Electrochemical Reduction of Arylsulfonamides

Peter T. Cottrell and Charles K. Mann*

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received November 6, 1970*

Abstract: The reduction of nine benzenesulfonamides at a mercury cathode was examined in MeCN. Reactions were shown to be quite similar to those of alkyl and aryl halides. A two-electron process forms an intermediate that undergoes scission of the S–N bond to produce sulfinate and amide ions in high yields. Primary and secondary sulfonamides lose a proton to the amide ion, producing a sulfonamide anion which is not electrochemically reactive and resulting in overall transfer of one, rather than two, electrons per molecule. The sulfinates produced from *p*-cyanobenzenesulfonamides undergo a one-electron reduction to the dianion radical, which is moderately stable under the experimental conditions. This radical was shown by esr spectroscopy to be identical with that formed by reduction of *p*-cyanobenzenesulfonyl chloride.

The utility of the toluenesulfonyl moiety as a removable protective group for the amino function in peptide synthesis has been long recognized.[1] It is used at present especially for protection of ω amino groups.[2] The fact that it is stable to the conditions commonly used for the removal of other protective groups, catalytic hydrogenation and treatment with acids, bases, and hydrazine, contributes to its usefulness. It is most often removed by action of metallic sodium in liquid ammonia solution.[3]

Recently Closson, *et al.*,[4] carried out reductive cleavage of sulfonamides by means of electron transfer from arene anion radicals. They reported that complete cleavage of tertiary sulfonamides to amine and sulfinate ion is obtained on reaction of 2 mol of reductant at −70°. At room temperature, reduction of the sulfinate ion occurs to produce hydrocarbons and inorganic sulfur compounds.

The electrochemical reduction of sulfonamides has received recent attention.[5–8] Horner and Neuman[5] carried out the reduction of a variety of sulfonamides in methanolic tetramethylammonium chloride at a mercury electrode. They observed a cleavage of the sulfur–nitrogen bond which permitted recoveries of amines in the range of 55–98% and of sulfinic acid in the range of 80–97%. The reaction was attributed to electrolytic formation of tetramethylammonium amalgam which reacted with the sulfonamide. Horner and Singer[6] measured polarographic half-wave potentials for a number of sulfonamides and correlated potential variations with substituent effects. They carried out the reduction of *N*,*N*-diphenyl-*p*-toluenesulfonamide in TEAP–MeCN and observed the formation of a red-brown product which gave an esr spectrum.[7]

Zuman, *et al.*,[8] reduced benzenesulfonamides, substituted with strongly electron-withdrawing groups, at mercury electrodes in aqueous borate buffers. They reported a reaction that involves cleavage of the carbon–sulfur bond to produce, for example from *p*-cyanobenzenesulfonamide, benzonitrile, SO_2, and NH_3.

We have examined the reactions of some of the same compounds studied by each of the two groups mentioned above, applying cyclic voltammetry, esr spectroscopy. and large-scale electrolysis with chemical product identification to their reactions in tetraethylammonium bromide (TEAB)–MeCN solutions at mercury electrodes. The solvent system chosen permitted examination of the effects of proton donors upon the reaction. Our results are in general agreement with those of Horner, *et al.*, in that we observed scission of the sulfur–nitrogen bond in all cases studied. We find, however, that proton availability influences the course of reaction of certain of the compounds. Under the conditions of these experiments, all but one of the examples studied were entirely converted to the amine and sulfinate.

Experimental Section

Reagents. Acetonitrile was purified, dried, and degassed as previously described.[9] Reagent grade tetraethylammonium bromide was purified by recrystallizing it three times from chloroform and carbon tetrachloride. After each recrystallization, the product was washed with anhydrous ether and finally dried under vacuum at 100°. All substituted *p*-toluenesulfonamides were prepared according to the procedure of deBoer and Backer.[10] Our experimental melting points agreed with the literature values for the following synthesized compounds: *N*-methyl-*p*-toluenesulfonamide, 75°; N-propyl-*p*-toluenesulfonamide, 52°; *N*,*N*-diethyl-*p*-toluenesulfonamide, 60°; and *N*,*N*-dimethyl-*p*-toluenesulfonamide, 79°. *p*-Toluenesulfonamide, *p*-cyanobenzenesulfonamide, and benzenesulfonamide were purchased and recystallized before being used. *p*-Cyanobenzenesulfonyl chloride was prepared from *p*-sulfaminebenzoic acid and PCl_5 according to the method of Remsen, Hartman, and Muckenfuss.[11] The crude product was allowed to stand overnight in ice water, dried in a desiccator over sulfuric acid, and finally recrystallized repeatedly from benzene–hexane. The purified product (mp 111°, lit. 111–112°) was used to prepare the *N*-propyl-*p*-cyanobenzenesulfonamide (mp 94°), using the method mentioned previously.[10]

Cyclic Voltammetry. Cyclic voltammetry measurements were obtained using the apparatus previously described.[12] Sweep rates were 10 V/sec, with a 3-msec step width. A mercury-plated Pt wire was used as the microelectrode. The Ag|$AgNO_3$ (0.10 *M*)–MeCN reference electrode was used for voltammetry and for all large-scale electrolyses.

---

(1) E. Fischer, *Chem. Ber.*, **48**, 93 (1915).

(2) J. F. W. McOmie, *Advan. Org. Chem.*, **3**, 159 (1963); M. Bodanszky and M. A. Ondetti, "Peptide Synthesis," Interscience, New York, N. Y., 1966, p 22.

(3) V. du Vigneaud and O. K. Behrens, *J. Biol. Chem.*, **117**, 27 (1937).

(4) W. D. Closson, S. Ji, and S. Schulenberg, *J. Amer. Chem. Soc.*, **92**, 650 (1970).

(5) L. Horner and H. Neumann, *Chem. Ber.*, **98**, 3462 (1965).

(6) L. Horner and R. J. Singer, *Tetrahedron Lett.*, 1545 (1969).

(7) L. Horner and R. J. Singer, *Justus Liebigs Ann. Chem.*, **723**, 1 (1969).

(8) O. Manousek, O. Exner, and P. Zuman, *Collect. Czech. Chem. Commun.*, **33**, 4000 (1968).

(9) P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969).

(10) Th. J. deBoer and H. J. Backer in "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 943.

(11) I. Remsen, R. N. Hartman, and A. M. Muckenfuss, *J. Amer. Chem. Soc.*, **18**, 150 (1896).

(12) C. K. Mann, *Anal. Chem.*, **37**, 326 (1965).

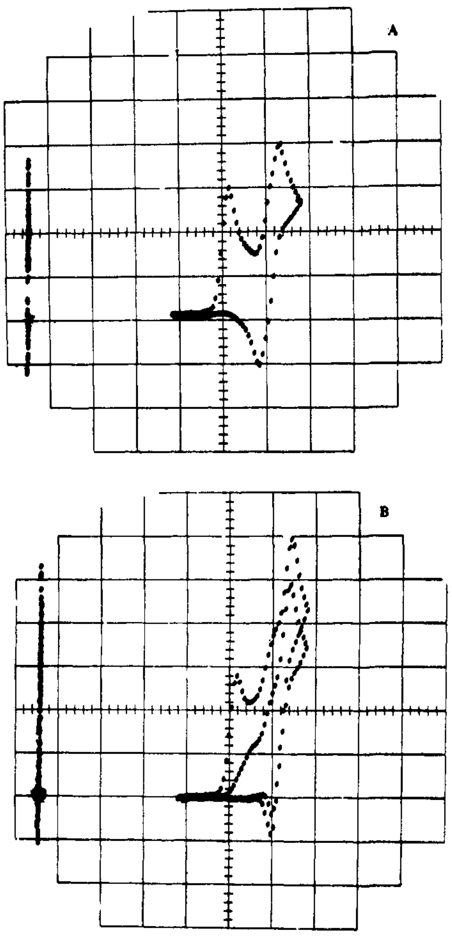


Figure 1. Voltammetric curve for *p*-cyanobenzenesulfonamide, vertical scale 150 μA/cm, horizontal scale 0.5 V/cm: (A) one-cycle scan, no phenol added; (B) two-cycle scan, phenol added.

Large-Scale Electrolyses. Large-scale electrolyses were carried out in three-electrode, divided cells, using an electronic potentiostat. In a typical reaction, 35 ml of degassed 0.2 *M* TEAB–MeCN in the cathode compartment was preelectrolyzed at a potential 100 mV more cathodic than the anticipated reaction potential. Preelectrolysis current decayed rapidly to less than 0.1% of subsequent initial reaction currents, with the passage of charge amounting to less than 1% of the subsequent reaction. On completion of the preelectrolysis, the cathode potential was adjusted to the value desired for the reaction and approximately 0.30 mmol of reactant was dissolved in the cathode solution. Change of reaction current with time is discussed below.

Product Analyses. Amine analyses were performed by direct gas–liquid chromatography of samples drawn from the cathode compartment. A 6 ft × 0.25 in. column packed with Dowfax 9N9-NaOH on Chromosorb W was used. It was found to be possible to chromatograph N-substituted benzene- and *p*-toluenesulfonamides on a 2.5 ft × 0.25 in. column of 100–140-mesh acid-washed glass beads coated with 0.6% Carbowax 20M, using temperatures in the range of 180–230° with H_2 carrier gas. Well-resolved and nearly Gaussian peaks were obtained for all six compounds examined. Conditions remaining constant, retention times increase in the order tertiary < secondary < primary. Cyano-substituted sulfonamides are not volatile enough to be analyzed by this method.

Unreacted sulfonamide was also identified by dissolving the residue that was recovered from cathode solutions in water and neutralizing the solution, after which the sulfonamide precipitated. After recrystallization, the material recovered was identified by comparing melting points and ir spectra with valid samples.

The Smiles test,[13] formation of a violet color on reaction of phenetole and sulfinic acid in concentrated sulfuric acid, was used to detect sulfinate. Since none of the other possible components of the product solution gave a color, this reaction was used as the basis for a quantitative colorimetric determination of sulfinate. The absorption measurement was made at 750 nm.

Esr Spectra. To obtain esr spectra, electrolyses were performed in a cell having a fitting in the cathode compartment through which a sample could be withdrawn into a previously degassed quartz tube. To be observable by this procedure, radicals must have half-lives of at least 30 min.

Results

Cyclic Voltammetry. The reactions of several sulfonamides have been examined; identifications of the compounds and the values of peak potentials are given in Table I. For benzenesulfonamides and *p*-toluenesulfonamides **1–6**, one irreversible reduction step in the range of −2.8 to −3.0 V is observed.

Table I. Cyclic Voltammetric Peak Potentials[a]

Compound[b]	Peak potential[c] $-E_p$, V		
1, *p*-toluenesulfonamide			2.97
2, benzenesulfonamide			2.82
3, *N*-methyl-*p*-toluenesulfonamide			2.91
4, *N*-propyl-*p*-toluenesulfonamide			2.87
5, *N*,*N*-diethyl-*p*-toluene sulfonamide	1.52 (1.34)[d]		2.93
6, *N*,*N*-dimethyl-*p*-toluenesulfonamide	1.46 (1.20)		2.85
7, *p*-cyanobenzenesulfonamide		2.21	2.79 (2.60)
8, *N*-propyl-*p*-cyanobenzenesulfonamide		2.01 (1.91)	2.62 (2.45)
9, *N*,*N*-diethyl-*p*-cyanobenzenesulfonamide	1.03 (0.93)	2.07 (1.94)	2.68 (2.56)

[a] Voltammetry at mercury-plated platinum wire, 10 V/sec sweep rate. [b] Concentration 5–10 m*M* in 0.2 *M* TEAB–MeCN. [c] Potential measured at ambient temperature of about 22° against a Ag|$AgNO_3$ (0.10 *M*) reference. [d] Oxidation peaks in parentheses.

Compounds which contain the electron-withdrawing *p*-cyano substituent, **7–9**, show different behavior. Each of these exhibits two reduction steps. Figure 1A shows the voltammogram observed for *p*-cyanobenzenesulfonamide (**7**). On this time scale, the first step appears entirely irreversible. The second step is apparently quasi-reversible on the basis of peak potentials. A continuous sweep restricted to the potential range of the first peak did not give any indication of reversibility. By contrast, the voltammogram for *N*,*N*-diethyl-*p*-cyanobenzenesulfonamide (**8**) in Figure 2 shows some reversible behavior for the first reduction step and a restricted continuous sweep produced symmetrical redox peaks, indicating an appreciable lifetime for the initial electron-transfer product. The curve of Figure 1B represents voltammetry on the same solution that was used for Figure 1A, except that a small amount of phenol had been introduced. The peak potentials are not shifted, but the second reduction peak is substantially larger with phenol added than without. The second peak produced by **9** did not change on addition of phenol.

Figure 1B also shows a second voltammetric scan, made without interruption after the first. The first reduction peak produced during the cathodic sweep of the first cycle is identical with the first peak of Figure 1A. It is barely evident, however, on the second cycle. On

---

[13] A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1962, p 1078.

Table II. Constant-Potential Sulfonamide Reduction[a]

Compound	Reaction potential, V[b]	n[c]	Product analysis[d] Starting material	Amine	Sulfinate
1	2.80	0.95 ± 0.02	51 ± 2	*e*	52 ± 10
2	2.80	0.96 ± 0.02	*f*	*e*	*g*
3	2.80	0.97 ± 0.02	*f*	45 ± 10	*g*
4	2.80	0.96 ± 0.02	51 ± 2	48 ± 2	47 ± 10
	2.80	1.96 ± 0.04[h]	0 ± 2	101 ± 2	*g*
5	2.80	1.96 ± 0.04	0 ± 2	94 ± 2	96 ± 10
6	2.80	1.94 ± 0.04	*f*	97 ± 5	*g*
7	2.70	0.94 ± 1[i]		*e*	*g*
8	2.70	1.00 ± 0.1[i]	50	44 ± 5	*g*
	2.70	2.0 ± 0.1[h,i]			
9	2.70	1.4		*j*	*g*
	2.20	1.7		*j*, *k*	*g*

[a] Reactions performed in 0.2 *M* TEAB–MeCN. [b] Ag|AgNO$_3$ (0.1 *M*)–MeCN. [c] Number of electrons per molecule of starting material. [d] Analyses expressed in mole per cent of starting sulfonamide. [e] Ammonia identified by glc. [f] Sulfonamide identified by glc after neutralizing reaction mixture. [g] Sulfinate identified by Smiles test. [h] Phenol added. [i] Electrolysis terminated at the estimated time of completion of the initial fast reaction. [j] Diethylamine identified by glc. [k] Glc indication of other products in addition.

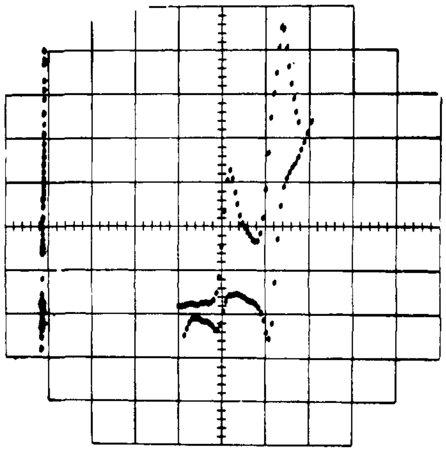


Figure 2. *N*,*N*-Diethyl-*p*-cyanobenzenesulfonamide, vertical scale 75 μA/cm, horizontal scale 0.5 V/cm.

scanning continuously, the first peak for any of the compounds **7–9** is eliminated if the second peak is included, indicating that the product of the second step reacts with the starting material. This is true whether or not phenol is added.

In addition to the features described above, it was noted that for N,N-disubstituted sulfonamides **5**, **6**, and **9**, additional peaks occur in the vicinity of −1.0 V. These are caused by reactions of the −2.93- and −2.85-V peaks of **5** and **6** and by reactions of the products from the −2.68-V peak of **9**. These peaks are eliminated by addition of phenol to the system.

Constant-Potential Electrolysis. Reactions of compounds **1–6** were carried out at potentials that approximated their voltammetric peak potentials. The variation of reaction current with time was followed. Typical curves are shown in Figure 3. This type of I-t behavior has been observed for reduction of alkyl halides[13] and alkyl tosylates[14] at Hg cathodes. Quantitative results are summarized in Table II. Addition of phenol in about 3.1 excess of the amount of sulfonamide has no effect upon the reaction of N,N-disubstituted compounds **5** and **6**, for which $n = 2$, where n is the number of electrons per molecule, determined coulometrically. For monosubstituted, **3** and **5**, and for unsubstituted compounds, **1** and **2**, for which $n = 1$ in the absence of

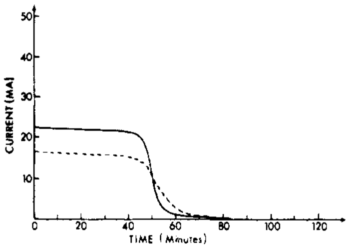


Figure 3. Current–time behavior for reduction of toluenesulfonamides: ——, ~30 m*M* *N*,*N*-diethyl-*p*-toluenesulfonamide; - - -, ~30 m*M* *N*-methyl-*p*-toluenesulfonamide.

proton donors, addition of phenol produces a two-electron reaction, but does not change qualitatively the shape of the current–time curve shown in Figure 3. Initial current densities were around 4.0 mA/cm^2. Reactions were terminated when current densities had decreased to around 0.01 mA/cm^2.

The behavior of cyano-substituted compounds when electrolyzed at the potential of the second voltammetric peak is different. The reaction is of course much faster, since it is performed at a potential 0.5 V more cathodic than the first voltammetric peak. For compounds **7**, **8**, and **9**, initial current densities were around 20 mA/cm^2. The qualitative shape of the curves obtained is similar to that shown in Figure 3; for a given number of moles of starting material, the time for reaction is necessarily much shorter. More importantly, after completion of the initial rapid reaction for which $n = 1$ for **7** and **8** and about 1.4 for **9**, a much slower reaction occurred which involved very slowly decreasing currents in the range of 0.8 mA/cm^2. Reduction of **7** and **8** in the presence of phenol requires two electrons per molecule to complete the rapid portion of the reaction. The reduction of **9** was carried out with the cathode potential held in the range of the first and also of the second voltammetric peaks. The current–time curve in each case had the shape illustrated in Figure 3. Considerably smaller initial currents are observed at the lower potential.

Products of these reactions were shown to consist of the sulfinate anion and ammonia or amine produced by sulfur–nitrogen cleavage and, in some cases, the deprotonated anionic salt of the starting sulfonamide. Quantitative results are summarized in Table II.

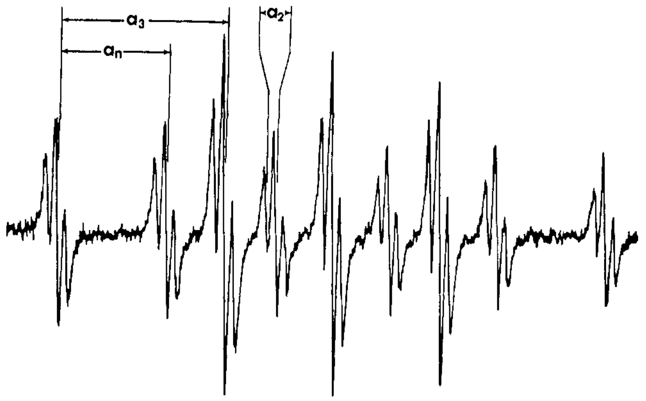


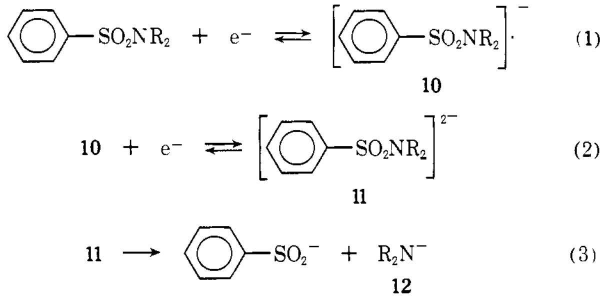
Figure 4. Esr spectrum of 4-cyanobenzenesulfonyl dianion radical.

The behavior of *N*,*N*-diethyl-*p*-cyanobenzenesulfonamide (**9**) was quite distinct from that of the other compounds studied in that *n* differed appreciably from an integral value and that there was an indication of formation of products other than those produced by sulfur–nitrogen scission. In examining each of the product mixtures, the product of sulfur–carbon scission, which would be benzene, toluene, or benzonitrile, was specifically sought. This was done by gas chromatography under conditions such that yields in the range of 1–10 mol % of starting sulfonamide would have been detected. There was no indication of hydrocarbon or nitrile formation for any of the compounds other than **9**. In this case, a glc peak was observed which had the same retention time as benzonitrile. If this identification is correct, it would have corresponded to 5–10 mol % of the starting material.

The slow following reaction of cyano-substituted sulfonamides produced, in each case, a brown product. The esr spectrum shown in Figure 4 was measured on a sample produced by electrolyzing until the fast stage of the reaction was complete, after which the brown product was formed. Immediately after sampling, the spectrum was very broad and poorly resolved. After approximately 30 min in the spectrometer, during which the initial high-spin concentration was reduced, a well-resolved spectrum could be obtained. Identical results were obtained for compounds **7** and **8** and for *p*-cyanobenzenesulfonyl chloride. No spectra were obtained for samples drawn during the fast stage of the reactions. Generally similar behavior was observed for **9**; however, it was not possible to obtain well-resolved spectra for the brown solutions.

Discussion

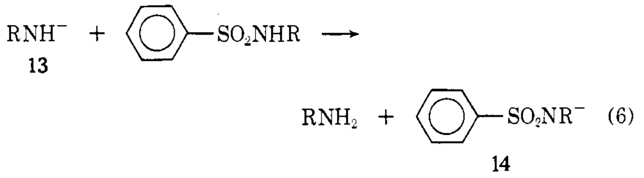
Tertiary Sulfonamides. The reaction scheme outlined in eq 1–5 is suggested for the reduction of tertiary benzene- and *p*-toluenesulfonamides **5** and **6**. This scheme is consistent with the observed two-electron reaction and the complete recovery of amine and sulfinate anion. The occurrence of a single irreversible voltammetric peak indicates that the potential required for step 1 is at least as cathodic as that for step 2 and that **11** is very unstable, making step 3 very rapid. Tertiary sulfonamides show anodic peaks at about −1.0 V which are eliminated by addition of proton donors. This is the same behavior which has been observed on reduction of alkyl halides[14] and alkyl tosylates.[15] It seems reasonable to attribute these to the depolarization of the microelectrode by very strong bases, possibly **12** in this example. Step 4 is included because it has been shown that, in reduction of alkyl halides,[14] MeCN does serve as a proton donor. The present case appears to be analogous. Step 5 is included because ethylene and triethylamine are detected, as is also true in alkyl halide reductions.

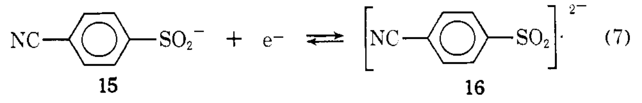


$$\mathbf{12} + CH_3CN \longrightarrow R_2NH + {}^{(-)}CH_2CN \qquad (4)$$

$$^{(-)}CH_2CN + Et_4N^+ \longrightarrow CH_3CN + CH_2{=}CH_2 + Et_3N \qquad (5)$$

Primary and Secondary Sulfonamides. For primary and secondary sulfonamides we suggest that steps 1–3 occur. However, when an acidic proton is available on the sulfonamide, the amide ion **13** reacts as indicated in step 6, rather than as in steps 4 and 5. This accounts for the occurrence of one-electron reactions of **1**, **2**, **3**, **4**, **7**, and **8** in the absence of proton donors, but of two-electron reactions with a proton donor present. It also accounts for the enhancement of the second cathodic peak in Figure 1B, produced by the addition of phenol. Recovery of half of the sulfonamide after neutralizing the residue from the cathodic solution when these compounds are reduced in an aprotic system is consistent with the occurrence of step 6. It would be expected that the formation of amide ions from the reaction corresponding to step 3 would cause us to observe anodic voltammetric peaks around −1.0 V. Their failure to appear can be attributed to the occurrence of step 6, which removes them. One would expect a similar depolarization by ions analogous to **14**; however, this is probably masked by depolarization caused by the bromide supporting electrolyte.





Cyanobenzenesulfonamides. We suggest that steps 1–5 also represent the rapid stage of the reduction of the cyanobenzenesulfonamides **7**, **8**, and **9**. The rapid reaction, thought to correspond to the first voltammetric peak of Figure 2, and therefore to be analogous to the single peak observed for **5** and **6**, would produce the amide ion and the sulfinate **15**. The second, quasi-reversible stage, is identified with formation of the dianion **16**, shown in reaction 7. This step would correspond to the reduction observed for benzonitrile,

---

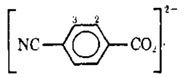
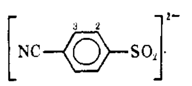
(14) J. L. Webb, C. K. Mann, and H. M. Walborsky, *J. Amer. Chem. Soc.*, **92**, 2042 (1970).

(15) P. Yousefzadeh and C. K. Mann, *J. Org. Chem.*, **33**, 2716 (1968).

tolunitrile, and *p*-cyanobenzoate.[16] These reactions are reversible and lead to mono- or to dianion radicals.

The spin resonance spectrum of the paramagnetic species produced during the exhaustive electrolysis of **7** or **8** is shown in Figure 4. The absorption centered at $g = 2.00$ shows a hyperfine pattern consistent with the interaction of a pair of equivalent hydrogen nuclei split by a single nitrogen nucleous further split by a second pair of equivalent hydrogen nuclei. Inspection of the spectrum shows all 27 lines resolved into the expected 1:2:1, 1:1:1, 1:2:1 intensity pattern. An obvious choice for the paramagnetic species, consistent with the compounds known to be in the product solution, would be the dianion of *p*-cyanobenzenesulfinic acid. The measured splitting constants for the numbered ring positions are compared in Table III with those obtained by Rieger, *et al.*,[16] for the *p*-cyanobenzoic acid dianion, and a considerable agreement is observed. Since the same spectrum is produced upon exhaustive electrolysis of *p*-cyanobenzenesulfonyl chloride under the same conditions, we feel that this is convincing evidence in favor of the assignment.

Table III. Comparison of Esr Data

Radical	Hfs, G
	$a^{\mathrm{N}} = 1.96^a$ $a_2^{\mathrm{H}} = 2.76^a$ $a_3^{\mathrm{H}} = 0.35^a$
	$a^{\mathrm{N}} = 2.05^b$ $a_2^{\mathrm{H}} = 3.15^b$ $a_3^{\mathrm{H}} = 0.18^b$

[a] Reference 16. [b] This work.

When a constant-potential electrolysis is run, the brown radical is not observed until the rapid phase of the reaction is completed. Since the slow phase must be taking place almost from the start and since the color of the radical is much deeper than the pale yellow of the intermediate products, this must indicate that **16** reacts with either the starting material or with one of the intermediates. In performing the cyclic voltammetry experiments, it was noticed that the first peak could not be seen if the second step had been occurring. This indicates that **16** must be reacting with the starting material, rather than with an intermediate. No attempt was made to investigate this process.

This electrochemical process appears to offer an attractive alternative to $NaNH_3$ removal of the tosyl group from peptides under certain conditions. This suggestion is advanced because cathodic reduction should offer flexibility that is otherwise unavailable. Our experiments have been carried out in acetonitrile, but cathodic reactions are routinely also performed in *N,N*-dimethylformamide and dimethyl sulfoxide, as well as in other solvents.[17] These are used in peptide synthesis and they may be simpler to work with than liquid ammonia. Difficulty is often encountered in removing inorganic salts that are unavoidably introduced with sodium reduction; this is especially troublesome when a water-soluble peptide is formed. The problem could be circumvented in a cathodic reduction by an appropriate choice of supporting electrolyte; for example, tetra-*n*-propylammonium perchlorate is adequately soluble in nonaqueous solvents and is only slightly soluble in water. Difficulty may be encountered from sodium cleavage of thiomethyl groups. Aliphatic sulfides, with the exception of dibenzyl sulfide, are not cathodically reduced.[18] When a peptide that contains reducible functions is of interest, the possibility exists of avoiding difficulty by utilizing the reaction potential selectivity that is inherent in electrochemical reactions. Use of a benzenesulfonyl having an electron-withdrawing substituent such as nitrile, rather than methyl, as the protective group would make it possible to perform the reductive cleavage at a lower potential.

There is a striking similarity between the electrochemical reduction of secondary and tertiary sulfonamides and their reaction with arene anion radicals studied by Closson, *et al.*[4] The types of products are the same. When reaction of the sulfinate is prevented by maintaining the temperature at −70°, reductive cleavage of sulfonamide requires 2 mol of arene anion/mol of sulfonamide; since the reaction of the arene anion radical is a one-electron process, sulfonamide reduction requires two electrons, as is true for electrochemical reduction.

In the previously reported work, the relative rates of cleavage of *N*-methyl-*N*-phenyl-*p*-toluenesulfonamide (I) and *N,N*-di-*n*-butyl-*p*-toluenesulfonamide (IV) were measured, using the following sodium salts as reductants: anthracenide, pyrenide, naphthalenide, and biphenylide. The Roman numeral designations are those used previously.[4] It was found that the relative cleavage rates, $k_{\mathrm{I}}/k_{\mathrm{IV}}$, were 36 for anthracenide, 10 for pyrenide, 1.26 for naphthalenide, and 1.31 for biphenylide. The fact that the relative rates are dependent upon the strength of the reductant shows that the first step of the reaction is rate determining. This was taken as indication that the first step is slow and irreversible. The proposed sequence is repeated here as

$$\mathrm{ArH}\cdot^- + \text{sulfonamide} \xrightarrow{\text{slow}} \text{intermediate(s)} \xrightarrow[\text{fast}]{\mathrm{ArH}\cdot^-} \text{products} \quad (8)$$

We suggest that the detailed similarities between the chemical and electrochemical reactions make it reasonable to expect that the mechanisms are similar and that the scheme outlined in eq 1–3 is applicable to both types of reaction.[19] Assuming that the potential for step 1 is at least as cathodic as that required for step 2 and that step 3 is fast, step 1 would be rate determining even though reversible. For the electrochemical reaction, the validity of these assumptions is indicated by the cyclic voltammetry curves, taken together with the coulometric results. This reaction scheme is in accord with the observed variation of $k_{\mathrm{I}}/k_{\mathrm{IV}}$ in the chemical experiments. Change in the identity of the reductant would be analogous to change in cathode potential, and the relative rates of electrochemical reduction of two compounds that exhibit different E^0 values would be expected to vary with change in cathode potential.

Acknowledgment. The support of the National Institutes of Health through Grant No. GM 10064 is acknowledged.

---

[16] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 85, 683 (1963).

[17] C. K. Mann in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, p 57.

[18] R. Gerdil, *J. Chem. Soc. B*, 1071 (1966).

[19] We are indebted to Professor Closson for bringing this to our attention.