constants in units of mol L.

in aqueous solution it is 26.3 kcal mol^{-1}, only 1.1 kcal mol^{-1} higher (Table 4).

Water molecules can also complex with the arenediazonium cation by interacting with the two nitrogens and with a hydrogen of the aromatic ring (MS5, Fig. 5). The enthalpy for the formation of this complex in the gas phase is calculated as −11.8 kcal mol^{-1}, and the Gibbs energy is −7.0 kcal mol^{-1} (Table 5). In water the Gibbs energy increases to 1.9 kcal mol^{-1} (Table 5). Water can attack the aromatic carbon bonded to nitrogen through two different pathways. One involves a transition state on the plane of the ring (TS7a) and the other corresponds to a transition state similar to that calculated for the reaction of the methanesulfonate, where the attack occurs from above the aromatic ring (TS7b). The reaction through TS7b is favored, having an activation free energy of 25.0 kcal mol^{-1} in the gas phase and 22.3 kcal mol^{-1} in aqueous solution (Table 4).

Gibbs energy profiles and the reaction mechanism. A point that deserves attention in Figs. 6 and 7 and Tables 4 and 5 is the similarity of the activation Gibbs energies for steps 1, 5 and 7 (Scheme 2) both in the gas phase and in aqueous solution. Although the pathways are different and the aqueous solution has very strong solvating properties, the $\Delta G^‡$'s are close to 25 kcal mol^{-1} (Table 4). According to our calculations, in aqueous solution, the formation of phenol (MS3, Scheme 2) is dominated by a bimolecular pathway (TS7b, Fig. 5) since the pseudo first-order rate constant for this reaction is 6.4×10^{-4} s^{-1}, which can be compared with the rate constant for the unimolecular mechanism (step 1, Scheme 2) that is 5.8×10^{-6} s^{-1} (Table 4). In the gas phase, which can be thought of as a very low polarity solvent, the bimolecular mechanism is even more favorable, with a rate constant of 4×10^{-1} L mol^{-1} s^{-1} compared with the unimolecular rate constant of 2.1×10^{-6} s^{-1} for step 1. However, in a low polarity solvent the water molecules will form a complex with the diazonium ion. In this case, we can consider that the mechanism occurs by the unimolecular rearrangement of the MS5 complex through TS7b, and we should observe a first order rate constant of 2.9×10^{-6} s^{-1}. Another aspect to be considered is the activation entropy. We have estimated that $\Delta S^‡$ is 15.1 cal mol^{-1} K^{-1} for the unimolecular mechanism in aqueous solution, while $\Delta S^‡$ is estimated to be 11.7 cal mol^{-1} K^{-1} for the bimolecular mechanism through TS7b (Table 4). In this case, since the arenediazonium ion is fully solvated by water molecules, we can consider the reaction as a unimolecular rearrangement of the MS5 complex through TS7b. Thus, this positive entropy is not inconsistent with nucleophilic attack of the water on the aromatic carbon. In addition, comparing this theoretical $\Delta S^‡$ with the experimental value of 10.5 cal mol^{-1} K^{-1}, we can note the good agreement between theory and experiment.[27]

The methanesulfonate anion should react with arenediazonium by a bimolecular mechanism (TS5) both in low polarity solvents or in an aqueous media where water molecules are solvating the diazonium ion. Upon unimolecular elimination of nitrogen one water molecule of the first coordination shell will form phenol, since this reaction has no activation barrier. Thus, the closest nucleophilic species will form a chemical bond with the aryl cation. The methanesulfonate anion will only compete with the water molecules when it is forming a tight ion pair with the arenediazonium cation and, in this case, the reaction will proceed by transition state TS5. When the reaction occurs in a low polarity solvent, methanesulfonate can form a stable ionic pair with the arenediazonium cation, and the reaction will also take place by a bimolecular mechanism, *i.e.* by nucleophilic attack of the methanesulfonate on the aromatic carbon.

Discussion

Products of the reactions of aryl cations with sulfates and sulfonates have been obtained in non-aqueous solvents. Phenyl benzenesulfonate, $PhSO_3Ph$, is obtained in good yield in the thermal decomposition of benzenediazonium tetrafluoroborate, PhN_2BF_4, in methyl and ethyl benzenesulfonate ($PhSO_3Me$ and $PhSO_3Et$).[28] The proposed mechanism for this reaction involves the formation of an aryl cation, upon spontaneous PhN_2BF_4 dediazoniation, followed by reaction with the sulfonyl-group oxygen. The intermediate formed is cleaved by fluoride or tetrafluoroborate giving $PhSO_3Ph$.[28] A similar mechanism can be used to rationalize the synthesis of methyl phenyl sulfate from dimethyl sulfate and benzenediazonium tetrafluoroborate.[16]

Here we have shown that dediazoniation of *z*-ArN_2^+, with or without micelles, produces the products expected for reaction of alkyl sulfate and alkanesulfonate with an aryl cation. Although it could be expected that in aqueous solutions an extremely reactive electrophile, such as the putative aryl cation, should react even with nucleophiles as weak as alkyl sulfates and alkanesulfonates, the products of such reaction had never been isolated. The assumption that the bisulfate ion is inert in the dediazoniation of benzenediazonium ion in solution can be understood from the instability of phenyl sulfate in 0.15 M sulfuric acid at 70 °C, the conditions necessary to maintain a high concentration of the bisulfate anion.[8]

Bravo-Diaz and co-workers studied the kinetics and mechanism of dediazoniation of several substituted methyl benzenediazonium salts in SDS in HCl (0.01 M).[29] They confirmed the formation of halides in SDS but did not report the formation of any other products.[29] From the kinetic data presented here it is clear that particular experimental conditions are necessary to identify the (unstable) product of the SDS and diazonium reaction.

^{1}H NMR data, obtained with 2-, 3- and 4-methylbenzenediazonium salts in SDS micelles, suggest that the aryl moiety of these probes is near the Cα and Cβ of SDS.[29] The association constant, K_s, of methyl-substituted arene diazonium ions with SDS ranges from 250 to 1390 M^{-1}.[29] Based on the effect of the hydrocarbon chain length on the association constant of the substrates and micelles, it can be expected that the value of K_s for 16-ArN_2^+ with SDS and SDSu is higher than 10^4 M^{-1}. Therefore, the diazonium probe should be totally bound to the SDS micelles under our reaction conditions.

The rate constants for the dediazoniation, k_φ, of 1-ArN_2^+ and 16-ArN_2^+ are very similar in 9 : 1 MeOH–H_2O (0.01 M HBr), *i.e.* 4.1×10^{-4} and 5.1×10^{-4} s^{-1}, respectively (40 °C).[1] Consistent with the known lack of significant solvent effect on dediazoniation rates, the value of k_φ for 1-ArN_2^+ in water (0.01 M HBr) is 5.4×10^{-4} s^{-1} .[1] However, 16-ArN_2^+ incorporation into CTAB micelles reduces the value of k_φ to 3.3×10^{-4} s^{-1}, a decrease of 40% when compared to the rate in water.[1] This inhibition is similar to that obtained upon dediazoniation of 1-ArN_2^+ in 3.0 M tetramethylammonium bromide, TMAB, where the value of k_φ is 4.2×10^{-4} s^{-1}, attributed to ionic strength effects on the pre-equilibrium fomation of halide·arene diazonium complexes.[1]

The value of k_φ for 16-ArN_2^+ dediazoniation in SDS and SDSu micelles was half of that observed in CTAB micelles and 4-fold lower than that of 1-ArN_2^+ in water (Table 1). The inhibition of dediazoniation of 16-ArN_2^+ in SDS (compared to the rate in CTAB) cannot be attributed to an ionic strength effect, since the local salt concentrations at the interface of SDS and CTAB micelles are comparable.[18] In water the presence of 3.0 M $NaMeSO_3$ or 3.0 M $NaMeSO_4$ decreased the value of k_φ for dediazoniation of 1-ArN_2^+ by 35% (Table 1). The inhibition caused by SDS can be rationalized by supposing that 16-ArN_2^+ binding to SDS results in ion pair formation favored by the hydrophobicity of both detergent and substrate and, consequently, stabilization of the initial diazonium ion. A similar effect of the interfacial charge on the relative stability of initial and transition states was proposed to explain the effect of charged micelles on the rate of spontaneous decarboxylation.[30]

The products of SDS or SDSu sulfonate reaction with 16-ArN_2^+, *i.e.* 16-$ArOSO_3Do$ and 16-ArO_3SDo, have different stabilities. The high stability of 16-ArO_3SDo is consistent with previous findings, which demonstrated that the hydrolysis of phenyl toluene-*p*-sulfonate, PTS, is slower than that of alkyl alkanesulfonates ($R'SO_3R$) and that no phenol is formed in the hydrolysis of PTS even after 3 weeks at 120 °C, in 60% aqueous dioxane.[17] The hydrolysis of PTS occurs in alkali, but involves an OH^- attack on sulfur with subsequent cleavage of the sulfur–oxygen bond. Hence, 1-ArO_3SMe and 16-ArO_3SDo are expected to be stable under our reaction conditions.

Hydrolysis of 1-$ArOSO_3Me$ and 16-$ArOSO_3Do$ is faster than that of the corresponding sulfonates and the rate constants for hydrolysis of these compounds in SDS and water–MeOH are consistent with previous data from the literature for compounds of similar structure (Table 2). The aryl sulfates formed in the hydrolysis of the diesters are stable and this allowed us to use chemical trapping to determine the monomer concentration in SDS micelles.

We stress here that the central assumption of the diazonium salt-based chemical trapping method is that the selectivities of long chain analogs incorporated in supramolecular structures towards two different nucleophiles are the same as the selectivity of their short chain analog towards the same nucleophiles in bulk solution. The validity of this assumption is clearly independent of the nature of the mechanism of the reaction between the nucleophiles and the diazonium ions and only requires that the mechanism in both media is the same. Hence, the slope of the standard curves, relating % yield of a particular anion with salt concentration, can be taken as the relative selectivity towards the nucleophile.[1] Our data, therefore, allows the comparison of the selectivities of $MeSO_3^-$, $MeSO_4^-$ and halides for the reaction with 1-ArN_2^+ in aqueous solution.

The standard curves of % yield of 2,4,6-trimethylphenyl chloride, 1-ArCl, and 2,4,6-trimethylphenyl bromide, 1-ArBr, against NaCl and NaBr in water are nonlinear above 0.1 M salt.[31] For both $MeSO_4^-$ and $MeSO_3^-$ the %1-$ArOSO_3Me$ and %1-ArO_3SMe increase linearly with salt (Fig. 3). Therefore, comparison of the relative selectivities between halides and alkyl sulfates and alkenesulfonates can only be made at a fixed salt concentration. At 1 M NaX the % yields of products for Br^-, Cl^-, $MeSO_4^-$ and $MeSO_3^-$ are 20, 12.5, 9 and 7, respectively. In 0.1 M salt the % yields of the products are 45, 23, 9 and 7 for Br^-, Cl^-, $MeSO_4^-$ and $MeSO_3^-$, respectively. Hence the limits of relative selectivity for the Br^-, Cl^-, $MeSO_4^-$ and $MeSO_3^-$ reaction with 1-Ar^+ with respect to $MeSO_3^-$ are 2.9, 1.8, 1.3 (1.0 M salt) and 6.4, 3.3 and 1.3 (0.1 M salt). These values, as well as other selectivities published previously for other sets of anions, are orders of magnitude lower than selectivities typically observed for anionic nucleophiles competing with water in reactions with stabilized carbocations or bimolecular reactions at saturated carbon.[1,7,32]

Such low selectivities are entirely consistent with pre-associative mechanisms, in which anion and ground state *z*-ArN_2^+ form a complex before bond breaking and making occurs. In fact pre-associative mechanisms have been proposed to explain both anionic and neutral nucleophile selectivity in the product distribution.[2,33,34]

In both cases however, the pre-association was followed by the currently accepted view, which assumes slow nitrogen loss from the diazonium ion, formation of an aryl cation·anion or aryl cation·molecule intermediate followed by a very fast reaction from the complex.

Recently this reaction has been explored theoretically and in the following section we suggest that the experimental data can be understood without recourse to the proposition of the existence of a phenyl cation intermediate, at least in aqueous solution. We have taken a model, namely benzenediazonium ion and compared the *ab initio* calculations with the experimental results obtained with 1-ArN_2^+.

Kinetic model

Based on the mechanism proposed in Scheme 2 and assuming that step 1 does not occur in aqueous solution, MS3 is generated in steps 7a and 7b, while MS2 is generated in step 5. The formation of the methanesulfonate–benzenediazonium ion pair (step 4, Scheme 2) will be considered. The equilibrium, K, and rate, k, constants for step n of Scheme 2 will be represented as K_n and k_n. For step 7, due to the occurrence of two transition states (TS7a and TS7b, Figs. 5–7) the rate constants are represented as k_{7a} and k_{7b} (Table 4). This notation is also used in Tables 4 and 5. In addition the following notation will be used: $D = ArN_2^+$, $S = CH_3SO_3^-$.

The total concentration of benzenediazonium (C_D) and its association equilibrium constant (K_4) is given by eqns. (13) and (14). The rate of ArN_2^+ dediazoniation, considering that water

$$C_D = [D] + [D \cdots S] \tag{13}$$

$$K_4 = \frac{[D \cdots S]}{[D][S]} \tag{14}$$

and $CH_3SO_3^-$ are in excess, can then be written as eqn. (15),

$$\frac{dC_D}{dt} = -k_S[S][D] - k_{H_2O}[H_2O][D] \tag{15}$$

where: $k_S = K_4k_5$ and $k_{H_2O} = K_6(k_{7a} + k_{7b})$. From these equations the following values are obtained: $k_S = 6.3 \times 10^{-5}$ L mol^{-1} s^{-1}; $k_{H_2O} = 1.2 \times 10^{-5}$ L mol^{-1} s^{-1}; and $K_4 = 1.9 \times 10^2$ L mol^{-1}.

Rearranging the equations above gives eqns. (16) and (17), and the yield of phenyl methanesulfonate (MS2) is is given by eqn. (18).

Table 6 Observed rate constants and yields of MS2 product in aqueous solution predicted by *ab initio* calculations[a]

[S] mol L^{-1}	MS2 (%)	k_{obs} ($K_4 = 190$)	k_{obs} ($K_4 = 1$)
0.001	0.0095	5.6×10^{-4}	6.7×10^{-4}
0.01	0.095	2.3×10^{-4}	6.6×10^{-4}
0.1	0.94	3.4×10^{-5}	6.1×10^{-4}
1.0	8.6	3.8×10^{-6}	3.6×10^{-4}

[a] $[H_2O] = 55.5$ mol L^{-1}, $k_s = 6.3 \times 10^{-5}$ L mol^{-1} s^{-1}, $T = 298.15$ K.

$$\frac{dC_D}{dt} = -k_{obs}C_D \tag{16}$$

$$k_{obs} = \frac{k_{H_2O}[H_2O] + k_S[S]}{1 + K_4[S]} \tag{17}$$

$$\frac{[MS2]}{[MS2] + [MS3]} = \frac{k_S[S]}{k_{H_2O}[H_2O] + k_S[S]} \tag{18}$$

The calculated product yields and rate constants for the reaction of benzenediazonium ion with methanesulfonate (Table 6) are similar to those obtained experimentally for the reaction of 1-ArN_2^+ with added sodium methanesulfonate (Fig. 3, Table 1) using $K_4 = 1$.

Reaction mechanism

The results of the *ab initio* calculations imply that ArN_2^+ dediazoniation occurs in aqueous solution by a bimolecular mechanism. The calculations also suggest that $CH_3SO_3^-$ reacts by a bimolecular path, *i.e.* through a nucleophilic attack on the carbon of the aromatic ring after the formation of a tight ion pair with ArN_2^+. These results are contrary to the currently accepted unimolecular mechanism that considers that nitrogen is lost without any participation of the nucleophile.[10]

The mechanism of the dediazoniation reaction has been extensively analysed and most authors have concluded that a bimolecular mechanism cannot be the main reaction pathway. In the current view, the unimolecular elimination of nitrogen with formation of the phenyl cation explains the experimental observations.[10]

In the following section, we propose that the reaction mechanism, depending on the medium, can be uni- or bimolecular and that this reaction pathway is consistent with experimental results.

The first point that deserves attention is the high reactivity of the phenyl cation. In our calculations, the elimination of nitrogen, as well as the addition of water and methanesulfonate, occurs without a saddle point on the potential energy surface even when the solvent is included by the continuum IPCM method. If this species were to be generated in aqueous solution, its lifetime would be in the picosecond time scale, and it would react with the nucleophile closest to the positively charged carbon. Thus, in aqueous solution, nucleophiles other than water will only react if they form a tight ion pair or ion•molecule pair with the diazonium ion. An ion•molecule pair with the ground state diazonium ion could be proposed even with N_2 or CO at high enough partial pressures, since both have been demonstrated to incorporate in the products of dediazoniation.[11]

Ground state formation of an ion pair or ion•molecule pair can influence the elimination of nitrogen and, since the outgoing nitrogen produces a positively charged carbon, the nearby nucleophile can form a bond with this carbon within the picosecond time scale. However, this mechanism generates a transition state on the potential energy surface with a variable degree of carbon–nitrogen bond-breaking and bond formation between carbon and the nucleophile. The present calculations show that in the transition state a charged species, such as $CH_3SO_3^-$, has a shorter carbon–oxygen distance (2.619 Å) than that calculated for a neutral species, such as water (2.937 Å for TS7b). These distances are large compared with a covalent bond. In particular, in the case of water, the reaction pathway is akin to a unimolecular mechanism, in the sense that at 2.937 Å essentially no carbon–oxygen bond has been formed in the transition state. However, the mechanism is *bimolecular*, since the explicit water generates the saddle point and alters the motion of the nitrogen moiety on the reaction path.

This mechanism, where water in the transition state does not form an appreciable O–C bond, is consistent with the necessity of using a dual substituent parameter to analyze substituent effects on the rate of dediazoniation.[10]

Our calculations suggest that a true unimolecular mechanism could occur only in a non-nucleophilic solvent. Now that the general aspects of the mechanism suggested by the *ab initio* calculations have been described, we analyse how the present mechanism is consistent with some of the experimental observations that led to the proposal of a phenyl cation as an intermediate.

Small dependence of the rate constant upon the nature of the nucleophile. The direct consequence of a transition state where the carbon–nucleophile distance is large is that the activation energy displays little dependence on the nature of the nucleophile, since the degree of new bond formation is small. The low selectivity of arenediazonium cations with respect to the nature of the nucleophile has been extensively illustrated.[6–8,10]

Table 4 shows that the calculated activation enthalpies in the gas phase for the reaction of ArN_2^+ with $CH_3SO_3^-$ and water from the respective complexes are 26.9 kcal mol^{-1} (TS5) and 28.5 kcal mol^{-1} (TS7b), respectively. Hence, the calculations show that, although the nucleophilicity of water and sulfonate are strikingly different, the activation enthalpies are essentially identical, in good agreement with experimental data.

Small solvent effect. Rate constants of dediazoniation of arenediazonium ions, as well as activation parameters, are extraordinarily solvent insensitive and this fact has been taken as one of the strongest pieces of evidence indicating a unimolecular heterolytic mechanism.[7,10,35] The present calculations (Table 4) show that the bimolecular mechanisms should indeed exhibit a very small solvent effect, as evidenced by the values of $\Delta\Delta G^{\ddagger}_{solv}$, calculated for aqueous solution. The difference in the solvent effect should be even smaller when comparing solvents with medium and high relative permittivities. This behaviour can be understood as arising from the location of the positive charge on the carbon–N_2 atoms, both the initial and the transition state where the new bond has yet to be formed. Thus, the *differential* solvation effect should be small, resulting in rate constants that are practically independent of the polarity of the medium. These observations, in conjunction with the low dependence of the rate constant upon the nature of the nucleophile, are consistent with experiment and show that the low solvent effect on the rate constants is consistent with a bimolecular mechanism.

Positive activation entropy. In aqueous solution, the diazonium ion interacts directly with the water molecules. The complex MS5 is a stable structure, with a formation enthalpy (from the diazonium ion and water fragments) of −11.8 kcal mol^{-1} in the gas phase. From the magnitude of the formation enthalpy and the water concentration, the reaction of ArN_2^+ with water can be considered as a unimolecular rearrangement of the MS5 complex through TS7b. In this case, the effect of the medium on the activation entropy should be small, and the gas phase value of 11.7 cal mol^{-1} K^{-1} can be taken as the $\Delta S^{\ddagger}$ in aqueous solution. This value is in good agreement with the experimental value of 10.5 ± 1.0 cal mol^{-1} K^{-1}.[27] Thus, the positive activation entropy is not inconsistent with a *bimolecular* mechanism in the sense that the transition state contains both the water molecule and the arenediazonium moiety.

Isomerization of isotopically labeled N_2 group. Studies with isotopically substituted nitrogen in benzenediazonium ions in aqueous solution show that the isomerization rate is smaller than that of the dediazoniation reaction of non-labeled analogs by a factor of 0.016.[35,36] Recent *ab initio* calculations by Glaser and Horan show that the isomerization of diazonium does not exhibit an intermediate, the free aryl cation, but a transition state, where the nitrogens are at equivalent distances from carbon.[37] This transition state allows for isomerization. Furthermore, the energy of the transition state is smaller than the dissociation energy. These observations are at odds with a unimolecular mechanism, since a lower barrier for isomerization should result in a higher rate constant. On the other hand, they are consistent with a bimolecular mechanism, because in this case water molecules are inducing the reaction, and are responsible for a reaction rate greater than the isomerization rate.

Reaction rates and water activity. A recent observation shows that, at constant tetraalkylammonium bromide concentration, the dediazoniation of 1-ArN_2^+ produces equal yields of 1-ArOH and 1-ArBr, although the water concentration varies 4-fold because of the differences of the tetraalkylammonium cation substituents.[38]

More strikingly, the value of the rate constants for benzenediazonium ion dediazoniation varies only 2.5-fold going from dilute (0.0001 mol L^{-1}) to very concentrated (18 mol L^{-1}) aqueous solutions of sulfuric acid.[7] Moreover, the rate constant varies less than 2% when the sulfuric acid concentration varies from 14 mol L^{-1} to 18 mol L^{-1}, corresponding to a variation in the activity of water of more than 1000-fold. These data have led to the exclusion of any bimolecular mechanism, leaving a unimolecular mechanism as the only alternative. However, Swain *et al.*[7] also comment on the possibility of a bimolecular mechanism with almost no formation of a covalent bond. The present calculations show that, in fact, there is almost no formation of a covalent bond, and the consequence is the low dependence of the rate constant with respect to the nature of the nucleophile. Even sulfuric acid molecules can act as nucleophiles and react with the benzenediazonium ion.

Thus, the present proposal is not at odds with the fact that the dediazoniation rate constant varies less than 2% when the concentration of sulfuric acid varies from 14 to 18 mol L^{-1}.

Phenyl cation has not been detected in solution to date. Scaiano and Kim-Thuan have used laser flash photolysis experiments in order to observe the phenyl cation generated from benzenediazonium ion in aqueous solution.[39] Although they were not able to observe this species, they have provided a rough estimate of its lifetime as less than 500 ps. This is in good agreement with the indications of the present calculations that predict a lifetime in the picosecond time scale. We are aware that photochemical generation of aryl cations is different from a thermal process. While it is possible that future laser flash photolysis studies with picosecond time resolution could detect the phenyl cation we believe that, in the thermal process, this species will not be generated in aqueous solution since the surrounding water molecules will alter the elimination reaction path, creating a saddle point on the potential energy surface as we have demonstrated in this work.

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