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On the Mechanism of Cleavage of Aryl Alkanesulfonates by Electron Donors[1]

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Abstract: In the cleavage of methane- and ethanesulfonates of phenols with arene anion radicals, 2 mol of the reducing species is consumed rapidly, resulting in formation of phenoxide and sulfinate ions. The mechanism involves initial rapid transfer of an electron from donor to sulfonate, followed by a considerably slower cleavage step. The effect of substituents on both these steps has been determined. With donors of higher reducing power, C–O cleavage yielding arene becomes more important. Tentative explanations for this latter effect are given.

Introduction

In our studies of the reaction of sulfonyl derivatives with electron donors we have discovered two rather different types of mechanisms of cleavage. With arenesulfonamides (**1**) the initial electron-transfer step is rate controlling and results in S–N cleavage exclusively.[2] This is followed by rapid further reduction resulting in formation of sulfinate and amide anions (eq 1).[3] With alkyl alkanesulfonates (**2**)

$$\underset{\mathbf{1}}{ArSO_2NR_2} \xrightarrow{e} ArSO_2^{-/\cdot} + NR_2^{\cdot/-} \xrightarrow{e} ArSO_2^- + NR_2^- \quad (1)^6$$

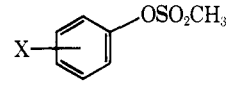
$$\underset{\mathbf{2}}{ROSO_2R'} \xrightarrow{e} \mathbf{2}^{\cdot-} \longrightarrow R\cdot + R'SO_3^- \quad (2)$$

$$\mathbf{2}^{\cdot-} \xrightarrow{e} RO^- + R'SO_2^- \quad (3)$$

$$\underset{\mathbf{3}}{(RO)_2\overset{\overset{O}{\|}}{P}{-}OAr} \xrightarrow{e} \mathbf{3}^{\cdot-} \longrightarrow (RO)_2PO^{-/\cdot} + ArO^{\cdot/-} \quad (4)^6$$

$$\mathbf{3}^{\cdot-} \xrightarrow{e} (RO)_2PO_2^{\cdot 2-/-} + Ar^{\cdot/-} \quad (5)^6$$

initial electron transfer results in a metastable substrate anion radical ($\mathbf{2}^{\cdot-}$) which, if nothing further transpires, undergoes C–O cleavage yielding alkyl radical and sulfonate anion (eq 2).[4] If, however, the concentration and/or reducing power of the electron donor is high enough, another electron is transferred and a different mode of cleavage, S–O, occurs (eq 3).[4] Recently, we have observed a slightly different version of this latter mechanism in the electron transfer reactions of aryl phosphates (**3**).[5] Here, the initial substrate anion radical ($\mathbf{3}^{\cdot-}$) undergoes P–O cleavage (eq 4), but if further reduced cleaves at the C–O bond (eq 5). In this work we wish to present an example of a sulfonyl derivative system, that of aryl alkanesulfonates (**4**), which appears to follow the reaction pattern of aryl phosphates. Also, we wish to present information on substituent effects on different steps of the reaction. Finally, we would like to propose explanations for the differences in behavior of these different classes of compounds on reductive cleavage.



4

a, X = H	h, X = *m*-CF_3
b, X = *m*-CH_3	i, X = *p*-*t*-C_4H_9
c, X = *p*-CH_3	j, X = *o*-CH_3
d, X = *m*-OCH_3	k, X = *p*-Br
e, X = *p*-OCH_3	l, X = *o*-OCH_3
f, X = *m*-Cl	m, X = *p*-C_6H_5
g, X = *p*-Cl	

Results and Discussion

Treatment of THF or DME solutions of aryl methanesulfonates with any of a wide variety of arene anion radicals results in rapid disappearance of the anion radical and formation of aryloxide and methanesulfinate ion in nearly

Table I. Rates of Reaction of Aryl Methanesulfonates with Sodium Anthracene[a]

Ester	Pseudo first-order rate, s^{-1}	Second-order rate, l./mol s	Rel rate
4f (*m*-Cl)	103.3	2065 ± 291	83.9
4a (H)	1.23	25.7 ± 3.2	(1.0)
4e (*p*-CH_3O)	0.0196	0.39 ± 0.07	0.016

[a] Concn of ester = 0.05 M; concn of sodium anthracene = $<10^{-4}$. Solvent, THF; temp 20°.

Table II. Relative Rates of Phenol Formation in Sodium Anthracene Cleavage of Aryl Methanesulfonates[a]

Ester	Rel rate[b]	Ester	Rel rate[b]
4h (*m*-CF_3)	30.0	**4c** (*p*-CH_3)	0.974
4f (*m*-Cl)	23.1	**4b** (*m*-CH_3)	0.457
4g (*p*-Cl)	9.86	**4i** (*p*-*t*-C_4H_9)	0.465
4d (*m*-CH_3O)	2.30	**4j** (*o*-CH_3)	0.372
4a (H)	(1.00)	**4e** (*p*-CH_3O)	0.313

[a] In THF at 0°. [b] Reproducibility was ±5%.

quantitative yields. Temperature, concentration, mode of mixing, structure of the sulfonate ester, and reduction potential of the electron donor have relatively little effect on the outcome of the reaction except that with anion radicals of higher reducing power (e.g., sodium naphthalene, $-E_{1/2}$ = 2.50 eV[7]) chloro or bromo groups may be partially removed from the aryl oxide and small amounts of **4** (5–15%) may be converted to the corresponding arene instead of phenol. The stoichiometry of the reaction was determined by measuring the yield of phenol obtained on treatment of solutions of **4** with known, insufficient quantities of anion radicals. "Titration plots" (yield of phenol, mmol, vs. mmol of added anion radicals) for **4b** in THF at 0° with sodium anthracene and at −78° with sodium naphthalene were quite linear up to ~100% reaction and had slopes of 0.49 and 0.47, respectively. This corresponds to anion radical: ester stoichiometries of 2.04 and 2.13, respectively, well within experimental error of the expected value of 2. From reactions with either sodium anthracene or sodium naphthalene, no more than traces of dihydroarene could be found, implying that proton abstraction by these species was not occurring.

The rate of disappearance of sodium anthracene on reaction with a few aryl mesylates was determined using a rapid mixing, stopped-flow device.[8] Data are reported in Table I. Rates of disappearance were cleanly first order in both anion radical and sulfonate ester and showed a rather large substituent effect. Though only three esters were examined a ρ value for the reaction of ca. 6.0 can be safely assumed.

The rate of disappearance of anion radical does not necessarily correspond to the rate of product formation, and so this step was examined by the somewhat cruder technique of competition kinetics.[9] In these experiments two or more esters in THF solution at 0° were treated with relatively small amounts of anion radical solution so that less than 10% of any ester was destroyed. Determination of the yield of phenol as a function of the initial concentration of its ester allows ready calculation of its relative rate of formation.[9] Data for several substituted phenyl methanesulfonates are presented in Table II. Clearly, the rates of disappearance of sodium anthracene and formation of product are not the same. The difference in the rate of anion radical disappearance between **4f** and **4e** is $\sim 5 \times 10^3$, while in the rate of phenoxide formation they differ by only a factor of 75. Using the data of Table II (except for **4j**) a value of ρ for product formation of 3.00 (r = 0.987) can be determined. The effect of changing the anion radical on the relative rate of product formation from **4b** and **4d** was also examined and the results are shown in Table III. Similar data for the competition cleavage of a pair of arenesulfonamides are also shown for comparison. It can be seen that the relative rates of cleavage of the sulfonamides are very sensitive to the nature of the electron source in keeping with the initial electron transfer being rate (and product) determining,[2] while relative rates of cleavage of the aryl mesylates are totally insensitive to this feature.

Table III. Relative Rates of Cleavage with Different Anion Radicals[a]

Anion radical	$E_{1/2}$ vs. SCE[b]	Relative rates[c] Methanesulfonates[d]	Relative rates[c] Sulfonamides[e]
Na^+ naphthalene·$^-$	−2.50	5.00	1.0
Na^+ anthracene·$^-$	−1.96	5.50	7.4
Na^+ fluoranthene·$^-$	−1.77	5.25	25.0

[a] In THF at 0°. [b] See ref 7. [c] Reproducibility was ±4%. [d] Rate of cleavage of **4d** relative to that of **4b**. [e] Rate of cleavage of *N*-methyl-*N*-phenylbenzenesulfonamide relative to that of *N*-ethyl-*N*-phenyl-*p*-toluenesulfonamide.

A kinetic scheme that would satisfy these observations is given in eq 6a–e. The key requirement is that the substrate

$$4 + \mathrm{ArH}\cdot^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 4\cdot^- + \mathrm{ArH} \quad (6a)$$

$$4\mathbf{x}\cdot^- + 4\mathbf{y} \overset{K_{yx}}{\rightleftharpoons} 4\mathbf{x} + 4\mathbf{y}\cdot^- \quad (6b)$$

$$4\cdot^- \xrightarrow{k_2} \mathrm{ArO}^{-/\cdot} + \mathrm{CH_3SO_2}^{\cdot/-} \quad (6c)$$

$$\mathrm{ArO}^{-/\cdot} + \mathrm{CH_3SO_2}^{\cdot/-} + 4\cdot^- \xrightarrow{k_3} \mathrm{ArO}^- + \mathrm{CH_3SO_2}^- + 4 \quad (6d)$$

$$\mathrm{ArO}^{-/\cdot} + \mathrm{CH_3SO_2}^{\cdot/-} + \mathrm{ArH}\cdot^- \xrightarrow{k_4} \mathrm{ArO}^- + \mathrm{CH_3SO_2}^- + \mathrm{ArH} \quad (6e)$$

anion radical have a finite lifetime and be capable of transferring an electron to another sulfonate ester (eq 6b). A fast equilibration of electrons between different esters would explain the insensitivity of the product-forming step (eq 6c) to the reducing agent. In fact, the relative rates in Table II would actually be combinations of equilibrium and rate constants:

$$\mathrm{rate_x/rate_y} = K_{xy}(k_{2x}[\mathrm{X}]/k_{2y}[\mathrm{Y}])$$

The initial step (6a) is probably also reversible but for most of the anion radicals examined equilibrium probably lies far to the right.

The sense of cleavage in step 6c is, of course, not known, but considering the relative pK_a's of phenols and sulfinic acids[10] one should probably expect phenoxy radical and sulfinate ion formation. This might also explain the relatively low ρ value for the product forming process as compared to the initial step. The equilibrium constant, K, might be expected to have a large positive value of ρ but k_2 might even have a negative value. Other reactions in which phenoxy radicals are generated often have negative reaction constants.[11] Conversion of any radicals generated in step 6c to anions by further reduction is probably a very rapid process[12] and may involve either or both $4\cdot^-$ and $\mathrm{ArH}\cdot^-$.

Bimolecular cleavage pathways for $4\cdot^-$ might also be considered (eq 7). The processes shown in (7) appear rather

Table IV. Relative Rates of Phenol Formation in Sodium Anthracene Cleavage of Aryl Ethanesulfonates[a]

Ester	Rel rate[b]	Ester	Rel rate[b]
5d (*m*-CH_3O)	1.19	**5c** (*p*-CH_3)	0.603
5a (H)	(1.0)	**5i** (*p*-*t*-C_4H_9)	0.469
5b (*m*-CH_3)	0.745	**5e** (*p*-CH_3O)	0.414

[a] In THF at 0° [b] Reproducibility was ±5%.

$$2\,4\cdot^- \xrightarrow{k_2'} 4 + ArO^- + CH_3SO_2^- \quad (7a)$$

$$4\cdot^- + ArH\cdot^- \xrightarrow{k_2''} ArH + ArO^- + CH_3SO_2^- \quad (7b)$$

unlikely since if ρ for the initial electron transfer from sodium anthracene is 6.0 the effect of substituents on introduction of a second electron should be even larger. The observed value of 3.0 does not support these cleavage mechanisms. In addition, conditions which would seem to favor double reduction of **4** (high concentrations of $ArH\cdot^-$ and high reduction potential of the reducing agent) appear to favor formation of different products (vide infra).

Aryl esters of certain other alkanesulfonic acids were examined briefly. The esters of α-toluenesulfonic acid were readily cleaved to phenoxide with either sodium naphthalene or anthracene but the reaction is complicated by the great sensitivity of the esters to base-catalyzed reactions[13a] and an apparent propensity for C–S cleavage. The ethanesulfonates (**5**), however, behaved quite similarly to the methanesulfonates but with a few puzzling differences. In competition experiments they were always two to four times more reactive than their mesylate counterparts. For example, **5b** is 1.9 times as reactive as **4b**, and **5d** is 2.7 times as reactive as **4d**. Their relative rates vs. each other are given in Table IV. From these data one can estimate a value of ρ for the product forming reaction of 1.24 (r = 0.982). Preliminary experiments suggest that the ethanesulfonates are ca. ten times as reactive as the methanesulfonates in the initial electron-transfer step. At present we have no explanation for this puzzling difference in reactivity.

The reactions of the para-halogenated mesylates (**4g** and **4k**) were examined in some detail. With sodium naphthalene under competition conditions (tenfold excess of ester) both esters yielded *p*-halophenol, dehalogenated ester, and traces of phenol. With sodium anthracene only the bromo compound yielded dehalogenated product. From the yields of different products one can estimate that the S–O/C–Br and S–O/C–Cl cleavage ratios are 1.7 and 4.9, respectively, for sodium naphthalene, and 21 and >1000, respectively, for sodium anthracene. The large differences in cleavage ratios between naphthalene and anthracene anion radicals implies that a simple competition between cleavage pathways by the mesylate anion radical (Scheme I) is not possible.[13b] The decision as to whether C–X or S–O cleavage will occur must be made in the *initial* electron transfer step (Scheme II). The choice between dissociative cleavage of the C–X bond in Scheme II and prior formation of aryl halide anion radical is not clear, but considerable evidence favors the intermediacy of the latter species in the reductive

Scheme I

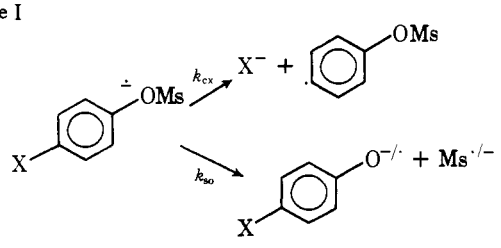
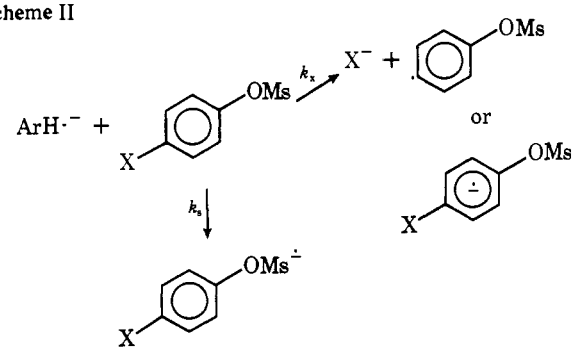


Table V. Yields of Arenes on Reduction of Aryl Methanesulfonates[a]

	Sodium naphthalene,[b] %		Sodium–liquid ammonia,[c] %	
Ester	Normal[d]	Inverse[e]	Normal[f]	Inverse[g]
4m (*p*-C_6H_5)	9	16		
4e (*p*-CH_3O)	<1	<1	68	95
4l (*o*-CH_3O)	3.5	16	77	100
4d (*m*-CH_3O)	15	20	53	65

[a] Results are averages of two or more experiments. [b] In THF at 0°; reproducibility is ca. ±5% of value quoted. [c] At −33°; reproducibility is ca. 10% of value quoted. [d] Slow dropwise addition of 0.1 M anion radical solution to a dilute (0.2 M) solution of ester. [e] Addition of ester to a large excess of ~0.7 M anion radical solution. [f] Slow addition of ~0.5 M Na/NH_3 solution in a dilute (0.05 M) solution of ester in THF. [g] Addition of ester to a large excess of 0.5 M Na/NH_3.

Scheme II

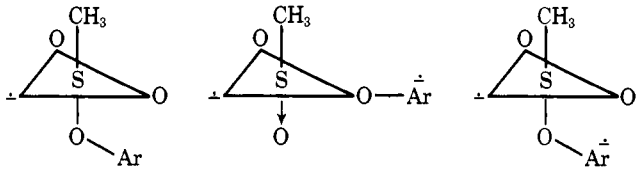


dehalogenation of many aryl halides.[14] If so, this implies that the k_s step in Scheme II (and probably k_1 in the reactions of aryl mesylates in general) must be rather intimately involved with the sulfonyl group. This set of reactions constitutes one of the few cases where all the evidence indicates that competition in mode of reaction of a small anion radical occurs because of initial placement of the extra electron.[15]

As mentioned previously, conditions that should favor double reduction of aryl phosphates (high concentration of electron donor and/or high reducing power of the donor) lead to formation of different products.[5] Thus, while reaction of **3** with sodium anthracene leads to no aryl product other than phenol, reaction with sodium naphthalene or donors of higher reduction potential leads to various amounts of arene, a product of C–O cleavage.[5] (Aryl oxides, the normal cleavage product, are quite inert toward further reaction.) Kenner and Williams noted that treatment of **4e** with sodium–liquid ammonia led to significant amounts of anisole.[16] In Table V we present data on several mesylates indicating how concentration and, particularly, reducing power of the electron donor affect the yield of arene. Variation of concentration of the electron donor does not produce as striking an effect on yield of arene as it does in the case of aryl diethyl phosphates,[5] but the effect of changing reducing power of the reagent is very large.

As in the case of phosphate esters (**3**) we feel C–O cleavage in **4** is a result of double reduction to a dianion, 4^{2-}. Admittedly, firm evidence for the existence of 4^{2-} is lacking, but it seems the most attractive way of explaining the results considering that $4\cdot^-$ clearly yields other products. One should note that S–O cleavage of 4^{2-} would have yielded two quite stable anions, phenoxide and sulfinate, yet this pathway is not followed. As in the case of **3** we believe we can explain the surprising differences in reaction of $4\cdot^-$

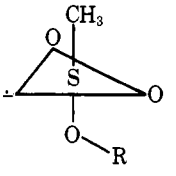
and 4^{2-} as follows: (1) Initial electron transfer is directly to the sulfur atom (except for minor amounts to the aryl ring in the cases of **4f, 4g,** and **4k**). (2) This anion radical adopts a trigonal-bipyramidal configuration with the extra electron occupying one of the basal positions. Considerable evidence for this configuration exists for many neutral and charged phosphoranyl radicals[17] and some for corresponding sulfur species.[18] Following the usual polarity rules[19] the aryloxy group would occupy an apical position as in **6.** (3) In accordance with the rules developed for phosphate ester hydrolysis,[19a] and which appear to hold for α-scission of neutral phosphoranyl radicals,[20] we postulate that the entire aryloxy group may be lost at this stage. (We should emphasize, however, that there is no evidence yet that the rules governing the entering and departure of groups from phosphorus actually apply to sulfur.) (4) Introduction of a second electron onto sulfur should be difficult and if one of the attached groups is of suitable electron affinity, e.g., the aryloxy group, it will be placed there. Such a group, now being electron rich, might migrate to a basal position as in **7,** but rates of pseudorotation about sulfur are thought to be rather slow.[3c,21] (5) If such a reduced group is in a basal position, and if the rules for phosphate ester displacements[19a] apply, then it cannot be expelled entirely but must fragment internally if it is to react at all. On the other hand, if the reduced aryloxy group remains apical (as in **8**), it may be that the expected weakening of the C–O bond brought about the negative charge in the aryl ring is sufficient to make β-scission an important, if not the preferred, course of reaction. It has been argued that for neutral phosphoranyl radicals both bond energy and stereoelectronic factors favor β-scission at an apical position.[20]



6 **7** **8**

Admittedly, this is a very simplified picture and does not take into account such effects as ion pairing, hydrogen bonding (in liquid ammonia), steric effects, etc. We hope to examine these effects in the future.

One might now consider reasons for differences in the electron transfer chemistry of other sulfonyl derivations we have examined. As noted, arenesulfonamides (**1**) appear to undergo only S–N cleavage and appear to do so in a fashion either concerted with uptake of the initial electron or very quickly thereafter.[2,3] One would achieve this situation if the lifetime of $\mathbf{1}\cdot^-$ were so short that it lacked opportunity either for equilibration with other species or for further reduction. The lesser electronegativity of N as compared to O should result in raising the energy of $\mathbf{1}\cdot^-$ relative to that of $\mathbf{4}\cdot^-$. Also, if $\mathbf{1}\cdot^-$ lasts long enough to orient itself with the S–N bond apical, one would expect this to be a weaker bond than the S–O bond in $\mathbf{4}\cdot^-$ if comparison with electronegativity effects on the strength of apical bonds in neutral sulfuranes is valid.[22] Unfortunately, studies on the exactly comparable system, $CH_3SO_2NR_2$, have yet to be made. Alkyl alkanesulfonates (**2**) definitely yield a metastable anion radical on reduction,[4] but this decomposes by C–O cleavage, rather than S–O, and on further reduction undergoes S–O cleavage. This is the reverse of the behavior of **4.** Considering electronegativities of attached groups $\mathbf{2}\cdot^-$ would almost certainly be more stable than $\mathbf{1}\cdot^-$ and may approach the stability of $\mathbf{4}\cdot^-$. The reason for C–O cleavage in $\mathbf{2}\cdot^-$ rather than S–O may be that β-scission is actually the preferred course of reaction as long as this β-bond is relatively weak. In $\mathbf{4}\cdot^-$, of course, this bond is anchored at an sp^2-hybridized carbon and such β-scission would be expected to be difficult. Further reduction of $\mathbf{2}\cdot^-$ must proceed in a manner different from that of $\mathbf{4}\cdot^-$. Likely sites for introduction of the second electron into $\mathbf{2}\cdot^-$ are the orbital that bears the odd electron and the antibonding orbital of the apical bond system.[22] Reaction at the latter site would lead directly to S–O cleavage. Increasing the electron density in the nonbonding orbital would tend to diminish s character in all other bonds to the sulfur[23] and thus probably weaken them.



$\mathbf{2}\cdot^-$

Table VI. Properties of Sulfonate Esters

Ester	Mp, °C	Lit. mp, °C
4a	61–62	61–62[a]
4b	22–24	25[b]
4c	43.5–44.5	43–44[c]
4d	(Bp 121/0.25 Torr)	*d*
4e	78.5–79	79.5–80[e]
4f	36–36.5 (bp 150/6 Torr)	(Bp 154/6 Torr)[f]
4g	68–69	68[a]
4h	7–9	*d*
4i	52.5–53.5	*d*
4j	20–22 (bp 80/0.2 Torr)	(Bp 80.5/0.2 Torr)[g]
4k	82–83	83[h]
4l	31–32.5	*d*
4m	151–152	*d*
5a	33–34	34–35[h]
5b	(Bp 104/0.15 Torr)	*d*
5c	Bp 136–137/6 Torr)	(Bp 154/13.5 Torr)[i]
5d	(Bp 135/0.25 Torr)	*d*
5e	37–40	*d*
5l	18–21	*d*

[a] O. Exner, Z. Fidlerova, and V. Jehlicka, *Collect. Czech. Chem. Commun.*, **33,** 2019 (1968). [b] R. N. Haszeldine, R. B. Heslop, and J. W. Lethbridge, *J. Chem. Soc.*, 4901 (1964). [c] J. H. Looker and D. H. Thatcher, *J. Org. Chem.*, **19,** 784 (1954). [d] Satisfactory C and H analysis (±0.4%) was reported. [e] See ref 16. [f] T. Kometani, O. Umezawa, K. Sekine, T. Oda, M. Ishiguro, and D. Mizuno, *Yakugaku Zasshi,* **84,** 237 (1964); *Chem. Abstr.*, **61,** 600 (1967). [g] See ref 13a. [h] C. Schall, *J. Prakt. Chem.*, **156,** 241 (1893). [i] O. R. Zaborsky and E. T. Kaiser, *J. Am. Chem. Soc.*, **88,** 3084 (1966).

Experimental Section

Materials and Equipment. Tetrahydrofuran (THF) was reagent grade and was dried by distillation from potassium benzophenone ketyl and stored under nitrogen. Elemental analyses were performed by the Department of Analytical Chemistry, University of Groningen, Groningen, The Netherlands. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard Model 5750 instrument equipped with flame ionization detectors, using a 10 ft × 0.125 in., 10% silicone rubber (UC-W98) on Chromosorb W, column. The NMR spectra were recorded using either a Varian A-60A instrument or an HA-100D instrument modified by a Digilab FTS-3 Fourier transform system.[24]

Sulfonate esters were prepared by treating the corresponding phenols with the appropriate sulfonyl chloride in pyridine or methylene chloride containing a slight excess of triethylamine at 0°. They were usually recrystallized from ethanol. Their properties are described in Table VI.

Table VII. Cleavage of Sulfonate Esters by Arene Anion Radicals

Sulfonate ester	Anion radical	Yield of phenol,[a] %
m-Methylphenyl α-toluenesulfonate	Naphthalene	98
4b	Naphthalene	96
5b	Naphthalene	102
4b	Anthracene	97
4c	Anthracene	99
4c	Fluoranthene	97

[a] Average of three or more determinations. Reproducibility of measurements was at least ±5%. No products of C–O cleavage were observed in these reactions.

Arene anion radical solutions were prepared and handled as described previously.[2] Their molarity was determined by quenching with water and measuring the amount of dihydroarene produced by GC.[25]

Reactions of Sulfonate Esters with Arene Anion Radicals. Titrations with sodium naphthalene and sodium anthracene were carried out as described previously for sulfonamides;[2] yields of phenol were determined by treating the reaction mixtures with an excess of bis(*N,O*-trimethylsilyl)trifluoroacetamide (BSTFA) and determining the amount of aryl trimethylsilyl ether by GC. Peak areas were determined by cutting and weighing, and *n*-alkanes were used as internal standards. The yields of phenol from complete reactions were determined as follows: approximately 0.2 mmol of sulfonate ester and ca. 0.15 mmol of *n*-decane (or other *n*-alkane) were weighed into a 4-dram vial. A small glass-covered stirring bar was then added and the vial capped with a rubber septum. Dry THF (1 ml) was then added via syringe; the vial was flushed with argon (several "evacuate and fill" cycles) and then placed in a cooling bath (sodium naphthalene reactions were usually carried out at ca. −70°, the others at 0°). Anion radical solution (0.1 to 0.2 M) was then added dropwise via syringe, with stirring, until the characteristic color persisted for at least 30 s. Any excess anion radical was then destroyed by opening the vial to the air, ca. 100 μl of BSTFA was added, and the mixture was analyzed by GC. Results for several experiments are shown in Table VII.

It was shown that unreacted sulfonate esters were stable in reaction mixtures that had been treated with BSTFA by experiments of the following type. To ca. 1.0 mmol of **4e** in 2 ml of dry THF (under argon) was added 0.5 ml of 0.15 M sodium anthracene. Next was added 100 μl of BSTFA and the resulting solution added to a solution of 0.25 mmol of **4b** and 0.19 mmol of *n*-decane in 1 ml of THF (under argon) at 0°. Analysis of this mixture after periods of up to 1 h showed no detectable *m*-methylphenyl trimethylsilyl ether. Warming the mixture at 40° for 1 h did give rise to a small amount (<2%) of the latter aryl ether. Similar control experiments showed that methane- and ethansulfonates in general were stable under these conditions but that α-toluenesulfonate esters of phenols were not. Sulfur-containing salts from the reactions were determined as follows. Phenyl methanesulfonate (0.312 g, 1.81 mmol) in 5 ml of THF under N_2 was treated with a slight excess of 0.25 M sodium anthracene at 0°. After the mixture was stirred for 10 min, 10 ml of water and 30 ml of ether were added, followed by several grams of dry ice. The aqueous layer was separated and washed twice with 30-ml portions of ether; water was then removed under vacuum. Anhydrous sodium acetate (0.0861 g, 1.05 mmol) was then added along with 3 ml of D_2O. The water was again removed under vacuum and the residue dissolved in 2 ml of D_2O and analyzed by NMR: acetate methyl (s) −117 Hz from external Me_4Si; methanesulfinate methyl (s) −23 Hz from acetate; methanesulfonate methyl (s) −56 Hz from acetate. Integration of the peaks and comparison with the acetate peak indicated 85 ± 5% of methanesulfinate and only 1–2% of methanesulfonate. Suspension of the dry salts in ethanol, addition of 0.47 g (2.2 mmol) of *p*-nitrobenzyl bromide, and heating at reflux for 3 h, yielded 0.203 g (0.946 mmol, 52%) of methyl 4-nitrobenzyl sulfone, mp 169–170 °C (chloroform) (lit.[26] 169–170 °C). A similar experiment using *p*-methoxyphenyl ethanesulfonate (**5e**) indicated a yield of 94 ± 5% of ethanesulfonate ion by NMR: triplet (J = 7.4 Hz) +50 Hz from acetate, quartet −25 Hz from acetate. Sodium ethanesulfonate (prepared by hydrolysis of the chloride) has a triplet (J = 7.4 Hz) +39 Hz from acetate and a quartet −61 Hz from acetate. Treatment of the salts from cleavage of **5e** with benzyl bromide in ethanol yielded ~60% of ethyl benzyl sulfone, mp 83–84 °C (ethanol) (lit.[27] 83–84 °C). Similar results were obtained using other arene anion radicals.

Competition Experiments. These were carried out by weighing desired amounts of competing substrates directly into either a 25-ml Erlenmeyer or a 4-dram vial. A small glass-covered magnetic stirrer was added and the vial closed with a rubber septum. Freshly distilled THF was added via syringe and the sample degassed by several evacuate and fill cycles using argon. Concentrations of individual sulfonates were in the range 0.2–1.0 M. The vial was then stirred in an ice bath for 5–10 min and the desired amount of anion radical solution (no more than enough to cleave 10 mol % of the sulfonate mixture) was then added dropwise via syringe. The reaction mixture was then immediately treated with an excess of BSTFA and analyzed for aryl trimethylsilyl ethers as described previously. It was found most convenient to run four or five different esters simultaneously, and almost all possible combinations were examined in order to ensure internal consistency of the relative rates. The data reported in Tables II, III, and IV are averages of several determinations each and were reproducible to at least ±5%.

Determination of absolute reaction rates of sulfonate esters and sodium anthracene in THF was carried out using equipment and techniques described previously.[8]

Measurement of Yields of Arene from Sulfonate Esters. For sodium naphthalene the reactions were carried out as follows. In "normal addition" a solution of ca. 0.1 M sodium naphthalene in THF was added dropwise to a solution of ca. 1 mmol of sulfonate ester in 5 ml of THF under argon. The solution was stirred rapidly and kept at about 0° (ice bath) during the reaction. After the green end point was reached, the excess anion radical was air quenched and the mixture analyzed by GC. For "inverse addition" 10 ml of ca. 0.7 M sodium naphthalene in THF was placed in a septum-sealed flask under argon and cooled to 0°. A solution of ca. 1 mmol of ester (plus internal standard) was added dropwise to the rapidly stirred anion radical solution via syringe. After addition was complete the solution was quenched with a little water, dried with magnesium sulfate, and analyzed by GC. The results from these sodium naphthalene experiments were fairly reproducible, repeat experiments usually giving results within a percent or two of the original. Some typical results were: **4d**, normal addition, 12.0% yield of anisole; inverse addition, 19.6% yield of anisole.

For the sodium–liquid ammonia experiments "inverse addition" was carried out by adding a solution of 1 mmol of sulfonate ester and 0.5 mmol of internal standard (usually ethylbenzene) in 2 ml of dry THF slowly to a stirred solution of 0.5 M sodium in liquid ammonia under nitrogen at ca. −33°. After stirring for 45 min, the ammonia was allowed to evaporate through a condenser, 10 ml of THF was added to the residue, and the resulting solution was analyzed by GC. For "normal addition" about 10 mmol of sodium was dissolved in 50 ml of liquid ammonia that was maintained in a dry ice jacketed dropping funnel. This was then added as slowly as possible to a stirred solution of 0.5 mmol of sulfonate ester and 0.4 mmol of ethylbenzene in 10 ml of dry THF under nitrogen. After addition was complete the ammonia was allowed to evaporate through a condenser and the residual solution analyzed by GC. Some typical results were: **4e**; inverse addition, 99% yield of anisole; normal addition, 69% yield of anisole.

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Structural Effects in Solvolytic Reactions. 14. Solvolysis of the 2-Aryl-2-benzonorbornenyl *p*-Nitrobenzoates. Application of the Tool of Increasing Electron Demand as a Test for π Participation in the High Exo:Endo Rate Ratios[1]

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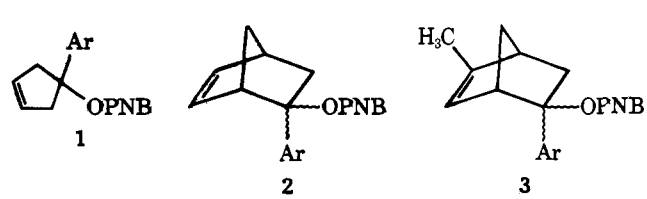
Abstract: 2-Aryl-2-benzonorbornenyl *p*-nitrobenzoates containing representative substituents in the 2-aryl ring were synthesized and their rates of solvolysis in 80% aqueous acetone determined. The exo:endo rate ratios observed are 3300 for *p*-CH_3O; 2900 for *p*-H, 2700 for *p*-CF_3, and 2800 for 3,5-$(CF_3)_2$. Thus the exo:endo rate ratio fails to exhibit any increase with increasing electron demand as anticipated for π participation as a factor in this ratio. The $\rho^+\sigma^+$ treatment reveals excellent linear correlations, with ρ^+ of −4.50 for the exo isomers and −4.51 for the endo isomers. The essential constancy of the exo:endo rate ratios with increasing electron demand is consistent with a mechanism involving no significant π participation in the transition state for the solvolysis reaction. It appears, therefore, that the high exo:endo rate ratio of approximately 3000 must arise from major steric difficulties in the ionization of the endo isomer.

The tool of increasing electron demand[3] offers promise of providing an unambiguous answer as to the importance in various systems of π or σ participation on the observed rates of solvolysis. Accordingly, we have undertaken an extensive program of testing this tool in the hope of establishing its reliability so that it could be applied to answer the vexing question of the importance of σ participation in the solvolysis of 2-norbornyl derivatives.[4]

We demonstrated that the tool could detect even small effects, as small as 1% of that postulated to be present in the 2-norbornyl system.[5] It provided an unambiguous answer as to the importance of σ electronic contributions in stabilizing the 3-nortricyclyl cation in solvolytic processes,[6] resolving conflicting proposals in the literature.[7]

Recently, we applied the tool to test for the importance of π participation in three closely related systems (**1**,[8] **2**,[9] **3**[10]).



1 **2** **3**

The results reveal the complete absence of π participation in **1**, in complete agreement with the earlier conclusion of Bartlett and Rice based on rate data for the solvolysis of the corresponding secondary derivative.[11]