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What is the cathodic behavior for α,β-ethylenic sulfoxides in solvents of very weak acidity?

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Summary — The title compounds were cathodically reduced in aprotic organic solvents either containing or not containing a proton donor. Both coupling and cleavage products were isolated. The proton availability product distribution depends on the electrolyte nature and the presence in β of the sulfoxide moiety of a substituent which lowers the LUMO level.

α,β-ethylenic sulfoxide / electrochemical reduction / cathodic cleavage

Résumé — Quel est le comportement cathodique pour les sulfoxydes α-insaturés en milieux de très faible acidité ? Les composés du titre sont réduits cathodiquement dans le diméthylformamide (électrolyte : tétrafluoroborate de tétrabutylammonium ou tétrafluoroborate de lithium) additionné ou non de donneur de proton (phénol). Des produits de coupure et de couplage sont isolés. Quelle que soit la teneur en donneur de proton du milieu électrolyte, la distribution des produits dépend fortement de la nature du cation de l'électrolyte et de la présence en β du groupement –SO– d'un substituant qui abaisse l'orbitale basse vacante.

sulfoxyde α-insaturé / réduction électrochimique / coupure cathodique

Introduction

Numerous results were obtained on the chemical oxidation and reduction of sulfoxides. The chemical oxidation of such compounds principally appears to be a mode of access to analog sulfones. For this, a large palette of methods is now available to achieve [1] - generally in acidic aqueous media – this kind of conversion. Among these, oxidations by nitric acid [2], by air in the presence of a suitable catalyst [3], by hydrogen peroxide [4] or by peroxyacids [5–7] are fully available within recent literature.

On the other hand, the chemical reduction of sulfoxides can be carried out according to two main routes using both aprotic solvents. The one consists formally in an exchange of oxygen atoms taking into account tri- [8] and even pentavalent [9] derivatives of phosphorus (examples: PI_3, PCl_3), trivalent derivatives of boron [10] like BBr_3), derivatives of silicium [11] (like $MeSiCl_3$). Such reactions may involve miscellar media [12]. The other method which affords chemically obtaining organic sulfides from sulfoxides mainly uses either hydrides in the presence of activating agents [13] (like $NaBH_4 + TiCl_4$) or metals [14] (like $Zn + TiCl_4$).

On the contrary, only a few studies were reported on the electrochemical behavior of sulfoxides. Anodic oxidation led normally to the formation of the corresponding sulfones [1, 15], whatever the nature (aqueous or organic aprotic) of the utilized electrolyte.

If cathodic reduction is now considered, it may be underlined that sulfide is widely considered as the main product obtained from the parent sulfoxide. Particularly this reaction is seen as general in the presence of an efficient excess proton donor. However, in aprotic organic solvents, the reduction of aromatic sulfoxides was found [16] to be more complex since product distribution could be explained by the hypothetic disproportionation reaction (catalyzed by electron transfer) and probably due to the fact that primary reduction products from aromatic sulfoxides are strongly nucleophile towards the starting materials. Later on, cathodic studies concerning phenyl methyl sulfoxide confirmed [26] to a certain extent the starting point proposal. Moreover, a very recent electrochemical study has demonstrated [27] (under electron transfer catalysis) deuterion/proton exchange with α,β-ethylenic sulfoxides in a quantitative yield. Nevertheless, several reactions achieved on α,β-ethylenic sulfones (like cyclodimerizations [25]) could not be achieved with parent sulfoxides. As a consequence, the following questions arise: What are the chances with α,β-ethylenic sulfoxides to lead to hydrodimers? Under which experimental conditions? Is it possible with such substrates to show the occurrence of disproportionation? In order to answer these questions, we

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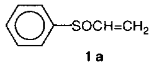
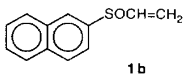
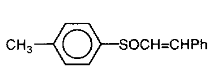
have chosen to study four different unsaturated sulfoxides **1a**, **1b**, **1c** (*Z* or *E*) and **1d** (*Z*) as target molecules.



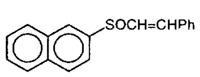
1a



1b



1c *E* or *Z*



1d *Z*

The chosen experimental conditions are essentially the aprotic ones (dimethylformamide (DMF) or dimethyl sulfoxide (DMSO)) containing quaternary ammonium salts or dried lithium perchlorate. Phenol, possibly added to these solutions, played the role of proton donor.

Experimental section

Supporting salts

Tetrabutylammonium tetrafluoroborate was synthesized from tetrabutylammonium bromide (Fluka) and sodium tetrafluoroborate (Fluka). It was then crystallized three times from a methanol/water mixture (1:1) and carefully dried for 48 h under vacuum. Lithium tetrafluoroborate was commercially available from Aldrich and used without any special purification.

Solvents and other specific chemicals

Dimethylformamide (DMF) from SDS (Solvants, Documentation, Synthèses) with less than 100 ppm of water was used without any purification. Aluminum oxide from Merck (Super I) was heated at 450 °C under vacuum for 24 h and used at once under argon atmosphere. Phenol and methyl iodide were pursached from Aldrich.

Cells and electrodes

All the electrochemical investigations were carried out in three-compartment cells. Anode, cathode and reference electrodes were in all cases separated by a glass frit (porosity: 3). All potentials refer to the system Ag/AgI/I^-, 0.1 M in DMF.

In the course of voltammetric investigations, the working electrode was either a 1 mm^2 stationary mercury drop or a 1 mm^2 stationary platinum disk. Micro- and macroelectrolyses were carried out with a mercury pool. In all cases, the counter electrode was a glassy carbon stick. All experiments were achieved under argon atmosphere. Three-electrode cells were connected to a PAR Model 173 potentiostat monitored with a PAR Model 175 signal generator and a digital coulometer PAR Model 179. Cyclic voltammetry curves were plotted on an *XY* SEFRAM-type TGM 164 recorder.

Experimental conditions

- *Controlled potential coulometries*

A mercury pool of about 1 cm^2 magnetically stirred was used as a cathode for electrolysis performed in DMF. DMF/Bu_4NBF_4, 0.1 M or DMF/$LiBF_4$, 0.1 M solutions were introduced in the cathodic and anodic (12 and 7 cm^3 respectively) compartments. For macroelectrolyses, a stirred mercury pool of 12 cm^2 was used as a cathode. DMF/Bu_4NBF_4 and DMF/$LiBF_4$ solutions were introduced into the cathodic and anodic compartments (volumes: 95 and 75 cm^3 respectively). Substrate was added to the catholyte (C: 3×10^{-3} M for microelectrolysis and 10^{-2} M for macroelectrolysis) and exhaustive reductions were then carried out at the level of the first wave peak potential. Electrolysis durations were usually about 1 h for microelectrolyses and 12 h for macroelectrolyses.

- *Specific work up*

After electrolysis completion, the catholyte in which CH_3I may be added in most of the cases was poured into water and the organic phase was extracted three times with ether from the aqueous solution. The ethereal phase was then washed with water and dried over $MgSO_4$ and finally evaporated. Lastly, reaction products were then chromatographed on a silica-gel column (Merck 60 H), eluting with cyclohexane–ethyl acetate.

Starting chemicals

NMR analyses were achieved with a Bruker AM 300 (300 MHz for ^1H, 75.5 MHz for ^{13}C). Chemical shifts δ are expressed in ppm downfield from internal tetramethylsilane as reference. High-resolution mass spectra were obtained on a Varian MAT 311 (Centre Régional de Mesures Physiques, Université de Rennes I). Phenyl vinyl sulfoxide **1a** was purchased from Aldrich and used as received. 2-Naphthyl vinyl sulfide **2b** was obtained according to the reported procedure [3]. *p*-tolyl styryl sulfide **2c** and 1-naphthyl styryl sulfide **2d** were prepared from phenylacetylene and analogous arenethiol by following the procedure given in [4]. Sulfoxides **1b–d** were obtained by oxidation of the corresponding sulfides using oxone (Aldrich) and wet alumina (Aldrich) according to [5].

- *2-Naphthyl vinyl sulfoxide* **1b**

^1H NMR, CD_3CN, δ: 5.89 (d, $^3J_{HCHA}$ = 9.5, H_C); 6.15 (d, $^3J_{HBHA}$ = 16.4, H_B); 6.75 (dd, $^3J_{HAHB}$ = 16.4, $^3J_{HAHC}$ = 9.5, H_A); 7.55–7.61 (m, =C*H*, 3H); 7.89–7.99 (m, =C*H*, 3H); 8.15–8.16 (d, *J* = 1.0, =C*H*, 1H).

^{13}C NMR, CD_3CN, δ (ethylenic system data): 121.0 (dd, $^1J_{CH}$ = 161, $^1J_{CH}$ = 164, CH_BH_C); 144.6 (dd, $^1J_{CH}$ = 177, $^2J_{CH}$ = 5, CH_A).

HRMS calc for $C_{12}H_{10}OS$ $[M]^+$: 202.045; found 202.046.

Yield: 65%; mp: 65–66 °C.

Analysis: $C_{12}H_{10}OS$; calc: C 71.25, H 4.97, S 15.85; found: C 71.21; H 5.01; S 15.88.

- *p-Tolyl styryl sulfoxide* **1c** *(Z)*

^1H NMR, CD_3CN, δ: 2.39 (s, CH_3, 3H); 6.43 (d, $^3J_{HAHB}$ = 10.6, H_A); 7.08 (d, $^3J_{HBHA}$ = 10.6, H_B); 7.28–7.45 (m, =C*H*, 5H); 7.54–7.59 (m, =C*H*, 4H).

^{13}C NMR, CD_3CN, δ: (ethylenic system data): 136.8 (d, $^1J_{CH}$ = 176, CH_A); 138.3 (dt, $^1J_{CH}$ = 156, $^3J_{CH}$ = 5, CH_B).

Yield: 75%; oil.

- *p-Tolyl styryl sulfoxide* **1c** *(E)*

^1H NMR, CD_3CN, δ: 2.37 (s, CH_3, 3H); 7.01 (d, $^3J_{HAHB}$ = 15.5, H_A); 7.35 (d, $^3J_{HBHA}$ = 15.5, H_B); 7.36–7.40 (m, =C*H*, 5H); 7.48–7.57 (m, =C*H*, 4H).

^{13}C NMR, CD_3CN, δ (ethylenic system data): 135.2 (dd degenerate, $^1J_{CH}$ = 179, CH_A); 135.9 (dt, $^1J_{CH}$ = 153, $^3J_{CH}$ = 4, CH_B).

Yield: 70%; mp: 56–57 °C.

HRMS calc for $C_{15}H_{14}OS$ $[M]^+$: 242.053; found 242.070 and $[M - O]^+$: 226.081.

Analysis: $C_{15}H_{14}OS$; calc: C 74.34; H 5.82; S 13.23; found: C 74.37; H 5.88; S 13.11.

This *trans* compound was obtained by oxidation of the *cis* ethylenic sulfide in acetic acid with one equiv of H_2O_2 at 110 °C.

- *2-Naphthyl styryl sulfoxide* ***1d*** *(Z)*

^{1}H NMR, CD_3CN, δ: 6.52 (d, $^3J_{HAHB} = 10.6$, H_A); 7.23 (d, $^3J_{HBHA} = 10.6$, H_B); 7.42–7.52 (m, =C–H, 3H); 7.58–7.66 (m, =C–H, 5H); 7.94–8.05 (m, =C–H, 3H); 8.26 (m, =CH, 1H).

^{13}C NMR, CD_3CN, δ (ethylenic system data): 137.9 (d, $^1J_{CHA} = 177$, CH_A); 139.9 (dt, $^1J_{CHB} = 157$, $^3J_{CH} = 4$, CH_B).

Yield: 75%; mp: 106–107 °C.

HRMS calc for $C_{18}H_{14}OS$ $[M]^+$: 278.076; found $[M - O]^+$: 262.082.

Analysis: $C_{18}H_{14}OS$; calc: C 77.70, H 5.03, S 11.51; found: C 77.40, H 4.57, S 11.22.

Products of electrolyses

- *Electrolysis of* ***1a*** *in DMF/Bu_4NBF_4, 0.1 M*

Methyl phenyl sulfone ***3a****: mp: 87–88 °C*

^{1}H NMR, $CDCl_3$, δ: 3.06 (s, CH_3, 3H); 7.55–7.69 (m, =CH, 3H); 7.93–7.97 (m, =CH, 2H).

HRMS calc for $C_7H_8O_2S$ $[M]^+$: 156.024; found: 156.025.

Methyl phenyl sulfide ***4a****: liquid*

^{1}H NMR, $CDCl_3$, δ: 2.48 (S, CH_3, 3H); 7.24–7.30 (m, =CH, 5H).

HRMS calc for C_7H_8S $[M]^+$: 124.034; found: 124.034.

- *Electrolysis of* ***1a*** *in DMF/Bu_4NBF_4, 0.1 M + phenol*

Phenyl vinyl sulfide ***2a****: liquid*

^{1}H NMR, $CDCl_3$, δ: 5.34 (d, $^3J_{HBHA} = 16.6$, HB); 5.35 (d, $^3J_{HCHA} = 9.6$, H_C); 6.54 (dd, $^3J_{HAHB} = 16.6$, $^3J_{HAHC} = 9.6$, H_A); 7.22–7.40 (m, =CH, 5H).

^{13}C NMR, $CDCl_3$, δ: (ethylenic system data): 115.4 (t, $^1J = 161$, CH_BH_C); 131.8 (ddd, $^1J = 173$, $^2J = 3$, $^2J = 5$, CH_A).

HRMS calc for C_8H_8S $[M]^+$: 136.034; found: 136.035.

- *Electrolysis of* ***1b*** *in DMF/Bu_4NBF_4, 0.1 M*

Methyl 2-naphthyl sulfone ***3b****: mp: 139–140 °C*

^{1}H NMR, $CDCl_3$, δ: 3.12 (s, CH_3, 3H); 7.53–7.80 (m, =CH, 2H); 7.90–8.09 (m, =CH, 4H); 8.55 (s, =CH, 1H).

HRMS calc for $C_{11}H_{10}O_2S$ $[M]^+$: 206.044; found: 206.036.

Methyl 2-naphthyl sulfide ***4b****: mp: 59–60 °C*

^{1}H NMR, $CDCl_3$, δ: 2.58 (s, CH_3, 3H); 7.3–7.5 (m, =CH, 3H); 7.59 (d, $J = 1.42$, =CH, 1H); 7.71–7.80 (m, =CH, 3H).

HRMS calc for $C_{11}H_{10}S$ $[M]^+$: 174.050; found: 174.052.

Methyl 2-naphthyl sulfoxide ***5b****: PF: 106–107 °C*

^{1}H NMR, $CDCl_3$, δ: 2.79 (s, CH_3, 3H); 7.58–7.62 (m, =CH, 3H); 7.96–8.00 (m, =CH, 3H); 8.21 (s, =CH, 1H).

HRMS calc for $C_{11}H_{10}SO$ $[M]^+$: 190.045; found: 190.046.

- *Electrolysis of* ***1b*** *in DMF/$LiBF_4$, 0.1 M*

3b*,* ***4b****, 2-Naphthyl vinyl sulfide* ***2b****: liquid*

^{1}H NMR, $CDCl_3$, δ: 5.38 (d, $^3J_{HBHA} = 16.6$, H_B); 5.40 (d, $^3J_{HCHA} = 9.5$, H_C); 6.62 (dd, $^3J_{HAHB} = 16.6$, $^3J_{HAHC} = 9.5$, H_A); 7.40–7.46 (m, =CH, 3H); 7.74–7.83 (m, =CH, 4H).

^{13}C NMR, $CDCl_3$, δ (ethylenic system data): 115.9 (dd, $^1J = 160$, $^1J = 162$, C_{HBHC}); 131.7 (ddd, $^1J = 174$, $^2J = 2$, $^2J = 5$, C_{HA}).

HRMS calc for $C_{12}H_{10}S$ $[M]^+$: 186.050; found: 186.050.

- *Electrolysis of* ***1b*** *in DMF/Bu_4NBF_4, 0.1 M + phenol and DMF/$LiBF_4$, 0.1 M + phenol:* ***2b***

- *Electrolysis of* ***1c*** *(Z) in DMF/Bu_4NBF_4, 0.1 M*

1c *(E), Methyl p-tolyl sulfone* ***3c****: mp: 88–89 °C*

^{1}H NMR, $CDCl_3$, δ: 2.45 (s, CH_3, 3H); 3.03 (s, SO_2CH_3, 3H); 7.36 (d, $^3J = 8.1$, =CH, 2H); 7.82 (d, $^3J = 8.1$, =CH, 2H).

HRMS calc for $C_8H_{10}O_2S$ $[M]^+$: 170.040; found: 170.040.

2,3-Diphenylbuta-1,3-diene ***6****: mp: 42–44 °C*

^{1}H NMR, $CDCl_3$, δ: 5.30 (d, $^2J_{HAHB} = 1.7$, $2H_A$); 5.54 (d, $^2J_{HBHA} = 1.7$, $2H_B$); 7.21–7.26 (m, =CH, 6H); 7.37–7.40 (m, =CH, 4H).

^{13}C NMR, $CDCl_3$, δ (ethylenic system data): 116.3 (t, $^1J_{CH} = 160$, $=CH_2$); 149.8 (sm, quaternary C of ethylenic system).

HRMS calc for $C_{16}H_{14}$ $[M]^+$: 206.109; found: 206.106.

- *Electrolysis of* ***1c*** *(Z) in DMF/$LiBF_4$, 0.1 M*

3c*, Methyl p-tolyl sulfide* ***4c****: liquid*

^{1}H NMR, $CDCl_3$, δ: 2.29 (s, CH_3, 3H); 2.43 (s, SCH_3, 3H); 7.07 (d, $^3J = 8.1$, =CH, 2H); 7.16 (d, $^3J = 8.1$, =CH, 2H).

HRMS calc for $C_8H_{10}S$ $[M]^+$: 138.050; found: 138.050.

- *Electrolysis of* ***1c*** *(Z) in DMF/Bu_4NBF_4, 0.1 M + phenol and DMF/$LiBF_4$, 0.1 M + phenol*

p-Tolyl disulfide ***8***

^{1}H NMR, $CDCl_3$, δ: 2.31 (s, CH_3, 3H); 7.09 (d, $^3J = 8.1$, =CH, 2H); 7.16 (d, $^3J = 8.1$, =CH, 2H).

HRMS calc for $C_{14}H_{14}S_2$ $[M]^+$: 246.052; found: 246.053.

- *Electrolysis of* ***1d*** *(Z) in DMF/Bu_4NBF_4, 0.1 M*

6*,* ***1d*** *(E)*

^{1}H NMR, $CDCl_3$, δ: 6.88 (d, $^3J_{HAHB} = 15.6$, H_A); 7.43 (d, $^3J_{HBHA} = 15.6$, H_B); 7.13–7.64 (m, =CH, 7H); 7.85–7.96 (m, =CH, 4H); 8.24 (d, $J = 0.93$, =CH, 1H).

^{13}C NMR, $CDCl_3$, δ (ethylenic system data): 132.8 (dd, $^1J = 173$, $^2J = 3$, CH_A); 136.75 (dt, $^1J = 157$, $^3J = 3$, CH_B).

HRMS calc for $C_{18}H_{14}SO$ $[M]^+$: 262.081; found: 262.082.

Methyl 2-naphthyl sulfone ***3b****: mp: 139–140 °C*

^{1}H NMR, $CDCl_3$, δ: 3.12 (s, CH_3, 3H); 7.53–7.80 (m, =CH, 2H); 7.90–8.09 (m, =CH, 4H); 8.55 (s, =CH, 1H).

HRMS calc for $C_{11}H_{10}O_2S$ $[M]^+$: 206.044; found: 206.036.

- *Electrolysis of* **1d** *(Z) in DMF/LiBF$_4$, 0.1 M*

3b, *Methyl naphthyl sulfide* **4b**: *mp: 59–60 °C*

^{1}H NMR, CDCl$_3$, δ: 2.58 (s, CH_3, 3H); 7.3–7.5 (m, =CH, 3H); 7.59 (d, J = 1.42, =CH, 1H); 7.71–7.80 (m, =CH, 3H).

HRMS calc for $C_{11}H_{10}S$ [M]$^+$: 174.050; found: 174.052.

- *Electrolysis of* **1d** *(Z) in DMF/Bu$_4$NBF$_4$, 0.1 M + phenol*

4b

Results

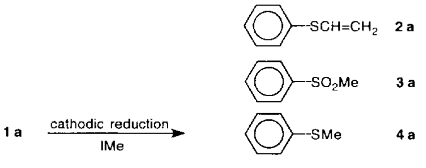
DMF-Bu$_4$NBF$_4$

Compounds **1a–d** reduced in DMF–TBATFB (0.1 M) all exhibited at least one reduction step (table I). Compound **1a** which very probably possesses the lowest LUMO gave one irreversible step which consumes much more than one-electron whatever the sweep rate. The corresponding peak potential was found to be highly negative. Currents were compared to a fully reversible one-electron system (here anthracen) under indentical experimental conditions. The three other substrates **1b**, **1c** and **1d** all showed a reversible one-electron step when the sweep rate v was made larger than 1 V s^{-1}. With slower sweep rates, the peak potential value changed with v. Slopes corresponding to the range 0.01 to 1 V s^{-1} (two decades of v) are given in table I.

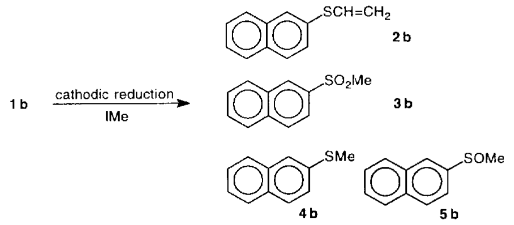
Results of macroelectrolyses carried out in DMF containing ammonium salts are gathered in table II. It can be noticed that sulfoxides **1** mainly afforded (although in rather low yield) the corresponding sulfinate ion. Small amounts of sulfide ions (in the order of 5%) were also found in the reduction mixture. Some moderate amounts of diphenyl butadiene **6** obtained with α-ethylenic sulfoxides **1c** and **1d** do attest the occurrence of a coupling reaction. Lastly, macroelectrolyses of **1c** and **1d** (isomers Z) afforded very low yields of E isomers, suggesting that reduction at the level of the Z isomer potential did not afford a total reduction of the parent E isomer.

Table II. Micro- and macroelectrolyses on sulfoxides **1** (in DMF–TBATFB, 0.1 M) at concentration $C_1 = 3 \times 10^{-3}$ M and $C_2 = 10^{-2}$ M respectively. Cathode: mercury pool; area: 10 cm^2; reference electrode: Ag/AgI/I$^-$, 0.1 M. Solutions were treated after electrolysis completion by methyl iodide during 12 h at room temperature.

Substrate	E_{red} *(V)*	*n(F mol^{-1})*		*Electrolysis products (isolated yield %)*
		C_1	C_2	
1a	−2.00	1.25	0.98	**3a** (18) **4a** (3)
1b	−1.55	1.30	0.99	**3b** (37) **4b** (5) **5b** (4)
1c (Z)	−1.50	1.72	0.98	**1c** (E) (4) **3c** (27) **6** (6)
1d (Z)	−1.30	1.25	1.09	**1d** (E) (4) **3b** (31) **6** (15)



Scheme 1



Scheme 2

Table I. Voltammetric data for sulfoxides (concentration: 3.0×10^{-3} M) obtained in DMF + TBATFB, 0.1 M. Working system electrode: stationary mercury microelectrode. Reference: Ag/AgI/I$^-$, Bu$_4$N$^+$ (0.1 M) in DMF.

Sulfoxide	*Peak potential*[a]				*Number of electrons*[c] *involved in VC*		*Slope*[d] $E_p = f(v)$ *(mV)*
	E_1	E_2	E_3	E_4	*0.1 V s^{-1}*	*100 V s^{-1}*	
1a	−1.85	–	–	–	1.42	2.71	35
1b	−1.48[b]	−1.93	−2.05	–	1.05	0.88	18
1c	−1.58[b]	−2.00	−2.23	–	1.00	0.93	15
1d	−1.43[b]	−1.74	−2.05	−2.20	1.55	0.91	30

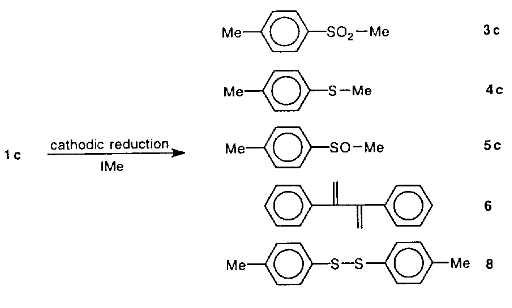
[a] Peak potentials were measured at a sweep rate of 0.1 V s^{-1}. [b] First step reversible when $v > 1$ V s^{-1}. [c] Number of electrons calculated from voltammetric experiments [23] when compared to anthracene. [d] Linear variation for peak potential within the range 0.1–1 V s^{-1}.

Table III. Coulommetric and macroelectrolysis results in the solvent–electrolyte couple DMF + $LiBF_4$, 0.1 M with sulfoxides **1b**, **1c** and **1d** (concentrations: $C_1 = 3 \times 10^{-3}$ M and $C_2 = 10^{-2}$ M). Macroelectrolysis data are given for concentration C_2. Working cathode: mercury pool (area: 10 cm^2); reference: $Ag/AgI/I^-$, 0.1 M in DMF. Catholyte solution was treated with methyl iodide in excess after total completion of the electrolysis.

Substrate	E_{red} *(V)*	*n (F mol^{-1})*		*Product distribution (isolated yield %)*
		C_1	C_2	
1b	−1.55	$2.30 < n < 3.10$	2.60	**2b** (14) **3b** (25) **4b** (14)
1c (*E*)	−1.40	$2.10 < n < 3.30$	3.20	**3c** (17) **4c** (14) **5c** (2)
1d (*Z*)	−1.38	$2.10 < n < 3.10$	3.05	**3b** (41) **4b** (56)

DMF–LiBF$_4$

Owing to its very negative reduction potential, compound **1a** could not be reduced in the presence of a lithium salt when a mercury cathode was used. On the contrary (see table III), the reduction of the three other starting substrates could be achieved. With **1b** and **1c**, the conversion sulfoxide → organic sulfide was obtained in higher yield than above, probably because the lithium ion can play the role of Lewis acid towards sulfoxide anion radicals. Moreover, lithium salts, which are known to be very hydroscopic, may probably favor the moisture admission into the electrolysis solution. Note the presence of small amounts of methyl sulfoxide (presumably formed – see the discussion hereafter – by methylation of the sulfenate ion attesting the cathodic cleavage of the C–S bond). In the presence of lithium ion, compound **1d** specifically afforded sulfide **4b** and sulfone **3b** in nearly equal amounts testifying the occurrence of disproportionation under electron transfer as already mentioned with other aromatic sulfoxides [24].



Scheme 3

Reduction in the presence of a proton donor

As underlined above, traces of moisture in the electrolysis solutions allow the limited cathodic conversion of sulfoxide into sulfide. As shown in figure 1 with sulfoxide **1b**, the addition of the stronger proton donor (like phenol) to the solution permitted to shift the first reduction step which comitantly increased. This step was checked to correspond to the bielectronic reduction (coulometry achieved at −1.55 V). Additionnally a second step merged at −1.8 V when a proton donor was added. This step should normally account for the two-electron cleavage of the ethylenic sulfide but the current was noted to be definitively larger than the one expected for a bielectronic step and relevant coulometries with this material revealed electricity consumption definitively higher than 3 F mol^{-1}. It is worth noting that a rather similar behavior was found with compound **1d**: the specific step of the organic sulfide did not appear either (fig 2) in aprotic solvent. On the contrary, voltammetry in the presence of phenol allowed to discover a step centered at −1.80 V. Similarly, the latter step assigned to the reduction of the sulfide did not appear anymore after a potentiostatic reduction of **1d** at −1.38 V. Additionally the existence of a disulfide bridge especially after electrolysis could easily be noticed (fig 3, curves c and d) at a mercury electrode (reversible system at −0.4 V).

A general overview of macroelectrolysis results is shown in table IV. Results with tetrabutylammonium and lithium salts were compared in the presence of phenol. Under protic conditions the formation of thioether or/and organic sulfide ion was checked. With **1c** and **1d** it was amazing to note the high electricity consumption which was found to be around 4 ± 0.2 F mol^{-1} especially with sulfoxide concentrations equal to or even larger than 10^{-2} M L^{-1}. This unexpected 'tetraelectronic' reduction step for ethylenic sulfoxide which was checked – by macroelectrolysis – to lead to the sulfide ion, was not noticed at all within voltammetric time scales. It was found to be provoked by a slow reaction of the phenate ion onto the α-ethylenic sulfide as mentioned in more detail in the discussion.

Discussion

All the electrolysis results gathered in tables II–IV clearly exhibit that the behaviour of aromatic sulfoxides (especially made unsaturated in the course of the present study) was found to be quite unexpected.

First of all, in electrolyte containing ammonium salts, some amounts of the corresponding sulfide (presence of the methylated thioether after treatment with an electrophile like methyl iodide which was checked to give a nearly quantitative marking of the sulfide ion after completion of the electrolysis) were often of the order of traces, eg 5%. Very similar results were noticed with other electrophiles like benzyl bromide. On the contrary, in the absence of an electrophile, the presence of –S–S– bridges was found either in voltammetry (specific oxidation of ArS^- at the mercury or platinum electrode) or during the work up (presence of disulfides in the electrolysis products, see figure 3 with a specific response of the S–S bridge at the mercury microelectrode). The presence of ArS^- cannot be provoked by the reduction of the sulfoxides into the corresponding α,β-ethylenic sulfides (by means of traces of water or

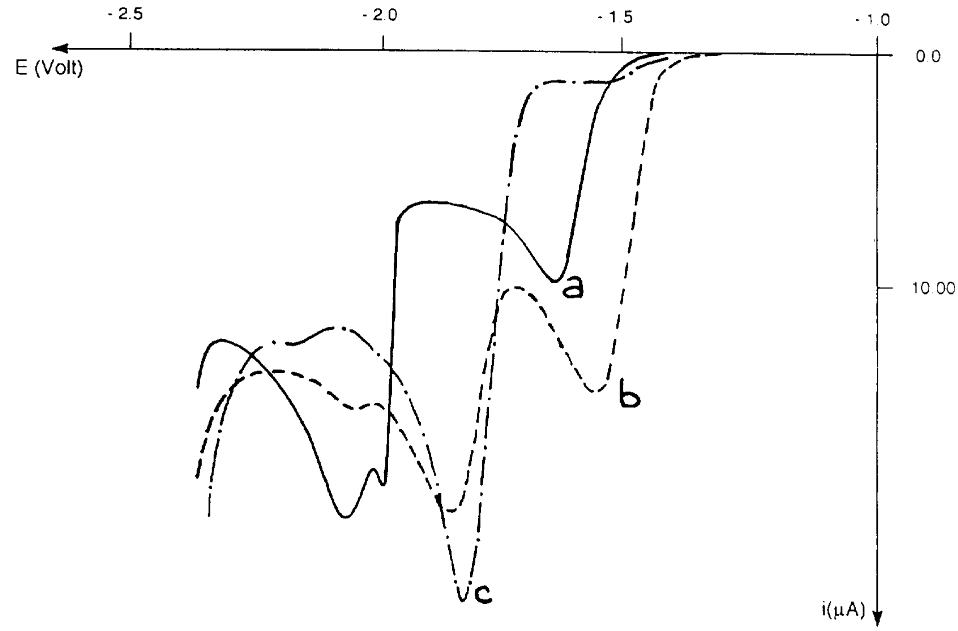


Fig 1. Voltammetry of a solution of **1b** (concentration: 3×10^{-3} M) in DMF/n-Bu_4NBF_4, 0.1 M. Mercury microelectrode; reference: Ag/AgI/I^-, 0.1 M; sweep rate 0.1 V s^{-1}. (a) Specific response for **1b**. (b) Preceding solution of **1b** containing now phenol in excess (concentration: 5×10^{-3} M). (c) After total reduction at a mercury pool cathode ($E = -1.55$ V with $n = 1.89$ F mol^{-1}).

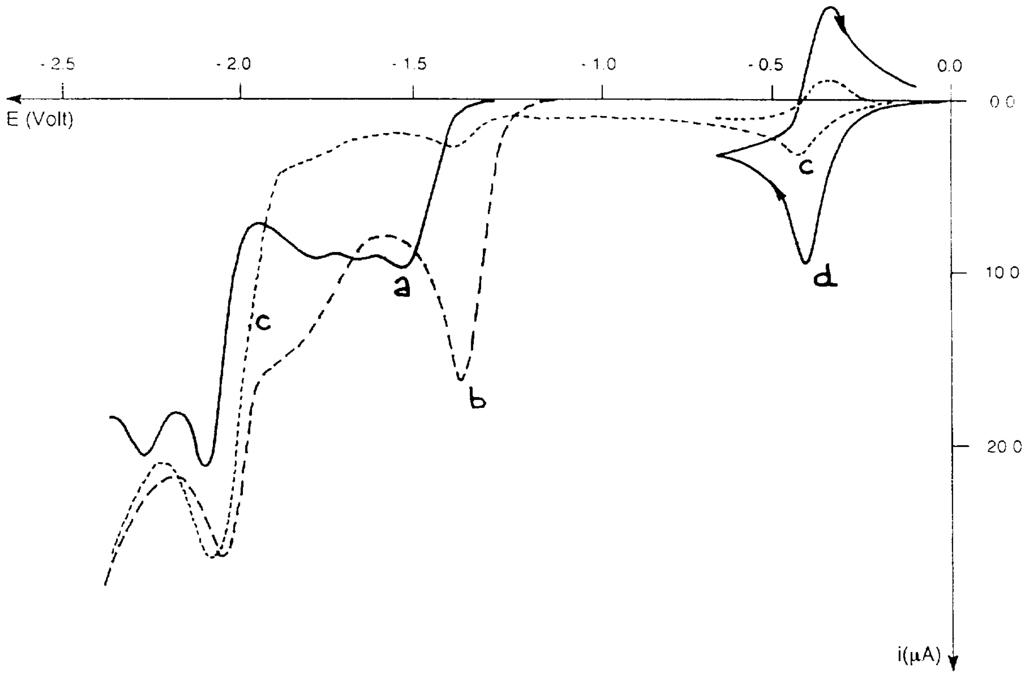


Fig 2. Voltammetric analysis of **1d** (concentration 3×10^{-3} M) in DMF + n-Bu_4BF_4, 0.1 M. Mercury microelectrode. Sweep rate: 0.1 V s^{-1}; reference: Ag/AgI/I^-, 0.1 M. (a) Response of **1d** in aprotic solution. (b) Solution (a) added with phenol in excess (concentration: 5×10^{-2} M). (c) After reduction of the preceding solution – protic conditions – at $E = -1.38$ V ($n = 2.9$ F mol^{-1}) at a mercury pool cathode. (d) Cyclic voltammetry – for comparison – of diphenyl disulfide (concentration: 3×10^{-3} M).

Table IV. Electrolyses carried out under protic conditions on starting sulfoxides (for two target concentrations: $C_1 = 3 \times 10^{-3}$ M and $C_2 = 10^{-2}$ M). Phenol concentration: 2×10^{-1} M; mercury pool cathode (area: 10 cm^2). The solution was treated after total completion of the electrolysis with methyl iodide in excess.

Sulfoxide	*Electrolyte*						*Electrolysis products (%)*
	DMF/Bu_4NBF_4/phenol			*DMF/$LIBF_4$/phenol*			
	E_{red} (V)	*n (F mol^{-1})*		*E_{red} (V)*	*n (F mol^{-1})*		
		C_1	C_2		C_1	C_2	
1a	−1.80	2.10	2.15	–	–	–	**2a** (75)[a]
1b	−1.50	1.90	2.06	−1.60	1.95	2.19	**2b** (80)[a] (70)[b]
1c	−1.35	2.90	4.15	−1.42	2.90	4.05	**8** (20)[a] (12)[b]
1d	−1.28	2.50	–	−1.30	2.60	4.21	**4b** (70)[a]

[a] Yields in DMF/Bu_4NBF_4. [b] Yields in DMF/$LiBF_4$.

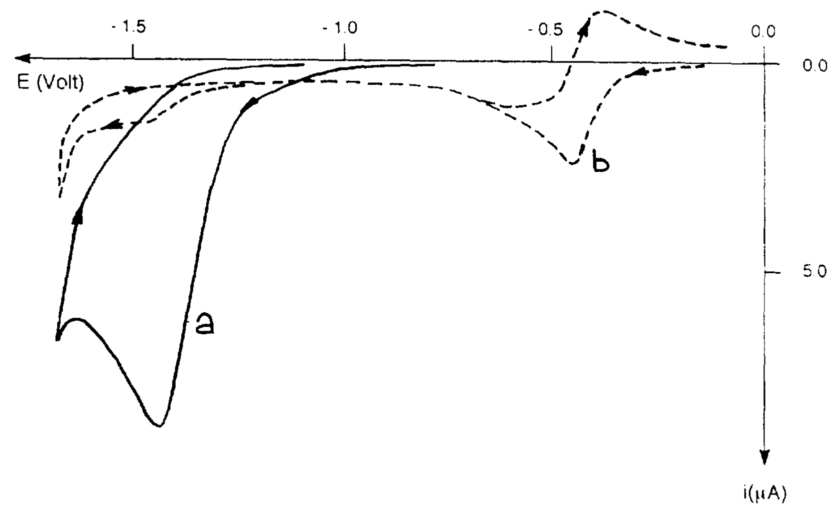


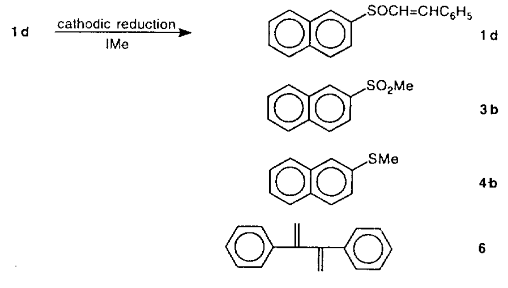
Fig 3. Cyclic voltammetry of **1c** (concentration: 3×10^{-3} M) in DMF-$LiBF_4$, 0.1 M. Working electrode: stationary mercury microelectrode. Reference: Ag/AgI/I^-, 0.1 M. Sweep rate: 0.1 V s^{-1}. (a) Before macroelectrolysis. (b) After electrolysis at a mercury pool cathode ($n = 3.10$ F mol^{-1}) at potential $E = -1.38$ V.

any acidic impurities present in the catholyte), possibly cathodically cleared at the potential of the primary reaction. As a matter of fact it has been verified that unsaturated sulfides were cathodically reduced at more negative potentials than the sulfoxide and that it seems unlikely that sulfides were reduced by the anion radical of the sulfoxide owing to a rather large potential difference between both the expected $E°$'s of each entity and the high chemical instability of sulfoxide anion radicals of the present series as developped below.

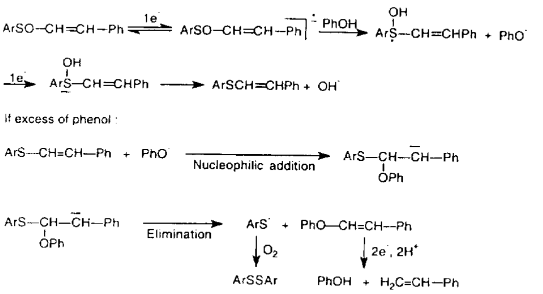
The most probable mechanism which might explain the limited amount of aromatic sulfide ion could be connected to the presence of acidic AH in very small amounts, acting as proton donor and consequently liberating the impurity as an electrogenerated nucleophile. Especially the presence of β-naphthol (4%) from **1c** might also be similarly explained by means of a nucleophilic aromatic substitution.

Secondly, all sulfoxides **1** reduced in aprotic conditions alternatively with a lithium salt as electrolyte undoubtedly led both to corresponding sulfides and sulfones (in fairly equivalent amounts). Corresponding electricity consumptions were in all cases definitively greater than 2 F mol^{-1}. As a typical experiment let us quote the reduction of **1d** in $LiBF_4$/DMF (table III) which afforded after addition of MeI both the corresponding methyl sulfone (isolated yield 41%) and methyl sulfide (yield 56%). Similar to previous experiments already reported with simpler aromatic sulfoxides [16], it is expected here that experimental conditions (particularly the presence of the Li^+ ion acting mainly as Lewis acid) favor a disproportionation-like process taking place under electron transfer and tentatively written as depicted in scheme 7.

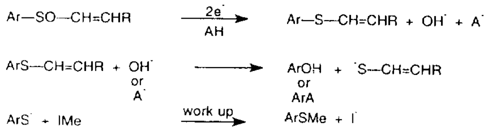
Since such a kind of disproportionation has been found until now with large Ar groups [24], it seems reasonable to consider the elementary reaction as a



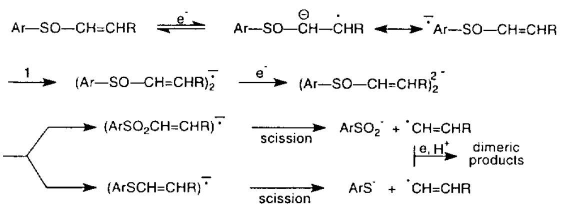
Scheme 4



Scheme 5



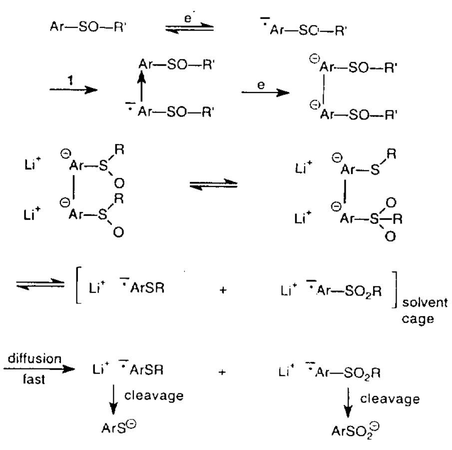
Scheme 6



Scheme 7

charge transfer complex formation between the anion radical and the substrate oxidized form followed by a second transfer (that is rather likely) and then a homolytic cleavage of the dianion might occur: as a matter of fact, the organic sulfide would be cleaved at a potential at which an electron transfer cannot quickly take place. The diffusion of the two anion radicals from the solvent cage should be fast. It remains however to explain why electron transfer does not occur and does not lead to the dianion of the aromatic sulfones (see scheme 8).

It was additionnally fully checked that such a so-called disproportionation does not occur in the presence of phenol as proton donor. For example, sulfoxide **1d** under such experimental conditions suffers a cleavage



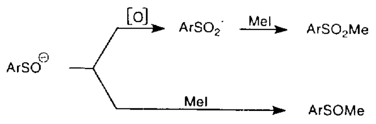
Scheme 8

since the relevant methyl sulfide **4b** was isolated nearly exclusively (yield 70%) while sulfoxide **1c** exhibits a classical reduction in sulfide also in good yield (70%).

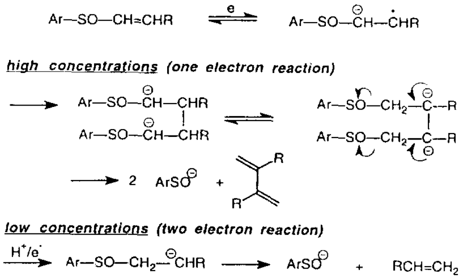
In the course of many experiments performed in tetraalkylammonium salts, large amounts of sulfinate ions (therefore leading to the corresponding methyl sulfone in the presence of MeI) were often noticed, especially when the work-up, after the electrolyses, was achieved in regular conditions, eg, in the presence of air. On the contrary, when the addition of the latter electrophile was realized in the cathodic compartment in careful conditions warranting as well as possible the absence of dioxygen, noticeable amounts of methyl sulfoxides were unexpectedly found (isolated yields up to 10–15%). These experimental facts have suggested that ethylenic sulfoxides **1** could be cleaved specifically under electron transfer:

$$1 \xrightarrow{e} 1^{\cdot -} \xrightarrow{\text{cleavage}} \mathrm{ArSO}^{\ominus} + {}^{\bullet}\mathrm{CH{=}CHR}$$

and the transient sulfonate ion may follow two chemical routes: either oxidation during the work-up, leading to the methyl sulfone, or alkylation in the absence of oxygen, affording a new sulfoxide formation:



For the moment, it seems too early to generalize the conditions for the formation of the sulfonate ion (for instance: cleavage at the level of the radical anion or even β-elimination). Particularly, the occurrence of an elimination reaction would be highly likely and might explain both the formation of dimer **6** and sulfonate (or sulfinate according to the condition of work up) ion: see scheme 9.



Scheme 9

The well-known tendency for olefin to lead to anionic or radical polymerization did not allow for the isolation of monomeric olefin. On the contrary, dimeric forms were isolated and fully characterized and moderate yields were explained in a similar manner. Lastly, the possible transformation of Z isomers into E isomers has already been noticed with geometric isomers of α-ethylenic sulfones [25]. The reason was the thermodynamic inequality $E_Z^{\circ} > E_E^{\circ}$ bound to the rate of rotation at the level of the anion radical with the more hindered isomer. A similar explanation for isomerization of the more stable isomer in the case of analogous sulfoxides is obviously very likely.

Acknowledgments

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