tri-*n*-butyltin deuteride (2.33 g, 8 mmol) in ether (50 mL) was irradiated for 6 h. The solvent was carefully removed in vacuo at room temperature and the residue was distilled at 0.1 mm. The distillate was mixed with silica gel (1 g). This mixture was heated to sublime pure cubane-*d* (306 mg, 65%, mp 131–132 °C in sealed capillary, lit.[8b] 131–132 °C). The IR (KBr) spectrum exhibited absorptions at 3000, 2250, 1220, and 840 cm^{-1}. The low-resolution mass spectrum exhibited peaks at *m/e* 106 (7.5), 105 (65) 104 (100), and 103 (7.4).

Registry No.—Tri-*n*-butyltin hydride, 688-73-3; adamantane, 281-23-2; 1-chloroadamantane, 935-56-8; 1-phenylbicyclo[2.2.2]octane, 23062-62-6; 9,10-dihydro-9,10-ethanoanthracene, 5675-64-9; norborane, 279-23-2; methyl 4-bromocubanecarboxylate, 37794-28-8; cubanecarboxylic acid, 53578-15-7; tri-*n*-butyltin deuteride, 6180-99-0; cubane-*d*, 59346-73-5.

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Reaction of Arylsulfonylalkyl Arenesulfonates with Hydroxide Ion. Nucleophilic Displacement at Sulfonate Sulfur

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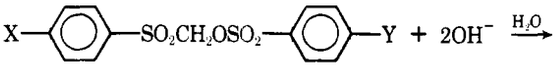
Recent studies have revealed that arylsulfonylmethyl arenesulfonates (1) react with sodium hydroxide in aqueous solution to yield sodium arenesulfinate, formaldehyde, and sodium arenesulfonate.[1] The reaction was thought to proceed



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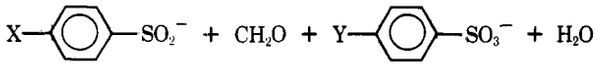


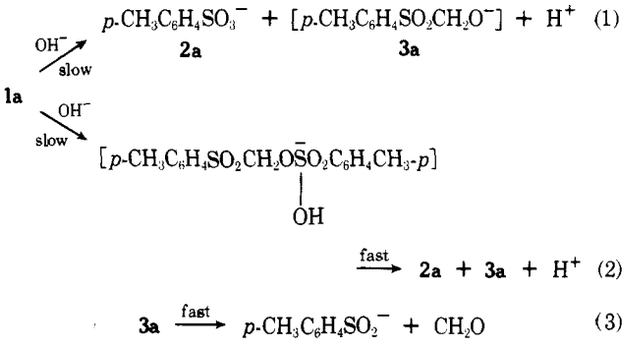
via a specific-base-catalyzed process involving rate-limiting decomposition of the corresponding α-sulfonyl carbanion. This mechanism, which is essentially different from that for the hydrolysis of arylsulfonylmethyl perchlorates[2a] and nitrates,[2b] was based on the following observations: (1) the absence of a measurable reaction with a series of nucleophiles (F^-, I^-, NO_2^-, and N_3^-) in methanol; (2) no enhanced reaction rates in 0.1 N NaOH upon addition of Br^- or F^- in concentrations as high as 0.1 M; (3) the solvent deuterium isotope effect [$k(OD^-)/k(OH^-)$ ca. 1.4]; and (4) fast CH/CD exchange at the α-sulfonyl carbon atom in 0.1 M NaOD in D_2O.

During the course of our investigation of microenvironmental effects on this reaction,[3] we obtained experimental data which cast considerable doubt on the correctness of the proposed mechanism. Therefore, we have investigated the mechanism in more detail and the results led us to propose that the sulfonates 1 preferentially undergo nucleophilic attack on sulfonate sulfur by hydroxide ion rather than hydrolyze via a specific-base-catalyzed process.

Results and Discussion

Reaction with ^{18}O-Enriched Hydroxide Ion. After reaction of 1a (X = Y = CH_3) in 50% (v/v) dioxane–water (at 67 °C) or in 33% (v/v) EtOH–H_2O (at 80 °C) containing 0.1 M NaOH and using ^{18}O-enriched water (1.5 atom % ^{18}O), the sodium *p*-toluenesulfonate formed was isolated as its *S*-benzylisothiouronium salt.[4] Mass spectrometric analysis of this product indicated that ^{18}O was incorporated in the sulfonate anion and the excess isotope abundance was in accord with exclusive S–O bond fission in the ^{18}O-labeled medium. The isotopic tracer did not appear in the starting material which was recovered before completion of the reaction. In a separate experiment it could also be shown[5] that under the same reaction conditions the *p*-toluenesulfonate anion does not exchange ^{16}O for ^{18}O. Therefore, we conclude that the ^{18}O-enriched *p*-toluenesulfonate anion is formed from either a one-step displacement of *p*-$CH_3C_6H_4SO_2CH_2O^-$ (3a) via attack of OH^- at the sulfonate sulfur atom of 1a (eq 1)[6] or via an addition–elimination type mechanism (eq 2) with rate-limiting attack by OH^- as the initial step (Scheme I). The

Scheme I



negative entropy of activation for the reaction ($\Delta S^{\ddagger} = -17$ eu for 1a)[1] is also consistent with a bimolecular rate-determining step. The *p*-tolylsulfonylmethoxide leaving group (3a) is known to decompose very rapidly into *p*-toluenesulfinate anion and formaldehyde (eq 3).[7]

These results clearly show the marked preference for nucleophilic attack at the sulfonate sulfur atom rather than C–O bond cleavage. This unusual situation is most compatible with the steric and field effects of the sulfonyl group[8] in the sulfonates 1 which will strongly hamper nucleophilic displacement at the α-sulfonyl carbon atom.[9]

Substituent Effects. Table I presents second-order rate constants (k_{OH^-}) for the reaction of four sulfonates *p*-$CH_3C_6H_4SO_2CH(R_1)OSO_2R_2$ (1a–d) with sodium hydroxide (0.3–2.0 M) in 33% (v/v) EtOH–H_2O at 47.4 °C and constant ionic strength (μ = 2.0 M). Most noticeable is the pronounced rate decrease by a factor of ca. 3×10^3 upon replacing R_2 = Me (1c) for R_2 = *t*-Bu (1d). Apparently, nucleophilic attack at the sulfonate sulfur atom of 1c is sterically hindered by the bulky

Table I. Second-Order Rate Constants for the Reaction of p-$CH_3C_6H_4SO_2CH(R_1)OSO_2R_2$ with Hydroxide and Hydrogen Peroxide Anion

Registry no.	Compd	R_1	R_2	Solvent	Temp, °C	$k_{OH^-} \times 10^3$, M^{-1} s^{-1}	$k_{HO_2^-} \times 10^3$, M^{-1} s^{-1}
14894-58-7	**1a**	H	p-$CH_3C_6H_4$	33% (v/v) EtOH–H_2O[a]	47.4	12.70	
	1a	H	p-$CH_3C_6H_4$	H_2O	24.7	3.74	
	1a	H	p-$CH_3C_6H_4$	H_2O	24.7		282[b]
62586-47-4	**1b**	C_6H_5	p-$CH_3C_6H_4$	33% (v/v) EtOH–H_2O[a]	47.4	5.95	
62586-48-5	**1c**	H	CH_3	33% (v/v) EtOH–H_2O[a]	47.4	8.68	
	1c	H	CH_3	H_2O	24.7	0.81	
	1c	H	CH_3	H_2O	24.7		74[c]
62586-49-6	**1d**	H	$(CH_3)_3C$	33% (v/v) EtOH–H_2O[a]	47.4	0.003	

[a] Ionic strength 2.0 M. [b] 1.6–3.4 × 10^{-3} M solutions of HO_2^- in 0.097–0.099 M NaOH. [c] 1.1–2.5 × 10^{-3} M solutions of HO_2^- in 0.098–0.100 M NaOH.

R_2 substituent.[10] The modest rate decrease upon replacing R_1 = H by R_1 = C_6H_5 is also not expected for a specific-base-catalyzed reaction because of the stabilizing effect of a phenyl substituent on an α-sulfonyl carbanion intermediate. The proposed nucleophilic displacement at sulfonate sulfur is further substantiated by the enhanced reaction rates of **1a** and **1c** in the presence of the α-effect nucleophile HO_2^- (Table I, $k_{HO_2^-}/k_{OH^-}$ = 75 for **1a** and 91 for **1c** at 24.7 °C in 0.1 M NaOH).[11]

The Hammett ρ values (ρ_x = 0.49, ρ_y = 2.12) obtained previously[1] from the linear plots of log k_{OH^-} vs. Hammett σ constants for a series of sulfonates **1** can be reinterpreted in terms of the present work as pointing to a transition state in which the negative charge of the incoming nucleophile is largely transferred to the electrophilic arenesulfonate reaction center. The relatively large ρ_x is most compatible with some S–O bond scission in the transition state as required by eq 1. However, in the absence of sufficient data on electronic effects for nucleophilic addition to sulfonate sulfur, the mechanism shown in eq 2 cannot be excluded.[12]

Reaction Products. GLC analysis of the products obtained after reaction of **1a** in 50% (v/v) etOH–n-$BuNH_2$ containing 0.13 M of NaOEt (20 °C) unequivocally established the presence of diethyl ether and formaldehyde. No trace of N-n-butyl-p-toluenesulfonamide could be detected. The most reasonable explanation for the formation of diethyl ether involves the reaction of excess ethoxide with ethyl p-toluenesulfonate,[13] the primary and only nucleophilic substitution product formed from **1a** under the employed reaction conditions.

Reaction Mechanism. From the evidence reported above it seems evident that the sulfonates **1** undergo nucleophilic attack at sulfonate sulfur by hydroxide ion. Bimolecular attack at sulfonate sulfur has only occasionally been studied[5,14,15] since C–O cleavage has been encountered much more frequently than S–O cleavage as a result of the excellent properties of sulfonate anions as leaving groups.[16] At least in one case it has been found that nucleophilic displacement at sulfonate sulfur is accompanied by inversion of configuration at the reaction center.[14,17] In the terminology of the theory of hard and soft acids and bases (HSAB), the sulfonate sulfur can be characterized as an electrophilic center of a considerable degree of hardness. Alternatively, nucleophilic displacement at tetracoordinated sulfur can be described as largely charge controlled in terms of the generalized perturbation theory of chemical reactivity.[18] In recent work it has been demonstrated that hydroxide ion is one of the most powerful non-α-effect nucleophiles toward a hard center.[18] For example, Kice[11,19] has shown that for nucleophilic attack at the sulfonyl moiety of phenyl α-disulfone (a much more reactive substrate than **1a**) in 60% (v/v) dioxane–water (25 °C) the hydroxide ion reacts ca. 4 × 10^2 times faster than the hard fluoride ion. Since $ArSO_2^-$ is presumably a much better leaving group than p-$CH_3C_6H_4SO_2CH(R_1)O^-$, the rate differences within a series of structurally different nucleophiles may be markedly larger for the reaction of the sulfonates **1**. These results may well explain the failure to detect measurable reactions of **1a** with a series of nucleophiles other than hydroxide ion in methanol as the solvent.[1,20] Finally, we note that the solvent deuterium isotope effect (k_{OD^-}/k_{OH^-} ca. 1.4) found for the reaction of the sulfonates **1** is not in contradiction with the proposed mechanism since the nucleophilicity[21] of OD^- is often 20–40% higher than that of OH^-.

Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. A. F. Hamminga. Melting points were determined using a Mettler FP1 melting point apparatus with a Mettler FP52 microscope attachment. NMR spectra were recorded using $CDCl_3$ as the solvent. The gas chromatographic analyses were with a Carbowax 20M column maintained at 70 °C.

Materials. The sulfonates **1a–d** were prepared from the corresponding α-diazosulfone and sulfonic acid using the general procedure reported previously.[1] The compounds were all purified by crystallization from methanol. Sulfonate **1a** has already been described.[1]

***α*-*p*-Tolylsulfonylbenzyl *p*-toluenesulfonate (1b)** was obtained from 3.5 mmol of p-tolylsulfonylphenyldiazomethane[22] in a yield of 64%. A sample exhibited mp 148.3–148.7 °C; NMR δ 2.39 (3 H, s, CH_3), 2.46 (3 H, s, CH_3), 6.13 (1 H, s, CH), 7.12–7.70 (13 H, m, aromatic H); IR 1150, 1170, 1185, 1295, 1305, 1325, 1375 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_5S_2$: C, 60.56; H, 4.84; S, 15.40. Found: C, 60.5; H, 4.7; S, 15.3.

***p*-Tolylsulfonylmethyl methanesulfonate (1c)** was obtained in a yield of 65%; mp 102.3–103.0 °C; NMR δ 2.47 (3 H, s, p-CH_3), 3.18 (3 H, s, CH_3SO_2), 5.10 (2 H, s, CH_2), 7.30–7.99 (4 H, m, aromatic H); IR 1145, 1165, 1175, 1295, 1325, 1365 cm^{-1}. Anal. Calcd for $C_9H_{12}O_5S_2$: C, 40.90; H, 4.58; S, 24.26. Found: C, 41.0; H, 4.7; S, 24.1.

***p*-Tolylsulfonylmethyl *tert*-butanesulfonate (1d)** was obtained in a yield of 44%. A sample had mp 132.0–133.0 °C; NMR δ 1.42 (9 H, s, t-Bu), 2.45 (3 H, s, p-CH_3), 4.99 (2 H, s, CH_2), 7.27–7.99 (4 H, m, aromatic H); IR 1140, 1150 (sh), 1300, 1310, 1335, 1350 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_5S_2$: C, 47.04; H, 5.92; S, 20.93. Found: C, 46.6; H, 5.9; S, 20.7.

Kinetics. Reaction rates were determined by following the change of the absorbance of **1a–d** at 235 nm. The reactions with **1a–c** were carried out in 2-cm quartz cells, which were placed in the thermostated (±0.05 °C) cell compartment of a Zeiss PMQ II spectrophotometer. The slow reactions of **1d** were followed using a Beckman Model 24 spectrophotometer employing 1-cm quartz cells placed in the thermostated (±0.05 °C) cell compartment. The conversions of **1a–c** were followed for at least 3 half-lives and infinity points were taken after 10 half-lives. For the reaction of **1d** the method of Guggenheim was employed. Satisfactory pseudo-first-order kinetics were observed. Second-order rate constants k_{OH^-} and $k_{HO_2^-}$ were obtained from plots of k_1 vs. c_{OH^-} and $c_{HO_2^-}$, respectively, and were reproducible to within 3%. Only for **1d** k_{OH^-} is less accurate (±20%) because of the very slow reaction. The UV spectra taken of the solutions after complete reaction were in accordance with those expected for the reaction products shown in Scheme I (as determined in separate experiments).

^{18}O Experiments. The water used in these experiments contained 1.5 atom % ^{18}O. The reaction of **1a** with hydroxide ion was carried out starting from 0.400 g (1.18 mmol) of **1a** in 20 mL of 50% (v/v) dioxane–^{18}O-enriched water, containing 0.080 g (2.0 mmol) of sodium hydroxide. The solution was kept at 67 ± 1 °C for 18 h. After cooling to room temperature, water and dioxane were removed in vacuo at

50 °C. The remaining white solid was partly dissolved in 30 mL of water. The undissolved material (0.070 g) was identical with an authentic sample of **1a** and did not contain excess ^{18}O as indicated by mass spectrometry.[23] The aqueous filtrate was acidified with 2 N H_2SO_4 (10 mL) and extracted with ether (2 × 20 mL). The combined ethereal extracts were washed with 2 N H_2SO_4 (10 mL) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded *p*-toluenesulfinic acid (0.150 g), identical with an authentic sample. The aqueous layer was made alkaline with 10 N NaOH and the water was removed in vacuo. The resulting white material was extracted in a Soxhlet apparatus with 100 mL of anhydrous ethanol for 4 h. After removal of the ethanol in vacuo, sodium *p*-toluenesulfonate was obtained, which was crystallized from anhydrous ethanol. The corresponding *S*-benzylisothiouronium salt was prepared according to a standard procedure[4] and exhibited mp 180.3–181.8 °C (lit. 182 °C)[4] after crystallization from 33% (v/v) ethanol–water. The same salt (mp 180.5–181.5 °C) was also prepared from a sample of sodium *p*-toluenesulfonate obtained from the reaction of 0.310 g (0.91 mmol) of **1a** in 33% (v/v) ethanol–^{18}O-enriched water (30 mL) containing 0.130 g (3.25 mmol) of sodium hydroxide (45 min at 80 °C). The mass spectrum of *S*-benzylisothiouronium *p*-toluenesulfonate shows a peak at *m/e* 172 for a $C_7H_7SO_3H^+$ fragment and a peak at *m/e* 174 for the same fragment enriched in ^{18}O. The ratio of the intensities of both fragments (I^{174}/I^{172}; estimated accuracy $\pm 0.1 \times 10^{-2}$) was determined on the monitor of the instrument. Comparison of this ratio ($I^{174}/I^{172} = 6.5 \times 10^{-2}$ in dioxane–^{18}O-enriched water) with that produced by using the *S*-benzylisothiouronium salt of natural *p*-toluenesulfonic acid ($I^{174}/I^{172} = 5.2 \times 10^{-2}$) indicated that exclusive S–O bond fission had occurred upon reaction of **1a** with hydroxide ion.[24]

A test reaction for oxygen exchange by the *p*-toluenesulfonate anion was run on a solution of 0.350 g (1.80 mmol) of sodium *p*-toluenesulfonate, 0.315 g (1.77 mmol) of sodium *p*-toluenesulfinate, and 0.120 g (3 mmol) of sodium hydroxide in 30 mL of 50% (v/v) dioxane–^{18}O-enriched water. After keeping this mixture at 67 ± 1 °C for 19 h, the *S*-benzylisothiouronium *p*-toluenesulfonate (mp 180.3–181.7 °C) was prepared as described above. Mass spectrometric analysis showed that no ^{18}O had been incorporated in the *p*-toluenesulfonate anion during the treatment in the alkaline medium.

Product Composition. Sulfonate **1a** (0.300 g, 0.88 mmol) was dissolved in 20 mL of 50% (v/v) ethanol–*n*-butylamine containing 0.180 g (2.6 mmol) of sodium ethoxide and kept at room temperature for 90 h. Gas chromatographic analysis of 2 mL of the reaction mixture unequivocally established the presence of considerable amounts of diethyl ether and formaldehyde as indicated by careful comparison with gas chromatographic data of reference solutions. The other 18 mL of the reaction mixture was evaporated to dryness and the resulting solid was dissolved in 15 mL of water. After acidification with 2 N H_2SO_4 no *N*-*n*-butyl-*p*-toluenesulfonamide could be detected.

Registry No.—*p*-Toluenesulfonic acid, 104-15-4; methanesulfonic acid, 75-75-2; *tert*-butanesulfonic acid, 16794-13-1; *p*-tolylsulfonylphenyldiazomethane, 52629-22-8; *p*-tolylsulfonyldiazomethane, 1538-98-3; hydroxide ion, 14280-30-9; *p*-toluenesulfinic acid, 536-57-2; *S*-benzylisothiouronium *p*-toluenesulfonate, 35469-22-8.

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Localized Photochemical Isomerization in a 1,4-Bichromophore. Photochemistry of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone Anil

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We wish to report an interesting case of an apparently localized rotational deactivation[1] in β,γ-unsaturated imine bichromophores. There is already considerable evidence that excited-state rotation (geometric isomerization) is an important governing factor in the photochemistry of the related 1,4-bichromophores, the di-π-[2] and oxa-di-π-methanes.[3,4] A germane illustration is the contrasting behavior of β,γ-unsaturated ketones **1** and **2** on photosensitized irradiation. Unconstrained ketone **1** undergoes only cis–trans isomerization,[3] whereas the structurally similar steroid **2**, for which geometric isomerization (rotational deactivation) would cause