Cathodic Cleavage of *ortho*-Alkyl Substituted Alkyl Aryl Sulfones

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The cathodic cleavage of methyl *o*-tolyl sulfone, methyl *o-tert*-butylphenyl sulfone, and benzyl *o-tert*-butylphenyl sulfone has been studied both in methanol and *N,N*-dimethylformamide solution at a mercury cathode. Whereas methyl phenyl sulfone undergoes exclusively alkyl-sulfur bond cleavage under these conditions, the *ortho* substituted methyl aryl sulfones also show aryl-sulfur bond cleavage to an extent that increases with the bulkiness of the *ortho* substituent. The cleavage mode is interpreted in terms of the preferred conformations of the sulfones. Benzyl *o-tert*-butylphenyl sulfone gives exclusively toluene and *o-tert*-butylbenzene-sulfinate ion, probably owing to the stability of the incipient benzyl radical.

The current-time dependence of the methyl aryl sulfone electrolyses suggests that an indirect reduction mechanism is operating. The tetraalkylammonium cation of the supporting electrolyte is assumed to act as a mediator in the overall charge transfer.

The cathodic cleavage at mercury of some cyclic sulfones having the general formula

$n = 1 - 4$
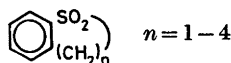
has been studied by Simonet and one of the present authors.[1] In contrast to methyl phenyl sulfone, which cleanly undergoes alkyl-sulfur cleavage to yield methane and benzenesulfinate ion,[2,3] the main ($n = 1, 4$) or exclusive ($n = 2, 3$) reaction for the cyclic sulfones is aryl-sulfur cleavage. The cleavage mode is thought to be governed by the orientation of the sulfonyl group with respect to the aromatic ring.[1] The preferred conformation of a representative cyclic sulfone ($n = 2$) and of methyl phenyl sul-

fone, respectively, is shown in Fig. 1. In the Koch and Moffitt terminology,[4] the cyclic compound is a Case I sulfone, and the other one represents Case II.[5]

It was pointed out to us by Dr. G. Jeminet (Université de Clermont-Ferrand, France) that an *ortho* alkyl substituted methyl phenyl sulfone might provide an interesting case for comparison. Inspection of Stuart-Briegleb models of methyl *o*-tolyl sulfone and methyl *o-tert*-butylphenyl sulfone suggested that these compounds might approach Case I. If the conformation is the decisive factor governing the cleavage mode, the *ortho* substituted methyl phenyl sulfones would be expected to show aryl-sulfur cleavage.

RESULTS

Synthesis of starting materials. The preparation of methyl *o*-tolyl sulfone followed a literature procedure.[6] Methyl *o-tert*-butylphenyl sul-
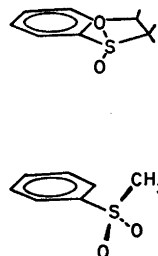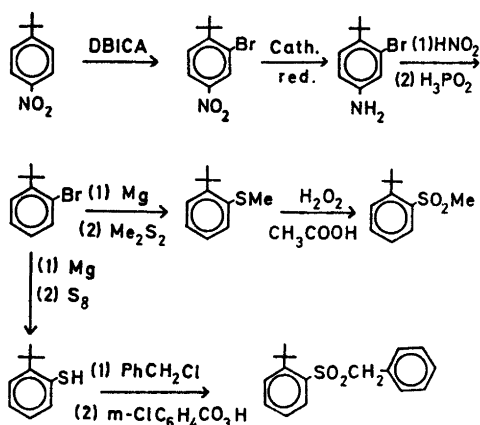

Fig. 1. Preferred conformations of 2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide, a Case I sulfone, and of methyl phenyl sulfone, a Case II representative.

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Scheme 1. Synthetic routes to benzyl and methyl o-tert-butylphenyl sulfone. DBICA = Dibromoisocyanuric acid.

fone was synthesized via a lengthy but straightforward route, illustrated in Scheme 1. Some steps in the synthesis were improved compared to earlier methods. Bromination of p-nitro-tert-butylbenzene was made with dibromoisocyanuric acid [7] instead of the expensive silver sulfate – bromine mixture.[8] Reduction of 2-bromo-4-nitro-tert-butylbenzene to the corresponding amine was carried out electrochemically rather than with iron and hydrochloric acid.[9] In the next-to-the-last step, a Grignard reagent was allowed to react with a disulfide. This reaction is known in the literature [10] but appears to have been seldom used.

Table 1. Polarographic half-wave potentials of some sulfones, recorded in DMF solution, tetrabutylammonium iodide 0.1 M. Sulfone concentration 10^{-3} M.

Sulfone	$E_{1/2}$/V [a]
Methyl phenyl	-1.73 [b]
Methyl o-tolyl	-1.73
Methyl o-tert-butylphenyl	-1.65
Benzyl phenyl	-1.60
Benzyl o-tert-butylphenyl	-1.43

[a] Potential vs. Ag,AgI/0.1 M Bu$_4$NI, DMF.
[b] Taken from Ref. 2 and reconfirmed in this work.

The electrolysis results prompted the inclusion of a third compound in the present study, namely, benzyl o-tert-butylphenyl sulfone. This compound was prepared as shown in Scheme 1.

Polarography. The half-wave potentials, recorded in DMF solution containing tetrabutylammonium iodide, 0.1 M, are listed in Table 1. The sulfone concentration was in all cases 10^{-3} M.

Electrolyses. The compounds were electrolyzed both in methanol and DMF solution. The starting amount in each run was $2-5$ mmol. The sulfinate ions formed upon cathodic cleavage were qualitatively and quantitatively determined via ^{1}H NMR spectroscopy. The results are presented in Table 2. For methyl o-tolyl sulfone and methyl o-tert-butylphenyl sulfone, the electricity consumption was always

Table 2. Product yields and conditions of electrolysis of some ortho-substituted sulfones.

Sulfone	Temp. °C	Supp. electrolyte	Cath. pot. Volt	Per cent cleavage alkyl-sulfonyl	aryl-sulfonyl	Ratio alkyl-sulfonyl/ aryl-sulfonyl
Methyl o-tolyl	10	MeOH, 0.05 M TMAC [a]	-2.2 [c]	83	18	4.6
	25	DMF, 0.05 M TEAP [b]	-1.8 [d]	93	7	13.3
	65	DMF, 0.05 M TEAP [b]	-1.8 [d]	93	7	13.3
Methyl o-tert-butylphenyl	10	MeOH, 0.05 M TMAC [a]	-2.2 [c]	7	91	0.08
	25	DMF, 0.05 M TEAP [b]	-1.85 [d]	7	91	0.08
	70	DMF, 0.05 M TEAP [b]	-1.85 [d]	16	84	0.19
Benzyl o-tert-butylphenyl	10	MeOH, 0.5 M TMAC [a]	-2.0 [e]	$-$ [g]	0	
	10	MeOH, 0.1 M LiCl	-2.1 [f]	86	0	

[a] TMAC Tetramethylammonium chloride. [b] TEAP Tetraethylammonium perchlorate. [c] vs. Ag,AgCl/ 0.05 M Cl⁻. [d] vs. Ag,AgI/0.1 M I⁻. [e] vs. Ag,AgCl/0.5 M Cl⁻. [f] vs. Ag,AgCl/0.1 M Cl⁻. [g] Not quantitatively determined.
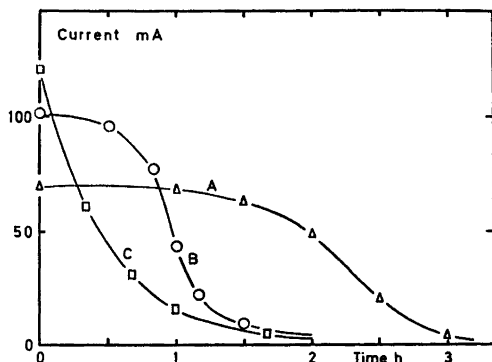
Fig. 2. Current-time dependence of sulfone electrolyses in methanol-tetramethylammonium chloride. Curve A, methyl *o*-tolyl sulfone, B, methyl *o*-*tert*-butylphenyl sulfone, C, benzyl *o*-*tert*-butylphenyl sulfone.

2 F mol^{-1} within a few per cent. With benzyl *o*-*tert*-butylphenyl sulfone, the current dropped to the background value after 1.5 – 1.7 F mol^{-1}. The current-time dependence was recorded for all runs in methanol. Fig. 2 illustrates the behaviour for the three sulfones. Simple exponential decay is only shown by benzyl *o*-*tert*-butylphenyl sulfone (curve C), whereas the methyl sulfones give an initially constant current (curves A and B).

An experiment to test the influence of changing the concentration of supporting electrolyte, not included in Table 2, was also performed. In a run with methyl *o*-tolyl sulfone in methanol, doubling the concentration of tetramethylammonium chloride caused a 33 % increase of the initial current.

DISCUSSION

Cleavage mode. Whereas methyl phenyl sulfone is exclusively cleaved between the methyl and sulfonyl groups,[1,3] the introduction of an *ortho* methyl group brings about some aryl – sulfonyl cleavage (see Table 2). With an *ortho tert*-butyl group, aryl – sulfonyl cleavage becomes the major mode.

The increasing trend towards aryl – sulfonyl cleavage as the bulkiness of the *ortho* substituent increases is believed to be caused by stereoelectronic effects of the type discussed in Ref. 2. It must be remembered, however, that steric repulsion between the *ortho* substituted aryl

group and the methanesulfonyl group will generally facilitate the breaking of the bond between them. Since the conformations of the *ortho* substituted sulfones are not independently known, it is impossible to assess the relative importance of the two factors which determine the cleavage mode. The chemical shifts of the methyl protons in the ^{1}H NMR spectra are too similar to allow any conclusions and might not be sensitive to conformational changes. They are, for phenyl, *o*-tolyl, and *o*-*tert*-butylphenyl methyl sulfone, respectively, δ (CDCl$_3$) 3.06, 3.06, and 3.11.
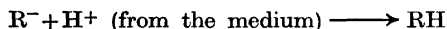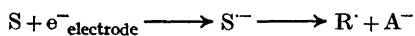
In the benzyl *o*-*tert*-butylphenyl sulfone, the cleavage takes place exclusively between the benzyl and the sulfonyl groups. Here the relative stability of the incipient benzyl radical explains the cleavage mode. Inspection of the polarographic half-wave potentials clearly bears this out. For benzyl and methyl *o*-*tert*-butylphenyl sulfone they differ by 0.22 V (Table 1), the benzyl sulfone being more easily reduced. For benzyl phenyl sulfone and methyl phenyl sulfone, the difference is less, 0.13 V. Steric effects may account for the discrepancy of the two differences.

Electrolysis of benzyl *o*-*tert*-butylphenyl sulfone provides a synthesis of *o*-*tert*-butylbenzenesulfinic acid (obtained as a salt). This compound has not been found in the literature and might be difficult to synthesize by any other route. For example, an attempted addition of sulfur dioxide to *o*-*tert*-butylphenylmagnesium bromide failed. Nor did *o*-*tert*-butylphenyllithium and sulfur dioxide yield the desired acid.

A close inspection of Table 2 reveals that the alkyl – sulfonyl/aryl – sulfonyl ratio for methyl *o*-tolyl sulfone is different in methanol and DMF. Also, there is a temperature effect on the ratio for methyl *o*-*tert*-butylphenyl sulfone in DMF, but not for methyl *o*-tolyl sulfone. We refrain from trying to explain these effects.

Current-time dependence. Typically, in electrolytic runs carried out at constant electrode potential, the current decreases exponentially with time. This first-order kinetic behaviour is shown by benzyl *o*-*tert*-butylphenyl sulfone (Fig. 2, curve C). The instantaneous current is proportional to the bulk concentration of electroactive substrate, and the usual and most simple interpretation is that electrons are
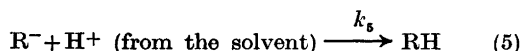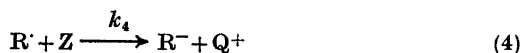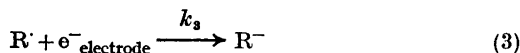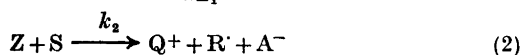
transferred directly from the electrode to the substrate. The reaction scheme is

$$S + e^-_{electrode} \longrightarrow S^{\cdot-} \longrightarrow R^{\cdot} + A^-$$

$$R^{\cdot} + e^-_{electrode} \longrightarrow R^-$$

$$R^- + H^+ \text{ (from the medium)} \longrightarrow RH$$

Whether the species $S^{\cdot-}$ is an intermediate or not is presently being investigated. In the mechanism above, S is sulfone, $R^{\cdot}$ alkyl radical, and A^- sulfinate anion.

A quite different behaviour is shown by the two other sulfones studied in this work (Fig. 2, curves A and B). The reaction rate is zero-order with respect to sulfone for a substantial part of the run, and at the end becomes first-order. This behaviour strikingly demonstrates a phenomenon recently brought to attention by Lund, Michel and Simonet,[11] namely, the participation of the supporting electrolyte in the reaction. A necessary condition for this is that the reduction potential of the substrate is not too far from that of the supporting electrolyte. The half-wave potential of benzyl *o-tert*-butyl-phenyl sulfone is too positive to allow the supporting electrolyte to participate.

A mechanism that will account for the observed kinetics is the following one:

$$Q^+ + e^-_{electrode} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z \qquad (1)$$

$$Z + S \xrightarrow{k_2} Q^+ + R^{\cdot} + A^- \qquad (2)$$

$$R^{\cdot} + e^-_{electrode} \xrightarrow{k_3} R^- \qquad (3)$$

$$R^{\cdot} + Z \xrightarrow{k_4} R^- + Q^+ \qquad (4)$$

$$R^- + H^+ \text{ (from the solvent)} \xrightarrow{k_5} RH \qquad (5)$$
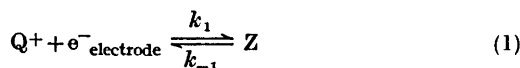
In the above scheme, equilibrium (1) represents the reversible, potential-dependent transfer of an electron from the cathode to the supporting electrolyte, yielding a species Z, "tetraalkylammonium radical" or "tetraalkylammonium amalgam". This equilibrium is far to the left. In reaction (2), charge is transferred from Z to the sulfone to regenerate the cation of the supporting electrolyte, Q^+, and bring about cleavage of S into a radical $R^{\cdot}$ and a sulfinate ion A^-. Reversible formation of a

radical anion $S^{\cdot-}$ followed by rapid cleavage would also be possible.

The radical $R^{\cdot}$ is further reduced, either *via* electron transfer from the electrode; (3), or by Z; (4), and finally, the resulting carbanion R^- is protonated by the solvent to form the corresponding hydrocarbon; reaction (5).

If we first assume that the conversion of $R^{\cdot}$ to R^- follows the homogeneous path (4) rather than the heterogeneous one, (3), we obtain

$$d[Z]/dt = k_1[Q^+] - k_{-1}[Z] - k_2[Z][S] - k_4[Z][R^{\cdot}] \qquad (6)$$

We also have

$$d[R^{\cdot}]/dt = k_2[Z][S] - k_4[Z][R^{\cdot}] \qquad (7)$$

Making the steady-state approximations that the time derivatives of [Z] and [R·] may be equalled to zero leads to

$$[Z] = k_1[Q^+]/(k_{-1} + 2k_2[S]) \qquad (8)$$

The reaction rate is given by the following expression:

$$-d[S]/dt = k_1 k_2[S][Q^+]/(k_{-1} + 2k_2[S]) \qquad (9)$$

If, on the other hand, reaction (3) rather than (4) is operating, the term $2k_2[S]$ in the denominator of (9) will be replaced by $k_2[S]$.

In the beginning of an electrolytic run, when [S] is large, it may be possible to neglect k_{-1} besides $2k_2[S]$ or $k_2[S]$, depending on the relative magnitude of the rate constants. This leads to

$$-d[S]/dt = k_1[Q^+]/2 \text{ or } k_1[Q^+], \text{ respectively.} \qquad (10)$$

The rate depends only on $[Q^+]$. Towards the end of the run, when [S] will have dropped to a low value, we may instead neglect the term $2k_2[S]$ or $k_2[S]$, respectively, and we obtain

$$-d[S]/dt = k_1 k_2[S][Q^+]/k_{-1} \qquad (11)$$

Eqns. (10) and (11) correspond to the zero- and first-order parts of the runs.

It is, in principle, possible to make a detailed mathematical analysis of the curves A and B, Fig. 2. However, a further complication must be considered in the present work. In the course of electrolysis, two cations are transported through the ion exchange membrane for each molecule of sulfone reacting. This causes $[Q^+]$ to increase in the cathode com-

partment, and since the initial concentrations of Q+ and S differ by less than a factor of 3, the concentration of Q+ can by no means be regarded as a constant. In fact, a close inspection of curve A reveals a slight upward drift in the beginning of the run, caused by an increase of [Q+].

The runs in DMF showed the same kinetic behaviour as described above for the methanol experiments, *i.e.*, for methyl *o*-tolyl sulfone and methyl *o-tert*-butylphenyl sulfone, the current remained constant for a large part of the reaction.

Eqn. (10) shows that the reaction rate (*i.e.*, the current) should be proportional to [Q+] for reactions being initially zero order with respect to [S]. In an experiment with methyl *o*-tolyl sulfone in methanol, the concentration of tetramethylammonium chloride was changed from 0.05 to 0.1 M. This caused a 33 % increase of the current, rather than the predicted 100 %. This apparent discrepancy is resolved by consideration of an ion-pair dissociation equilibrium for the supporting electrolyte. The dissociation constant for tetraethylammonium chloride in methanol is 0.1,[12] and that of tetramethylammonium chloride should be smaller. It then follows from Ostwald's dilution law that the concentration of dissociated quaternary ions will increase roughly as the square root of the stoichiometric concentration of the salt. It is assumed that only the free ions partake in the electrochemical mechanism postulated above.

EXPERIMENTAL

Syntheses. Melting points have been determined on a Kofler Hot Stage microscope. Pressures are given in SI units. 1 Pa = 7.5 × 10⁻³ mmHg.

Methyl o-tolyl sulfone was prepared from *o*-thiocresol (Fluka AG).[6] Yield 83 %, m.p. 54 – 56 °C, lit.[6] 55 – 57 °C.

2-Bromo-4-nitro-tert-butylbenzene. A solution of 38.5 g (0.2 mol) of 4-nitro-*tert*-butylbenzene [13] in 100 ml of ice-cold 92 % sulfuric acid was first prepared. A suspension of 28.7 g (0.1 mol) of dibromoisocyanuric acid [7] in 300 ml of ice-cold 92 % sulfuric acid was added at such a rate that the temperature did not rise above 25 °C. During the addition and 2 h afterwards, the reaction mixture was mechanically agitated and cooled in an ice-bath. It was then poured into 2 l of ice-water, and the solid material was

collected on a suction filter, washed with water and allowed to dry. Continuous extraction with ether in a Soxhlet apparatus separated the product from the ether-insoluble isocyanuric acid. Evaporation of the ether solution to dryness and recrystallization of the residue from 95 % ethanol gave 35.6 g (69 % yield) of 2-bromo-4-nitro-*tert*-butylbenzene, m.p. 94 °C, lit.[8] 94 °C.

o-Bromo-tert-butylbenzene. A solution of 25.8 g (0.1 mol) of the preceding compound in 300 ml of 95 % ethanol and 15 ml of conc. hydrochloric acid was placed on top of a 5 mm layer of mercury in a thick-walled 1 l beaker. Electrical contact with the mercury was made *via* a short piece of platinum sealed in glass. The anode, a piece of lead sheet, was immersed in 10 % sulfuric acid in a ceramic cup serving as a diaphragm and placed inside the beaker. The cathode surface was mechanically agitated and the cell was cooled in water during the electrolysis. A current of 8 A was fed through the cell. The reduction required 16.2 Ah theoretically and in fact, when this amount had been introduced, a vigorous hydrogen evolution started at the cathode. In order to ensure complete reduction, the current was gradually diminished to zero during 30 min in such a way that the hydrogen evolution was barely visible. The catholyte was separated from the mercury and evaporated to dryness *in vacuo*, giving a quantitative yield of 4-*tert*-butyl-3-bromoaniline hydrochloride as a white, crystalline mass. This was redissolved in 250 ml of water and 20 ml of conc. hydrochloric acid and diazotized with a solution of 7.9 g (0.1 mol) of sodium nitrite in 20 ml of water. The temperature was kept below −2 °C by cooling in a Dry Ice – acetone bath. Without undue delay, 250 ml of 50 % phosphinic acid was added and the solution kept overnight at 5 °C. The product was isolated through extraction with ether, washing with 2 M sodium hydroxide solution to remove phenolic impurities, drying over anhydrous sodium sulfate and distillation. The yield was 15.7 g or 74 %, b.p. 88 – 92 °C/1 kPa, lit.[9] 96 – 98 °C/1.6 kPa.

Methyl o-tert-butylphenyl sulfone. A Grignard reagent was prepared [9] from 6.4 g (0.03 mol) of *o*-bromo-*tert*-butylbenzene. A solution of 3 ml (appr. 0.03 mol) of dimethyl disulfide in 10 ml of absolute ether was added, causing a mildly exothermic reaction and the gradual appearance of a gray precipitate. After a reflux period of 5 h, enough 2 M hydrochloric acid was added to dissolve the precipitate, and the resulting two phases were separated. The ether phase was washed with water, sodium carbonate solution and water, dried over anhydrous sodium sulfate and filtered. Vacuum distillation gave 2.7 g (50 %) of a colorless oil, b.p. 108 – 110 °C/930 Pa. This sulfide was dissolved in 15 ml of glacial acetic acid, and 8 ml of 30 % aqueous hydrogen peroxide (appr. 0.08 mol) was added. The reaction mixture was refluxed

for 30 min and poured onto ice. The solid material which precipitated was collected and recrystallized from 50 % ethanol to give 2.7 g (85 %) of colorless crystals, m.p. 69 – 69.5 °C. ^{1}H NMR (60 MHz, CDCl$_3$): δ 1.60 (9 H, s), 3.11 (3 H, s), 7.25 – 7.75 (3 H, m), 8.10 – 8.35 (1 H, m).

o-tert-*Butylthiophenol.* A Grignard reagent was prepared[9] from 10.7 g (0.05 mol) of *o*-bromo-*tert*-butylbenzene. Elemental sulfur, 1.6 g (0.05 gram atom), was added in portions and the mixture was kept at reflux for 3 h. About 0.2 g of lithium tetrahydridoaluminate was added in order to reduce any disulfide formed, and 40 ml of 5 M hydrochloric acid was added. After separation of the two phases, the ether phase was washed with water and conc. sodium chloride solution and dried over anhydrous sodium sulfate. Distillation gave 3.3 g (40 %) of product, b.p. 115 – 118 °C/2.4 kPa, lit.[14] 99 °C/1.3 kPa.

Benzyl o-tert-*butylphenyl sulfide.* A solution of 1.2 g (0.03 mol) of sodium hydroxide in 2 ml of water was added to a solution of 3.3 g (0.02 mol) of *o-tert*-butylthiophenol and 2.5 g (0.02 mol) of benzyl chloride in 25 ml of methanol. A moderately exothermic reaction took place. The mixture was left overnight at room temperature and then evaporated *in vacuo*. The remaining oil was freed from inorganic solids by dissolution in ether, washing with water, drying over Sikkon ® and reevaporation *in vacuo*. The residue was 5.1 g (100 %) of the sulfide, a colourless oil.

Benzyl o-tert-*butylphenyl sulfone.* Of the preceding sulfide, 3.0 g (0.012 mol) was dissolved in 60 ml of dichloromethane. *m*-Chloroperbenzoic acid (Fluka AG, 85 % grade), 5 g (0.025 mol peracid), was added in portions over a period of 5 min. After another 10 min, the solution was washed with 1 M sodium hydroxide solution to remove acids, dried over anhydrous sodium sulfate and evaporated *in vacuo* to yield 3.5 g of colourless oil (theoretical yield of sulfone 3.4 g). After 6 months at 5 °C the oil had not crystallized. IR (film): bands at 1130, 1155, and 1320 cm^{-1}. Sulfones are reported[15] to have strong bands at 1175 and 1325 cm^{-1}. Sulfoxides have a strong band in the 1000 – 1050 cm^{-1} region,[15] in which no strong absorption of the present sample was observed. ^{1}H NMR (60 MHz, CDCl$_3$): δ 1.60 (9 H, s), 4.40 (2 H, s), 7.0 – 8.0 (9 H, multiplet). The sulfoxide most probably would have shown an AB pattern for the benzyl group, but a singlet was observed.

Purification of supporting electrolytes and solvents. Tetramethylammonium chloride (Fluka AG) was recrystallized from a mixture of methanol and ether and dried *in vacuo*. Tetraethylammonium perchlorate was prepared from the bromide and sodium perchlorate, preelectrolyzed until free from sodium ion and recrystallized five times from water. Tetrabutylammonium iodide was "polarography grade"

from Fluka AG. The methanol was from May and Baker, reagent grade, and used as received. The DMF was purified as in earlier work.[3]

Polarography. The half-wave potentials at a dropping mercury electrode were recorded in DMF solution using the same conditions as in earlier work.[3] A three-electrode apparatus similar to the Heath Model EUW 401 was used.

Electrolyses. An H-type cell with a cation exchange membrane (Amfion ® type C-311), clamped between two flat-flange joints, was used. The supporting electrolyte was a 0.05 – 0.5 M solution of tetramethylammonium chloride or lithium chloride in methanol. The cathode was a 20 cm^2 mercury layer and the anode a bundle of graphite rods. A silver chloride coated silver wire in a glass capillary containing supporting electrolyte served as the reference electrode. The catholyte was agitated by a stirrer which did not touch the mercury surface. The cell was immersed in ice water and the catholyte was kept deaerated with nitrogen. Current was supplied by a 200 V/1 A potentiostat built in this laboratory. The instantaneous current as well as its time integral were registered on a two-channel recorder. This arrangement, recommended by Fry,[16] made possible some important kinetic observations which have been commented on. An oscilloscope was connected across the cell to monitor the stability of the system. According to our experience some potentiostats (including commercial ones) cause oscillation in the 10 – 20 kHz region with some cells. The oscillation can reach an amplitude close to the full voltage swing of the potentiostat and has the consequence that the electrolysis does not take place at constant electrode potential. The remedy is to change the transfer function of the potentiostat by suitable damping.

After preelectrolysis, a weighed amount (2 – 5 mmol) of sulfone was added to the cathode compartment. The potentials of electrolysis are given in Table 2. The initial current was about 100 mA, and the experiments were run to exhaustion, at least 2 h. The half-life for the cases showing first-order kinetics was about 20 min. After completion of each run, a known amount of sodium 2,2,3,3-tetradeuterio-3-trimethylsilylpropionate (Merck), about 50 mg (0.3 mmol), was dissolved in the catholyte to serve as calibration substance as well as internal shift reference in the following analysis. The mercury was separated off and the methanol solution evaporated *in vacuo*. A few ml of deuterium oxide (99.5 % grade) was added and the evaporation repeated. The residue was dissolved in the minimum amount (1 – 3 ml) of deuterium oxide. The ^{1}H NMR spectrum was recorded on a Varian A-60 or T-60 instrument. The absolute amounts of the sulfinate ions could be calculated from the corresponding integrals of the peaks. Tetramethylammonium ion, when present in the supporting electrolyte, gave a huge peak at δ 3.2, but this

Table 3. 60 MHz ¹H NMR data for some sulfinate ions.

Ion	Chemical shift in ppm (D₂O, ref. (CH₃)₃SiCD₂CD₂COONa)
Methanesulfinate	2.29 (s)
o-Toluenesulfinate	2.54 (3 H, s), 7.25 − 7.95 (4 H, m)
o-tert-Butylbenzene-sulfinate	1.52 (9 H, s), 7.45 − 8.15 (4 H, m)

did not interfere with any sulfinate ion signal needed for quantitative analysis in the present work.

The chemical shifts for the various sulfinate ion signals are given in Table 3.

In the analysis of the catholyte after electrolysis of benzyl o-tert-butylphenyl sulfone, signals from o-tert-butylbenzenesulfinate ion were observed. In the lithium chloride run, no signals were found between 3.0 and 6.0 ppm, the expected region for the methylene protons of phenylmethanesulfinate ion. Aryl-sulfonyl cleavage had apparently not taken place. (The absence of tert-butylbenzene in the catholyte was also verified by GLC analysis.)

For comparison, some runs were also made in DMF containing tetraethylammonium perchlorate (0.1 M). A cell with a glass frit as separator between the cathode and anode compartments was used since some runs were made at elevated temperatures. The reference electrode was a silver iodide coated silver wire in 0.1 M tetrabutylammonium iodide (in DMF), contained in a glass capillary. Identification of the sulfinate ions was made through ¹H NMR analysis as above after evaporation of the solvent *in vacuo*.

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