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Substituent Effects on Reductive Cleavage of *N*-Methylarenesulfonanilides. Cleavage by Sodium Anthracene and Electrochemically at the Vitreous Carbon Electrode

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The relative rates of cleavage of ten para-substituted *N*-methylbenzenesulfonanilides by sodium anthracene in tetrahydrofuran at 25 °C were determined. The rates of those with less electronegative substituents (*p*-dimethylamino through *p*-fluoro) give a moderately good correlation with σ constants, $\rho = 1.91$ ($r = 0.987$). More strongly electron-withdrawing substituents, however, result in a cleavage rate much slower than expected due to reduction of the substituent rather than of the sulfonyl group. Electrochemical reduction in acetonitrile solution at a vitreous carbon electrode proceeds via an irreversible two-electron process. The peak potentials of all the sulfonamides give an excellent correlation with σ^n constants, $\rho = 1.07$ V ($r = 0.995$). Whether this is an eec or ece process is discussed, as well as possible causes for the large differences between homogeneous and electrochemical reduction. A suggested value of σ^n for the *p*-methanesulfinyl group is +0.54.

Arenesulfonamides of secondary amines have been investigated in considerable detail with respect to their reductive cleavage reactions.[2-6] Manousek, Exner, and Zuman showed that 4-cyanobenzenesulfonamide undergoes electrochemical cleavage in aqueous solution at the carbon–sulfur bond (eq 1),[5] while Cottrell and Mann observed only S–N cleavage in

$$ArSO_2NH_2 + 2e + H^+ \rightarrow ArH + {}^-SO_2NH_2 \xrightarrow{H_2O} HSO_3^- + NH_3 \quad (1)$$

electrochemical reduction of several arenesulfonamides in acetonitrile.[4] They proposed an irreversible, two-electron reduction followed by rapid cleavage to two anions (eq 2).

$$ArSO_2NR_2 \xrightarrow{2e} ArSO_2NR_2^{2-} \rightarrow ArSO_2^- + {}^-NR_2 \quad (2)$$

Asirvatham and Hawley noted that Cottrell and Mann's results could also be explained by either the *ece* mechanism shown in eq 3, where the nitrogen- or oxygen-centered radical

$$ArSO_2NR_2 \xrightarrow{e} (ArSO_2NR_2)^{-\cdot} \longrightarrow \begin{cases} ArSO_2^- + \cdot NR_2 \\ \text{or } ArSO_2\cdot + {}^-NR_2 \xrightarrow{e} ArSO_2^- + {}^-NR_2 \end{cases} \quad (3)$$

would be rapidly reduced at a potential less cathodic than that of the initial reduction, or by a rate-determining disproportionation process (eq 4).[5] Either of these processes would

$$2(ArSO_2NR_2)^{-\cdot} \xrightarrow{slow} ArSO_2NR_2^{2-} + ArSO_2NR_2 \xrightarrow{fast} ArSO_2^- + {}^-NR_2 \quad (4)$$

account for the products and n values reported.[4] The only arenesulfonamide of a secondary amine (*N*,*N*-dimethylnitrobenzenesulfonamide) examined by Asirvatham and Hawley, however, underwent reversible, stepwise reduction, yielding the corresponding dianion.[5] Cleavage to amine was not reported.[5]

Kovacs and Ghatak reported that sodium–liquid ammonia reduction of tosylamides leads primarily to C–S cleavage, similar to the results of Manousek et al.,[5] but with a minor pathway involving S–N cleavage.[2] From their data it was not possible to ascertain more information on the mechanism of cleavage. One might expect that reduction of arenesulfonamides with arene anion radicals in ether solvents might proceed in a fashion similar to that in liquid ammonia, but our earlier work using sodium biphenyl, naphthalene, and anthracene in tetrahydrofuran (THF) and dimethoxyethane (DME) showed only the occurrence of S–N cleavage.[3] In addition though we found that the selectivity of cleavage of arenesulfonamides in competition experiments was quite different for sodium anthracene vs. sodium naphthalene.[3] This observation rules out a disproportionation mechanism similar to eq 4 and would be best explained by a mechanism similar to eq 3, where the initial electron transfer is rate determining. Further study of the relative reactivities of different sulfonamides toward sodium anthracene, which would have been useful in refining the cleavage mechanism, was hampered by poor reproducibility.

In this work we wish to present a study of the relative rates of cleavage of a series of *N*-methylarenesulfonanilides by sodium anthracene in THF, a cyclic voltammetric study of the redox behavior of the same series of sulfonamides using the vitreous carbon electrode in acetonitrile, and a discussion of the similarities and differences of these two types of reduction.

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Table I. Relative Rates of Aniline Formation in Sodium Anthracene Cleavage, and Peak Potentials for S–N Reduction of *N*-Methylarenesulfonanilides

Sulfonanilide[a]	Registry no.	Relative rate[b]	*E* vs. SCE (V)[c]
1 (H)	90-10-8	1.0	−2.45
2 (CH_3S)	64999-90-2	1.04	−2.33
3 (CH_3)	599-62-2	0.54	−2.59
4 (F)	360-09-8	0.92	−2.43
5 (Cl)	16358-34-2	1.2[d]	−2.24
6 (Br)	64999-91-3	*d*	−2.26
7 (CH_3O)	16358-36-4	0.19	−2.63
8 [$(CH_3)_2N$]	53973-86-7	0.024	−2.71
9 (CH_3SO)	64999-92-4	0.63	−2.04[e]
10 (CN)	64999-93-5	0.60	−1.76[f]
11 (NO_2)	64999-94-6	0.078	−1.68[g]
12 (CH_3)[g]		0.45[h]	

[a] The para substituent is given in parentheses. [b] Reproducibility was ±5%. [c] Peak potential was measured in the cyclic voltammetric scans on 10^{-3}–5×10^{-3} M solutions of sulfonamide in 10^{-1} M $TBAPF_6$ in acetonitrile at a scan rate of 200 mV/s. [d] Dehalogenation occurred in competition with S–N cleavage. [e] Exhibited irreversible peak at −2.73 V as well. [f] Exhibited reversible peak at −2.37 V in addition. [g] Also exhibited reversible peak at −0.86 V. [h] Relative rate for *N*-ethyl-*p*-toluenesulfonanilide was used as a reference compound.

Results

Cleavage with Sodium Anthracene. Originally we had tried to determine the relative rates of cleavage of different sulfonamides by straightforward competition techniques,[7] which worked well in a similar study of the reductive cleavage of aryl alkanesulfonates.[8] This technique, adding a small amount of anion radical solution to a solution containing an excess of two or more sulfonamides and determining the amount of reaction of each by measuring the yields of the different amines, easily showed the great differences in selectivity between sodium naphthalene, sodium pyrene, and sodium anthracene.[3] Attempts to obtain reproducible relative rate data with sodium anthracene, however, were unsuccessful until it was discovered that the selectivity was very sensitive to sodium ion concentration.[8] It was found that adding a quantity of sodium salt (sodium perchlorate) about equal to the total concentration of sulfonamides (ca. 0.2 M) in the competition mixture allowed quite reproducible results to be obtained. Without this sodium ion buffer not only was reproducibility quite poor, but selectivity between different sulfonamides also appeared to be much lower. The poor reproducibility in the absence of sodium buffer is probably a result of rapidly changing reaction rates as the sodium ion concentration changes from 0 to ca. 0.04 M during the competition experiment.

The cause of this effect is almost certainly related to the state of ion pairing of the anthracene anion radical in THF. Both ESR and conductimetry data have shown that sodium anthracene is largely ion paired in THF,[10,11] and it is to be expected that ion-paired species should be less reactive (and therefore more selective) toward electron-transfer reactions than free ions.[12] An attractive explanation for our results would be that free anthracene anion radical is present at very low sodium anthracene concentrations and cleaves sulfonamides in a much less discriminating fashion than do ion-paired species; buffering with sodium perchlorate merely keeps the equilibrium shifted toward ion-paired species throughout the competition experiment. On the other hand, Bank and Bockrath, through a kinetic analysis of the effect of sodium tetraphenylboron on the rate of reaction of sodium anthracene with water in THF, ruled out the presence of significant amounts of free anthracene ions in concentrations as low as 5×10^{-5} M.[13] Obviously, further work is necessary to define the role of sodium ion in these reactions.

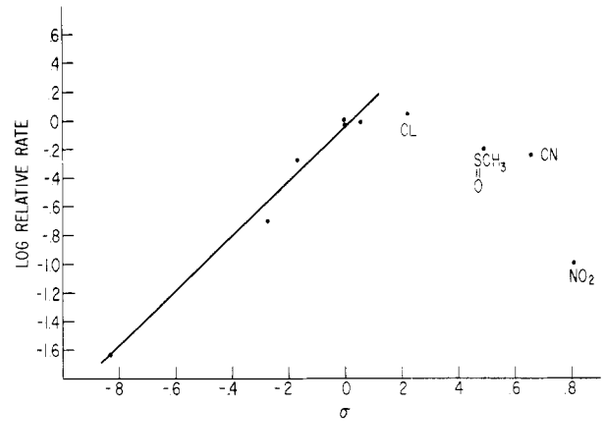
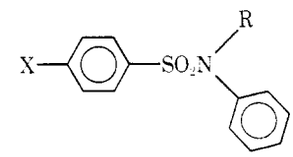


Figure 1. Plot of log of relative rates of sulfonamide cleavage by sodium anthracene vs. σ constants. Least-squares slope for the first portion, 1.91; correlation coefficient, 0.987.

Arenesulfonanilides **1–12** were prepared by standard

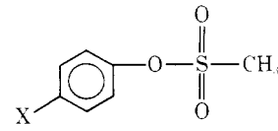


1, X = H; R = CH_3
2, X = SCH_3; R = CH_3
3, X = CH_3; R = CH_3
4, X = F; R = CH_3
5, X = Cl; R = CH_3
6, X = Br; R = CH_3
7, X = OCH_3; R = CH_3
8, X = $N(CH_3)_2$; R = CH_3
9, X = $S(O)CH_3$; R = CH_3
10, X = CN; R = CH_3
11, X = NO_2; R = CH_3
12, X = CH_3; R = CH_2CH_3

techniques, and their relative rates of reaction with sodium anthracene at 25 °C in THF in the presence of 0.04 M sodium perchlorate were determined by competition techniques. The relative rate data for all but **6** are presented in Table I.

From the data in Table I it can be seen that neither strong electron-donating nor electron-withdrawing substituents accelerate the rate of cleavage. Indeed, the two least reactive compounds (toward cleavage) are those with dimethylamino and nitro substituents. For the electron-donating substituents (including fluorine), a Hammett plot may be obtained using σ constants, with a ρ value of +1.91 (r = 0.987). Use of either σ^n or σ^0 gave definitely poorer fits (r = 0.713 and 0.957, respectively). No good correlation of the rates of the sulfonamides with electron-withdrawing substituents could be obtained with any of these substituent parameters (see Figure 1).

The value of ρ is lower than that observed for either of the two steps in S–O cleavage of aryl methanesulfonates (**13**) with sodium anthracene (ca. +6 for the initial electron-transfer step and +3.0 for the product-forming step).[8] The initial electron-transfer step in the cleavage of **13** is closest in nature to



13

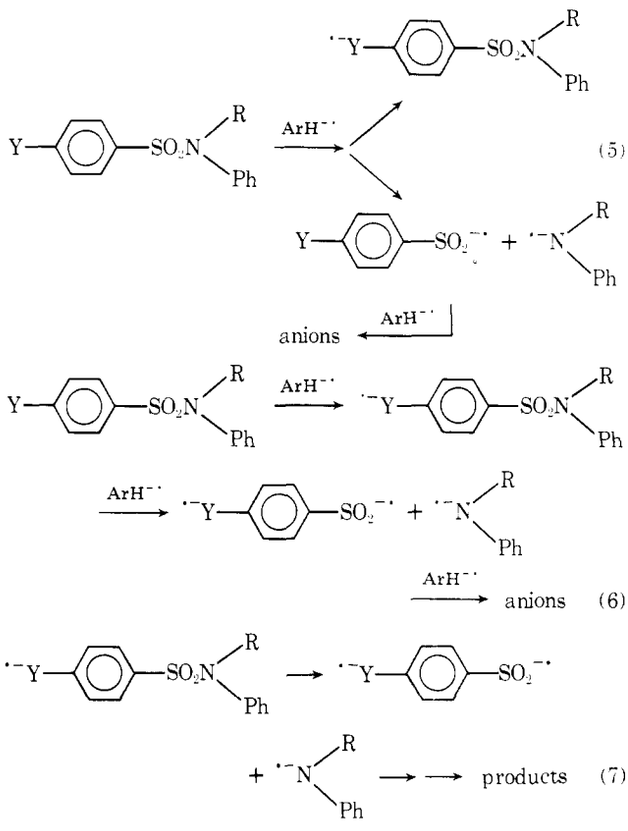
the rate-controlling step in sulfonamide cleavage, and the large difference in reaction constant is striking. In **13** the substituent is also insulated from the sulfonyl group by an additional oxygen atom, which might be expected to attenuate the substituent effect. Probably the best explanation for the large

difference in ρ is that the methanesylfonyl group is inherently less easily reducible than an arenesulfonyl group (alkyl methanesulfonates are not reduced by sodium anthracene but alkyl arenesulfonates are;[14] likewise, anthracene anion radical readily cleaves arenesulfonanilides,[3] but methanesulfonanilides react slowly via a proton-abstraction process[15]), and thus the transition state occurs earlier on the reaction coordinate for the sulfonanilide reaction.

In the case of the *p*-chlorosulfonamide **5** it was shown that dehalogenated, uncleaved sulfonamide **1** was present in the reaction mixture after the competition experiment was performed. This competition between C–Cl and S–N cleavage is similar to that observed between C–X and S–O cleavage in the reaction of halogenated versions of **13** with arene anion radicals[8] and certainly causes the measured reactivity to be less than expected. The bromine-substituted sulfonamide **6** would be expected to be more prone to this side reaction and was not examined. Pertinent to this is the fact that titration plots (yield of amine vs. amount of anion radical added) of **5** and **6** with sodium anthracene in 1,2-dimethoxyethane (DME) solution gave slopes of 0.42 and 0.24, respectively, rather than the value 0.5 expected for 1:2 stoichiometry.[3] This would imply that **5** undergoes some dechlorination prior to S–N cleavage, but that the *p*-chlorobenzenesulfinate ion is fairly stable toward further reaction under these conditions. In the case of **6** the data are probably best interpreted as indicating almost equal reactivity of the C–Br and S–N bonds, with the reactivity of the C–Br bond in *p*-bromobenzenesulfinate ion being considerably less reactive. (The titration plots were measured only to about 30% of the total theoretical yield of amine. At higher extents of reaction one would expect complications due to the buildup of halogenated sulfinate ion and increasing amounts of reaction of this with the electron donor.)

The other sulfonamides with electronegative substituents (**9, 10,** and **11**) are also almost certainly undergoing reduction of the substituent in competition with the cleavage reaction at the sulfonyl center. The cleavage that is observed may be occurring by either or both of the mechanisms outlined in eq 5 and 6. In eq 5, amine anion is produced in competition with reduction of the substituent in the initial electron transfer; in eq 6, amine anion is generated in a second reduction of the substrate which now bears a negatively charged substituent. This latter sort of electron transfer would be expected to be rather slow since the substituent should now be electron releasing. (It has been reported that the σ^0 constant of a *m*-nitro group changes from +0.70 to about −0.16 upon one-electron polarographic reduction.[16]). A third possibility, use of the electron already in the substituent for a subsequent cleavage reaction at the sulfonyl center (eq 7), might also be considered. In order for this to result in a lesser yield of amine than expected, the cleavage step would either have to have a rate as slow as the time scale of the experiment (a few minutes) or be in competition with other reactions of the reduced substituent.

Some preliminary experiments carried out on sulfonamide **11** with the more potent electron donor sodium naphthalene are pertinent to the question of the cleavage step of **11**. Titration of **11** with sodium naphthalene in DME at 25 °C required ca. 4.7 mmol of anion radical to produce 0.8 mmol of *N*-methylaniline from 1.0 mmol of sulfonamide. Further addition of sodium naphthalene did not increase the yield. A plot of yield of amine vs. amount of anion radical added gives a rather scattered set of points, but some amine is clearly formed after addition of quite small amounts of electron donor. This early production of amine would seem to favor the mechanism given in eq 5. The continued production of amine and the abnormal stoichiometry (the slope of the plot is about 0.2 rather than the expected value of 0.5[3]) would better fit the



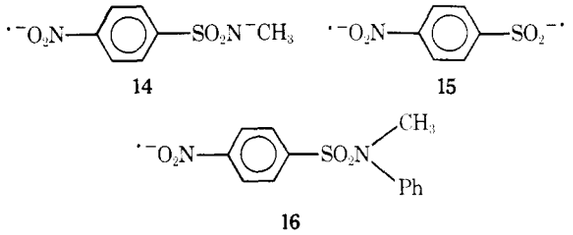
(5)

(6)

(7)

mechanism given in eq 6. (Much anion radical is probably also used up on a variety of other reduction processes typical of aryl nitro groups.[17]) About all that can be concluded is that the pathway of eq 6 almost certainly occurs, but some reaction may be occurring via that of eq 5. The process shown in eq 7 appears very unlikely.

The deep red solution resulting from reaction of **11** with about 2 equiv of sodium naphthalene in DME at 25 °C was examined by ESR and found to give a rather poorly resolved nine-line spectrum. This could be interpreted in terms of hyperfine splittings due to one nitrogen ($a_N \sim 9.6$ G) and a pair of equivalent hydrogens ($a_H \sim 3.2$ G). The poor resolution and broadness of some of the peaks suggest the presence of two or more structurally similar paramagnetic species. Asirvatham and Hawley reported that the hyperfine coupling constants for the ion radicals **14** and **15** were $a_N = 9.41$ G, a_{o-H}



14 **15**

16

= 3.33 G, and $a_{m-H} = 1.06$ G, and $a_N = 10.02$ G, $a_{o-H} = 3.33$ G, and $a_{m-H} = 1.07$ G, respectively.[5] It would seem reasonable that our ESR signal might well be the result of a mixture of **15** and **16**.

Cleavage via Electrochemical Reduction. The same series of sulfonamides was examined by cyclic voltammetry, using a vitreous carbon electrode in acetonitrile and tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. Several other electrode–solvent systems were examined, but this combination seemed superior, exhibiting an electrochemical window of +1 to −3.0 V vs. SCE.

Most of the sulfonamides showed no electrochemical ac-

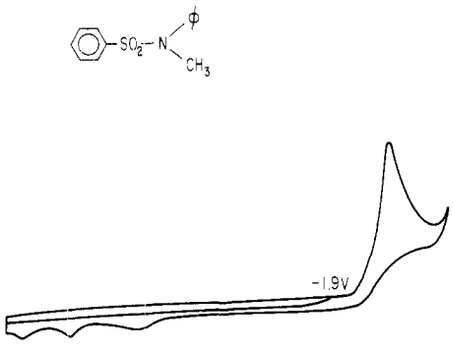


Figure 2. Cyclic voltammogram of *N*-methylbenzenesulfonanalide in acetonitrile with $BTAPF_6$ (0.2 M) as the supporting electrolyte. Scan rate, 200 mV/s; scan direction, negative; initial potential, +1.00 V; final potential, −2.90 V; range, 1 MA.

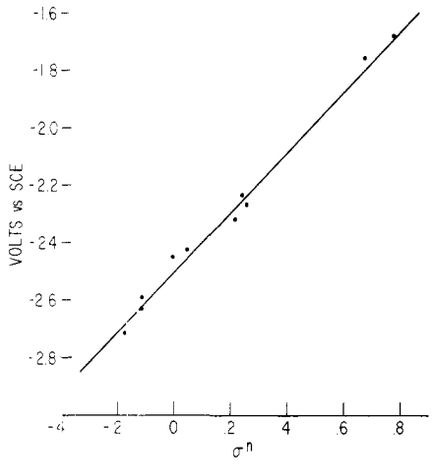


Figure 3. Plot of sulfonamide peak potentials vs. σ^n constants. Least-squares slope, 1.07 V; correlation coefficient, 0.995.

tivity until a single irreversible reduction wave was observed in the vicinity of −2.0 V vs. SCE. On reversal of the scan, oxidation peaks could be observed. Through comparison with known samples, these peaks could be identified as being due to *N*-methylaniline and arenesulfinate ions, the expected cleavage products. A sample scan for **1** is shown in Figure 2. Sulfonamides **5**, **6**, **9**, and **10** exhibited somewhat different behavior. The scans of **5** and **6** were rather similar to that of **1** except that the areas and shapes of the reduction peaks were inconsistent with a two-electron process as judged by comparison with known two-electron reductions.[18] Reductive dehalogenation was suspected and proved by showing that *p*-bromobenzenesulfinate ion undergoes an irreversible reduction at a potential very close to that of **6**. Therefore, this increase in peak area is probably due to overlapping of the S–N and C–X reduction waves. The methanesulfinyl- and cyano-substituted sulfonamides **9** and **10** also exhibited irregularities. The scan of **9** exhibited two irreversible waves at −2.04 and −2.73 V. Reversal after the first peak showed the usual oxidation waves due to methylaniline and sulfinate salt, so this one can be assigned to reductive cleavage of the sulfonamide group; the peak at the more negative potential is probably due to reduction of the methanesulfinyl moiety. The cyano compound **10** showed an irreversible peak at −1.76 V due to S–N cleavage, followed by a reversible wave at −2.37 V. This is similar to the electrochemical behavior of several *p*-cyanobenzenesulfonamides reported by Cottrell and Mann,[4] and we attribute the second wave to reversible reduction of *p*-cyanobenzenesulfinate ion as did these authors. The cyclic voltammogram of the nitro-substituted compound

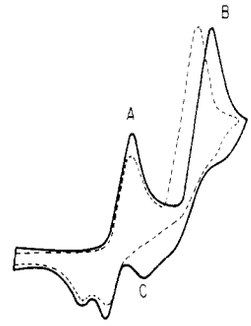


Figure 4. Cyclic voltammogram of *N*-methyl-*p*-nitrobenzenesulfonamide in acetonitrile with $TBAPF_6$ (0.2 M) as the supporting electrolyte; initial potential, 0.0 V; final potential, −2.0 V; scan rate, etc., as in Figure 2. Peak A, reduction of nitro group; peak B, reductive cleavage of S–N bond; and peak C, oxidation of nitrobenzenesulfinate dianion radical. Dashed curve is the cyclic voltammogram in presence of 0.18 M water.

11 also showed unusual features, but this will be discussed later.

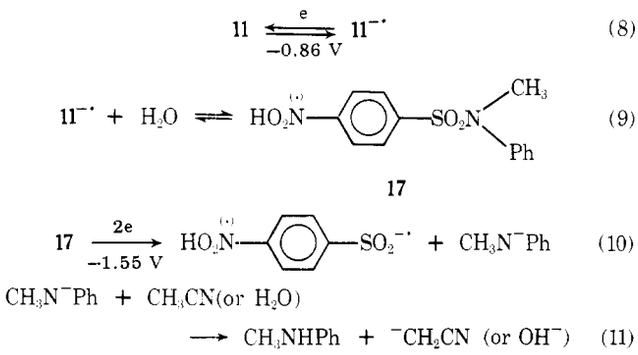
The peak potentials for S–N cleavage of the sulfonanilides are given in Table I. In all cases except for those of **5** and **6** this peak was shown by means of dc pulse polarographic techniques[19] and controlled potential electrolysis to have a current density corresponding to $n = 2$. In Figure 3 the peak potentials are plotted vs. σ^n. This yields a "reaction constant" of "ρ" = 1.07 V, with an excellent correlation coefficient of 0.995. (Although plotted in Figure 3, the value for the nitro compound **11** was not used in determining "ρ", for reasons to be discussed later.) Correlation of peak potentials with σ and σ^0 gave somewhat poorer fits (r = 0.939 and 0.973, respectively). At the time of printing, no literature value for the σ^n constant for the *p*-CH_3SO group could be found. From our data a value of 0.54 can be postulated. This is a reasonable value considering that the methanesulfinyl group is less electronegative than is the methanesulfonyl group,[20] for which a $\sigma^n{}_p$ value of 0.686 has been established.[21]

The nitro-substituted compound **11** undergoes a one-electron reversible reduction at −0.86 V vs. SCE, followed by a two-electron irreversible wave at −1.68 V. The magnitude of the oxidation peaks at −1.1 and −0.45 V are dependent on the scan rate and the final potential of the scan. A typical cyclic voltammogram of **11** is shown in Figure 4. Addition of water (0.18 M) to the system alters the scan by causing oxidation peak C to disappear and the position of peak B to shift to a less negative potential. When alumina is added peak C reappears and B reverts to its original position. Peak C has been attributed to oxidation of the anion radical of *p*-nitrobenzenesulfinate ion (**15**).[5] In the presence of water, protonation of the reduced nitro group would seem feasible, and the resulting species (**17**) would not be expected to be oxidized at the same potential. Scheme I is proposed to account for the behavior of **11** in the presence of a proton donor.

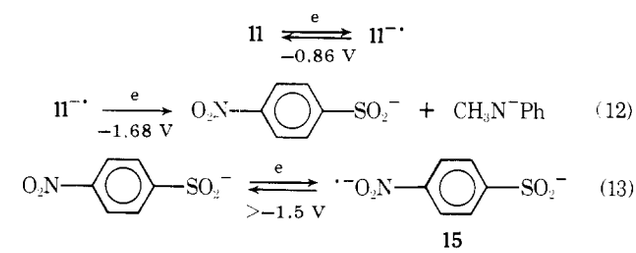
If step 9 is fast and equilibrium lies far to the right, the potential necessary for cleavage of the N–S bond should occur at a less negative value. In the absence of a proton donor we postulate the sequence of steps shown in Scheme II. The second irreversible reduction wave was shown to involve the transfer of two electrons. Since reduction of *p*-nitrobenzenesulfinate has been reported to occur at −1.10 V (in DMF), it would probably be reduced as rapidly as formed and give rise to the observed consumption of two electrons (step 13) and the appearance of oxidation peak C on reversal of polarity.

The above argument would indicate an eec (e) process for electrochemical cleavage of **11**, and the question arises as to whether this is general for this class of sulfonanilides. It has

Scheme I



Scheme II



been argued that a distinction cannot be made between an eec and an ece mechanism for this sort of reaction,[5] but the evidence seems fairly good for our interpretation of the electrochemistry of **11**. Two possibilities seem to exist. One is that the other sulfonamides are reacting by ece processes, and it is fortuitous that the σ^n_p constant of $NO_2^{-\cdot}$ is very close to that of NO_2. This seems rather unlikely. The other is that all are undergoing eec reactions, but in the process of introducing the second electron into $11^{-\cdot}$, the first electron is somehow "moved" from its low energy position in the nitro group into the vicinity of the sulfonamide group, and the full inductive effect of the nitro group comes into play. This sounds even more tortured. If nothing else, our results should serve as a warning toward making general conclusions from electrochemical data obtained from compounds in which nitro groups are present.

Comparison of Homogeneous and Electrochemical Reduction. In general, the data obtained from the sodium anthracene reactions support the originally proposed mechanism, and the correlation of reactivities with Hammett σ constants appears to be typical of these sorts of reactions. Of practical significance, there is no benefit in ease of cleavage derived from introducing substituents more electronegative than hydrogen. Introduction of such substituents merely diverts a portion of the reaction into reduction of the substituent itself, which usually results in making S–N cleavage more difficult. In contrast, the vitreous carbon electrode appears to be much more selective for reduction of the sulfonamide function. In practical terms, even its curious behavior with respect to **11** does not impair its usefulness for regenerating amine from sulfonamide.

An even more striking difference is the correlation of the electrochemical peak potentials with σ^n rather than σ. Particularly noticeable are the data for the *p*-dimethylamino group, which fall extremely close to the correlation line in both Hammett plots; yet, the difference between its σ and σ^n constants is 0.66 units. We thus feel that there is an important difference in reaction mechanism between the two processes. One attractive explanation is that while sodium anthracene reacts with a normal moderately solvated sulfonamide, where the effect of a para substituent will be the usual mix of resonance and inductive interactions, the electrochemical results are probably attributable to heterogeneous surface phenomena at the graphite electrode. If the main site of interaction is the aromatic ring, as might seem reasonable for a vitreous carbon electrode, this may disrupt resonance interactions between substituent and sulfonyl group, while still allowing modest inductive effects.

Table II. Properties of Para-Substituted *N*-Methylbenzenesulfonanilides

Substituent	Mp, °C	Lit. mp, °C
H (**1**)	79–79.5	79[a]
CH_3S (**2**)	80–81	*b*
CH_3 (**3**)	92.5–93.5	94[a]
F (**4**)	65.7–66	67[c]
Cl (**5**)	95–95.4	*b*
Br (**6**)	93–94.5	92[d]
CH_3O (**7**)	109–110.3	109–110[e]
$(CH_3)_2N$ (**8**)	132–133	132–133[f]
CH_3SO (**9**)	101.5–102.5	*b*
CN (**10**)	113–114	*b*
NO_2 (**11**)	131–132	*b*
CH_3 (**12**)[g]	84.5–85	87[a]

[a] Z. Rappoport, "Handbook of Tables for Organic Compound Identification", 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, Table XVIII. [b] Satisfactory analytical data (±0.4% for C, H) were reported for these new compounds. [c] R. Nodzu, T. Osaka, H. Kitano, and K. Fukui, *Nippon Kagaku Zasshi*, **76**, 775 (1955); *Chem. Abstr.*, **51**, 17793 (1957). [d] C. S. Marvel and F. E. Smith, *J. Am. Chem. Soc.*, **45**, 2696 (1923). [e] S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson, and P. Wriede, *ibid.*, **89**, 5311 (1967). [f] S. J. Shafer and W. D. Closson, *J. Org. Chem.*, **40**, 889 (1975). [g] *N*-Ethyl derivative.

Experimental Section

Materials and Equipment. Tetrahydrofuran (THF) was reagent grade and was dried by distillation from lithium aluminum hydride and stored under nitrogen. Acetonitrile was spectroscopic grade and was dried either with molecular sieves or alumina before use. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard Model 5750 instrument equipped with flame ionization detectors, using a 6 ft × 0.125 in, 10% silicone rubber (UC-W98) on Chromosorb W column. Triangular wave stationary electrode cyclic voltammetry was performed on a Princeton Applied Research Model 170 electrochemical system using a three-electrode system fitted with a grid to keep the electrodes in the same juxtaposition to maximize the reproducibility of the results. A vitreous carbon or a 2-mm diameter platinum sphere was used as the working electrode. An aqueous saturated calomel electrode was used throughout as the reference. A scan rate of 200 mV/s was employed in obtaining the cyclic voltammograms. The ESR spectra were obtained using a Varian V-4502 PER instrument.

Arene anion radical solutions were prepared and handled as described previously.[3] Their molarity was determined by quenching with water and measuring the amount of dihydroarene produced by GC.[22]

Sulfonamides were prepared by standard techniques from commercially available sulfonyl chlorides and amines, except in the cases noted below. Their properties are described in Table II.

***N*-Methyl-*p*-methanesulfinylbenzenesulfonanilide (9)** was prepared from the corresponding *p*-methylthio compound **2** as follows. To 0.60 g (2.04 mmol) of **2** dissolved in 5 mL of dichloromethane under a nitrogen atmosphere was added 0.49 g (2.16 mmol) of 85% technical grade *m*-chloroperbenzoic acid dissolved in 5 mL of dichloromethane. The mixture was stirred at 22 °C for 40 min, and then 2 mL of 10% aqueous sodium sulfite was added. The mixture was washed with 5% sodium bicarbonate solution until the aqueous extracts remained basic. The organic layer was then dried, the solvent removed under reduced pressure, and the residual solid recrystallized from ethanol, yielding 0.40 g (1.29 mmol, 64%) of white crystals, mp 101.5–102.5 °C.

***N*-Methyl-*p*-cyanobenzenesulfonanilide (12)** was prepared from the corresponding bromo compound **6** after the manner of Friedman and Shechter.[23] A mixture of 8 g of **6** (0.024 mol) and 2.45 g (0.027 mol) of cuprous cyanide was reflexed for 5 h in 20 mL of dimethylformamide. The mixture was then poured into a solution of

Table III. Titration of N-Methyl-p-chlorobenzenesulfonanilide with Sodium Anthracene in DME at 25 °C

Sodium anthracene, mmol	Yield of N-methylaniline,[a] mmol	Amine/electron-donor ratio
0.308	0.129	0.419
0.532	0.222	0.417
0.720	0.331	0.460
0.910	0.364	0.400
		(0.42 ± 0.01)[b]

[a] Each sample contained 1.23 mmol of sulfonamide in 10 mL of DME. [b] Average value of ratio.

0.6 g of ferric chloride in 17 mL of 1.7 M hydrochloric acid. Extraction with benzene, drying, and concentration yielded a brown material which was purified by liquid chromatography on silica gel (dichloromethane eluent). Recrystallization from ethanol yielded 3.3 g (0.012 mol, 50%) of tan crystals, mp 113–114 °C.

Sodium p-bromobenzenesulfinate was prepared from p-bromobenzenesulfonyl chloride after the manner of Whitmore and Hamilton.[24] A 62% yield of white crystals, mp 370 °C dec, was obtained by crystallization from water.

Tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) was prepared by a modification of the procedure reported by Ferguson.[25] To a stirred solution of 100 g of tetra-n-butylammonium iodide in 700 mL of acetone was slowly added a solution of 50 g of ammonium hexafluorophosphate in 175 mL of acetone. The resulting solution was filtered to remove some of the precipitated ammonium iodide, and then ca. 1 L of water was slowly added to precipitate the $TBAPF_6$. The resulting salt was collected on a filter funnel and washed several times with water. It was then redissolved in 250 mL of acetone along with 5 g of ammonium hexafluorophosphate and reprecipitated by the slow addition of ca. 150 mL of water. The material was collected by filtration and then recrystallized from ethanol–water. The white solid was dried under vacuum (0.5 mm) at 100 °C, affording 75 g (72%) of product, which was used without further treatment.

Competition experiments were carried out by dissolving a total of 0.4 mmol of an N-methylsulfonamide and the reference compound 12 in 2 mL of dry THF, which also contained 0.4 mmol of dry sodium perchlorate and ca. 0.02 mmol of n-decane, used as an internal standard. The reaction vial was then sealed with a septum and deoxygenated by alternately evacuating and filling with nitrogen. To the stirred solution, at 25 °C, was added slowly ca. 0.44 mL of 0.18 M sodium anthracene solution. After several minutes a few drops of water were added, and the mixture was analyzed by GC. All results are the average of two or more determinations; reproducibility was at least ±5%.

Titrations of sulfonamides with anion radical solutions were carried out in the manner described previously.[3] The data for a typical titration plot are given in Table III.

Electrochemical experiments were carried out as follows. A solution of 0.2 M $TBAPF_6$ in acetonitrile was prepared immediately before use. Using this solution, an amount of sulfonamide was added to give a concentration of 4×10^{-3} M. All measurements were carried out under a nitrogen atmosphere and are the average of three or more determinations. A reference voltammogram of anthracene was run at the start and finish of each series of measurements to ensure against any drift in potential. A scan rate of 200 mV/s was employed.

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Addition of Halogens to Cyclopropylacetylene

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The halogenation of cyclopropylacetylene (1) with chlorine, bromine, trichloramine (NCl_3), and iodobenzene dichloride (IBD) is reported. Chlorine reacts with 1 primarily by an ionic pathway, while bromine can react by either an ionic or radical methanism. IBD and NCl_3 were found to react only by a radical process. The reactivity of 1 with these halogenating reagents is used to make some statements about the relative energy of the transition states in these reactions.

Chlorine (Cl_2),[1a,c] bromine (Br_2),[1b,c] trichloramine (NCl_3),[1d,2] and iodobenzene dichloride ($C_6H_5ICl_2$) (IBD)[1e,2] are known to react with olefins and dienes by an ionic or radical process under the appropriate reaction conditions. The reactions of these halogenating reagents with acetylenes has not been studied extensively. Bromine reacts with acetylenes by an ionic mechanism in acetic acid as solvent.[4] Nazarov and Bergel'son examined the stereochemistry of the radical addition of bromine to a variety of substituted acetylenes.[5] They found that the cis isomers were favored due to the preference of a trans relationship of the bulky substituents in the intermediate **3a**.[6] Poutsma reported that chlorine reacts only by

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