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Cathodic Cleavage of Methyl and Benzyl Naphthyl Sulfones

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The cathodic behaviour of the methyl and benzyl naphthyl sulfones has been investigated at a mercury cathode in *N*,*N*-dimethylformamide/tetraethylammonium perchlorate or methanol/tetramethylammonium or lithium chloride.

Methyl α-naphthyl sulfone gives exclusively naphthalene and methanesulfinate ion, and the β isomer gives also some 1,2-dihydronaphthalene. The latter compound is believed to result from hydrogenation followed by cleavage. In aprotic solvent, either isomer displays reversible formation of the corresponding radical anion.

The benzyl naphthyl sulfones give toluene and the corresponding naphthalenesulfinate ions as the main products. Even in aprotic solvent, the first electron transfer appears to be irreversible for both isomers.

The cathodic reduction of methyl phenyl sulfone at mercury is known to yield methane and benzenesulfinate ion, both in methanol[1] and in *N*,*N*-dimethylformamide (DMF).[2] On the other hand, if a strongly electron-attracting group, *e.g.*, carboxyl, cyano, or methanesulfonyl, is introduced in the aromatic ring of methyl phenyl sulfone, aryl-sulfonyl cleavage takes place, leading to methanesulfinate ion and a monosubstituted benzene.[3]

We now report a study of the cathodic behaviour of methyl α-naphthyl sulfone (*1*), methyl β-naphthyl sulfone (*2*), benzyl α-naphthyl sulfone (*3*), and benzyl β-naphthyl sulfone (*4*) at mercury in DMF containing tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. For comparison, some preparative electrolyses have also been carried out in methanol containing lithium chloride or tetramethylammonium chloride.

Table 1. Polarographic data for sulfones.

$E_{1/2}$/V [a] [i_d/μA] ($E_{1/4}-E_{3/4}$/mV)	$E_{1/2}$/V [b] [i_d/μA] ($E_{1/4}-E_{3/4}$/mV)
Methyl α-naphthyl	
−1.89, −2.44	−1.91
[2.5] [1.85]	[5.0]
(56) (85)	(60)
Methyl β-naphthyl	
−2.00, −2.49	−2.02
[3.1] [3.1]	[4.8]
(60) (55)	(60)
Benzyl α-naphthyl	
−1.77, −2.30, −2.53	−1.78, ?[c]
[7.5] [2.3] [3.5]	[9.0]
(55) (60) (60)	(70)
Benzyl β-naphthyl	
−1.93, −2.42, −2.64	−1.97, −2.55
[6.3] [2.9] [2.3]	[8.0] [3.0]
(85) (55) (55)	(55) (55)
Methyl phenyl	
−2.28	
[3.9]	
(65)	
trans-Cinnamyl methyl	
−2.08	
[2.8]	
(70)	

[a] Sulfone conc. 5×10^{-4} M, solvent 0.1 M TEAP in DMF, pot. *vs.* SCE. [b] Phenol conc. 2×10^{-3} M, conditions otherwise same as in *a*. [c] Poorly defined wave.

RESULTS AND DISCUSSION

Methyl naphthyl sulfones. The polarographic data are given in Table 1. Comparison of the wave heights of *1* and *2* with that of methyl phenyl sulfone, which is known to give a two-electron wave,[2] and application of Tomes' criterion[4] showed that in aprotic DMF, both *1* and *2* are reversibly reduced to radical anions. These are irreversibly reduced at more cathodic potentials. Addition of phenol gives irreversible two-electron waves as expected, since the radical anions are rapidly protonated by phenol to electroactive radicals.

Cyclic voltammetry at a hanging mercury drop verifies these results. Figs. 1 and 2 show the behaviour of *1* in aprotic and phenol-containing DMF, respectively. The overlapping peaks at -2.45 and 2.54 V in Fig. 1 represent the formation of substrate dianion and the one-electron reduction of naphthalene, respectively. These two processes occur at the same potential for *2*, so that only one peak is observed in this potential range. For *2* in aprotic DMF, $E_{pc} = -2.05$ and -2.55 V, $E_{pa} = -1.98$ V. Addition of phenol doubled the height of the first peak and shifted it to -2.07 V, and caused a 20 % increase of the height of the second peak. No anodic peaks were obtained upon sweep reversal.

That the peak at -2.54 V indeed represents reduction of naphthalene was verified by determination of E_{pc} for authentic naphthalene. In a separate experiment, this value was found to be -2.57 V (all potentials are *vs.* SCE). One would have expected reversibility of the third peak in Fig. 1, but since this was scarcely observed, we must conclude that the naphthalene radical anion reacts rapidly. Homogeneous electron transfer to fresh substrate is a possibility.[5] The second peak in Fig. 2 (protic DMF) represents the two-electron reduction of naphthalene to its 1,4-dihydro derivative which is observed in protic solvents.[6]

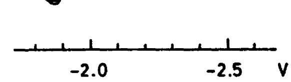


Fig. 1. Cyclic voltammogram of a 5×10^{-4} M solution of methyl α-naphthyl sulfone in DMF. Supporting electrolyte TEAP, 0.1 M. Sweep rate 165 mV s^{-1}. Potentials *vs.* SCE: $E_{pc} = -1.93, -2.45, -2.54$ V, $E_{pa} = -1.87$ V. One trace represents sweep reversal at -2.25 V.

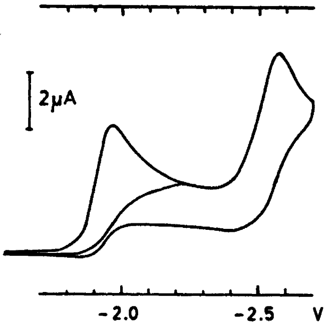


Fig. 2. Cyclic voltammogram of a 5×10^{-4} M solution of methyl α-naphthyl sulfone in DMF containing TEAP, 0.1 M, and phenol, 1.5×10^{-3} M. Sweep rate 165 mV s^{-1}. Potentials *vs.* SCE. One trace represents sweep reversal at -2.24 V.

The results from gram-scale runs are collected in Table 2. Both *1* and *2* undergo aryl-sulfonyl, but no alkyl-sulfonyl cleavage. Methyl phenyl sulfone gives exclusively alkyl-sulfonyl cleavage under similar conditions.[1,2]

Besides naphthalene, 1,2-dihydronaphthalene (*5*) was also obtained from *2*, but not from *1*. Since naphthalene is not electroreducible at the potential used, *5* must be formed from *2* *via* cathodic hydrogenation to methyl β-(1,2-dihydro)-naphthyl sulfone, followed by cleavage. Attempts at isolating the postulated intermediate from the catholyte were unsuccessful. Being an allylic sulfone, its cathodic cleavage is easily understood.[1] A referee suggested that cinnamyl methyl sulfone be studied as a model compound. The *trans* isomer of this showed $E_{1/2} = -2.08$ V, $E_{pc} = -2.13$ V, and since *2* was electrolyzed at -2.0 V, the proposed mechanism (Scheme 1) is plausible.

Scheme 1 with appropiate modifications can also be applied to the reduction of *1*. It has been pointed out by others[3] in similar cases that

Table 2. Preparative electrolysis results for sulfones.

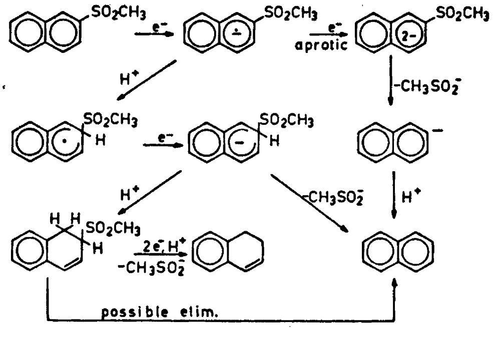
Sulfone	Supporting electrolyte[a]	Cathode pot./V	Charge/ F mol^{-1}	Hydrocarbons produced; yield (%)[b]
1	MeOH, LiCl[c]	-1.9^{d}	2.03	Naphthalene (85)
1	DMF, TEAP	-1.9^{e}	2.08	Naphthalene (85)
2	MeOH, Me_4NCl	-2.0^{d}	3.31	Naphthalene 1,2-Dihydronapht.
2	DMF, TEAP	-2.0^{e}	3.36	Naphthalene (61) 1,2-Dihydronapht. (24)
3	DMF, TEAP	-1.8^{e}	3.23	Toluene (72) Naphthalene (5)
3	DMF, TEAP[f]	-2.0^{e}	1.88	Toluene (56)
4	DMF, TEAP	-1.9^{e}	2.96	Toluene (63) Naphthalene (1)
4	DMF, TEAP[f]	-2.0_{e}	1.73	Toluene (58) Naphthalene (2) Bibenzyl (< 1)
4	DMF, TEAP[f]	-2.4^{e}	2.66[g]	Toluene (58) Naphthalene (< 2)

[a] All salts 0.1 M. In DMF runs, twice the stoichiometric amount of phenol (with respect to substrate) was usually added as proton donor. [b] No number indicates qualitative identification. [c] A similar run with Me_4NCl gave identical results. [d] Potential *vs.* Ag,AgCl/0.1 M Cl^- in MeOH. [e] Potential *vs.* SCE. [f] No phenol present. [g] The current had not reached the background value when the run was stopped.

the reaction leading to naphthalene may be regarded as nucleophilic aromatic substitution by hydride ion, though the analogy is a strictly formal one. Hydride ion cannot be cathodically generated in the systems used in this work.

It is possible to explain the formation of naphthalene *via* base-catalyzed β elimination as indicated on the bottom line of Scheme 1, and a similar route can be constructed for *1*, but we can see no reason to favour this alternative compared to the direct loss of methanesulfinate ion from the anionic intermediate shown in the centre of Scheme 1.

Benzyl naphthyl sulfones. Both isomers of methyl naphthyl sulfone have thus been shown to give exclusively aryl-sulfonyl cleavage. One possibility of bringing about alkyl-sulfonyl cleavage, which has been successfully used in a study of *ortho* alkyl substituted alkyl aryl sulfones,[7] is to replace the methyl group by a benzyl group. In order to check if the same change of the cleavage mode takes place with naphthyl sulfones, the benzyl α- and β-naphthyl sulfones, *3* and *4*, were investigated.



Scheme 1. Mechanisms of cathodic cleavage of methyl β-naphthyl sulfone in aprotic or protic solvent.

The polarographic data for *3* and *4* are given in Table 1. They are not easy to interpret quantitatively. Cyclic voltammetry at a hanging mercury drop was more informative. In aprotic DMF, *3* gave peaks at $E_{pc} = -1.79$, -2.29 and -2.54 V in the approximate ratio 2:1:2. No anodic peaks were seen, except for a small peak at -2.48 V. Addition of phenol gave two peaks of similar height at $E_{pc} = -1.80$ and -2.54 V, respectively. Similar behaviour was observed for *4*. The cyclic voltammogram is shown in Fig. 3. E_{pc} in aprotic solvent: -1.86, -2.33 and -2.56 V. Addition of phenol caused the second peak to disappear.

Preparative electrolyses in phenol-containing DMF, and also in aprotic DMF, showed that both isomers yield toluene as the main hydrocarbon (Table 2). Minute amounts of naphthalene and in one case, a trace of bibenzyl, were also detected.

From the cyclic voltammograms and the preparative results, a detailed cleavage mech-

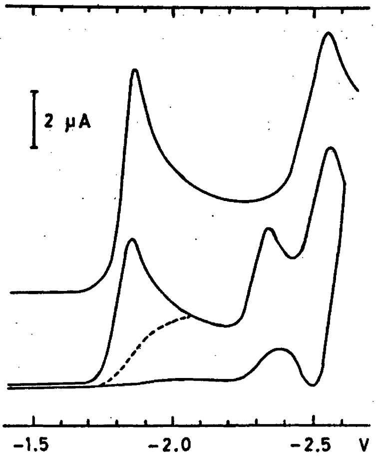


Fig. 3. Cyclic voltammogram of benzyl β-naphthyl sulfone, 5×10^{-4} M solution in DMF. Supporting electrolyte TEAP, 0.1 M. Sweep rate 165 mV s^{-1}. Potentials *vs.* SCE. Phenol concentration for lower trace, 0, for upper trace, 2×10^{-3} M. The dotted line represents sweep reversal at −2.03 V.

anism may be deduced. Initial one-electron transfer to the substrate, followed by unimolecular fragmentation, gives a benzyl radical and a naphthalenesulfinate ion (first peak in the voltammograms). In aprotic DMF, the benzyl radical reacts with mercury to a benzylmercury radical, which is reduced to benzyl anion and mercury at a more negative potential (second peak). The same behaviour is shown by benzyl bromide.[8] The benzyl anion forms toluene by proton abstraction from residual water. In phenol-containing DMF, the benzyl radical abstracts an H atom from phenol to yield toluene and a phenoxy radical, which is rapidly reduced to phenoxide ion, giving an apparent two-electron process (first peak grows larger, second peak vanishes). The naphthalenesulfinate ion is also reducible (third peak), as was verified by a comparison with authentic β-naphthalenesulfinate ion. The latter, as the tetrabutylammonium salt, gave a peak at $E_{pc} = -2.48$ V.

The trace of naphthalene obtained in the preparative runs is probably formed *via* the same route as for *1* and *2*. Bibenzyl may be formed from benzyl radicals or through thermolysis of dibenzylmercury upon GLC analysis.

EXPERIMENTAL

General. ^{1}H NMR spectra were recorded on a Varian A-60 or a Bruker WH-270 instrument. A mass spectral analysis was made on an AEI MS 902 high-resolution instrument. For GLC, a Perkin-Elmer 3920 B instrument was used with a Hewlett-Packard 3380 A integrator. The columns were 3 m, 3 mm i.d., SE-30 silicone grease on Chromosorb. Melting points were determined on a Kofler hot stage microscope.

Syntheses. Methyl α-naphthyl sulfone. Following a route used in earlier work,[7] the Grignard reagent from α-bromonaphthalene was treated with dimethyl disulfide, and the resulting sulfide was oxidized with hydrogen peroxide in acetic acid. After recrystallization from methanol, an overall yield of 69 % was secured, m.p. 101 – 102 °C, lit.[9] 102 – 103 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.23 (3 H, s), 7.4 – 8.5 (7 H, m).

Benzyl α-naphthyl sulfone. This compound was prepared like the preceding one, dibenzyl disulfide being used instead of dimethyl disulfide. The yield after recrystallization from 95 % ethanol was 52 %, colourless needles, m.p. 111.5 – 112.5 °C, ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.52 (2 H, s), 6.9 – 8.2 (12 H, m). IR (KBr disc): Sulfone bands at 1309 and 1123 cm^{-1}.

Methyl β-naphthyl sulfone. Reduction of β-naphthalenesulfonyl chloride with sodium sulfite was carried out in aqueous suspension at 70 °C for 3 h, following a literature procedure.[10a] The sulfinate was extracted into dichloromethane as the tetrabutylammonium salt,[11] and alkylation of this ion-pair with iodomethane gave the sulfone. After recrystallization from methanol, the overall yield was 53 %, m.p. 142 – 143 °C, lit.[9] 142 – 143 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.18 (3 H, s), 7.5 – 8.2 (6 H, m), 8.75 (1 H, s).

Benzyl β-naphthyl sulfone. Alkylation of tetrabutylammonium β-naphthalenesulfinate (see the preceding compound) with benzyl chloride gave the sulfone. After recrystallization from toluene, 58 % yield was obtained as colourless scales, m.p. 192 – 193 °C, ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.38 (2 H, s), 6.9 – 8.1 (11 H, m), 8.27 (1 H, s). IR (KBr disc): Sulfone bands at 1321, 1157 and 1133 cm^{-1}.

1,2-Dihydronaphthalene. This compound was prepared according to the literature[12] except that 85 % phosphoric acid was used for dehydration of α-tetralol. The latter was prepared from α-tetralone with sodium tetrahydridoborate in ethanol solution.[13] The overall yield was 75 %, b.p. 56 °C at 1 – 2 mmHg.

trans-*Cinnamyl methyl sulfone.* This compound was prepared following the literature;[14] overall yield from cinnamyl alcohol 40 %, m.p. 124 – 125 °C, lit.[14] 125 – 125.5 °C.

Tetrabutylammonium β-naphthalenesulfinate. A sample of commercial β-naphthalenesulfonyl chloride (Th. Schuckardt) was recrystallized from a benzene – pentane mixture. Hydrogenation was carried out in ether solution in a low-pressure Parr apparatus. The catalyst was 10 % palladium on charcoal.[10b] At about twice the atmospheric pressure, the hydrogen uptake was complete in 30 min. The ether solution was filtered, evaporated to dryness *in vacuo*, and the residue was dissolved in water. Excess tetrabutylammonium hydroxide solution was added, and the sulfinate was extracted as an ion-pair salt into dichloromethane. Drying over magnesium sulfate, filtration and evaporation of the solvent gave an almost colourless mass which was recrystallized from ethyl acetate. M.p. 119 – 120 °C, yield almost quantitative.

Polarography and cyclic voltammetry. The solvent (DMF) and supporting electrolyte (TEAP) were purified as described before.[15,16] A three-electrode polarograph built in this laboratory, similar to the Heath Model EUW 401 was used. The substrate concentration was 5×10^{-4} M, and that of TEAP, 0.1 M. Phenol, when present, was 2×10^{-3} M.

Preparative electrolyses. The cells used with methanol and DMF, respectively, and the potentiostat and coulometer have been described previously.[7] In the case of a methanol run, the catholyte, after electrolysis, was extracted with pentane, which was analyzed for other hydrocarbons by GLC and in one case, MS. Evaporation of the pentane gave a residue which was weighed and analyzed by ^{1}H NMR. The yields given in Table 2 are lower limits because of the volatility of the hydrocarbons. The methanol phase was also evaporated, and the remaining salts were redissolved in deuterium oxide. This solution was qualitatively analyzed by ^{1}H NMR.[7]

Work-up the DMF catholytes involved dilution with the tenfold volume of water and extraction with ether. The ether extracts were analyzed by GLC and in one case, MS. To obtain the yields of hydrocarbons, a known amount of *tert*-butylbenzene was added as an internal standard.

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REFERENCES

1. Horner, L. and Neumann, H. *Chem. Ber. 98* (1965) 1715.
2. Simonet, J. and Jeminet, G. *Bull. Soc. Chim. Fr.* (1971) 2754.
3. Manoušek, O., Exner, O. and Zuman, P. *Collect. Czech. Chem. Commun. 33* (1968) 3988.
4. Fry, A. J. *Synthetic Organic Electrochemistry*, Harper and Row, New York 1972, p. 38.
5. Lund, H., Michel, M.-A. and Simonet, J. *Acta Chem. Scand. B 29* (1975) 217.
6. Dietz, R. In Baizer, M. M., Ed., *Organic Electrochemistry*, Dekker, New York 1973, p. 260.
7. Lamm, B. and Ankner, K. *Acta Chem. Scand. B 31* (1977) 375.
8. Brown, O. R., Thirsk, H. R. and Thornton, B. *Electrochim. Acta 16* (1971) 495.
9. Otto, R., Rössing, A. and Tröger, J. *J. Prakt. Chem.* [2] *47* (1893) 94.
10. Muth, F. In *Methoden der Organischen Chemie* (Houben-Weyl), 4th Ed., Thieme, Stuttgart 1955, Band IX; *a.* p. 306; *b.* p. 311.
11. Brändström, A. *Preparative Ion-Pair Extraction*, Apotekarsocieteten/Hässle läkemedel, Stockholm 1974.
12. Hock, H. and Lang, S. *Ber. Dtsch. Chem. Ges. 75* (1942) 313.
13. Brown, H. C. *Hydroboration*, Benjamin, New York 1962, p. 242.
14. Baliah, V. and Shanmuganathan, S. *J. Indian Chem. Soc. 35* (1958) 31.
15. Lamm, B. and Simonet, J. *Acta Chem. Scand. B 28* (1974) 147.
16. Lamm, B. and Ankner, K. *Acta Chem. Scand. B 32* (1978) 31.

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