

examined by HPLC as described above. Peak areas were determined by triangulation. Results (mmol PPh<sub>3</sub>, ratio of 1:2): 0, 1.76 (2% of nicotine was formed); 0.024, 1.34; 0.045, 0.96; 0.062, 0.69. These values correspond to an 87% preference for reaction with I.

**Acknowledgements.** We thank Mrs. Lena Liedgren for running NMR spectra. This work has been supported by the Swedish Tobacco Company and by grants from Stiftelsen Bengt Lundqvists Minne (to L.L.).

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Received October 20, 1977.

## Homogeneous Electron Transfer Reactions. Increased Selectivity in Reduction of Some Disulfones Using Indirect Electrolysis

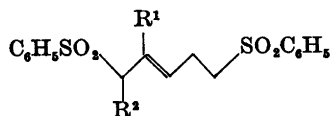
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Electrocatalytic reductions in organic electrochemistry have recently been the subject of several papers.<sup>1-11</sup> Anion radicals or dianions are generated electrochemically, and these species transfer electrons to the substrate. Quite frequently such a homogeneous electron transfer occurs without consumption of the catalyst, whereas in other cases, especially when the substrate is an aliphatic halide,<sup>3</sup> the catalyst concentration decreases due to a coupling reaction.

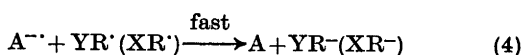
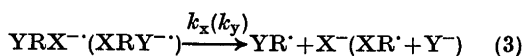
Indirect electrolysis has certain advantages and disadvantages compared to direct electrolysis. Among the advantages of indirect electrolysis is the relative independence of cell-design. In an ordinary laboratory cell the current distribution at the working electrodes is not uniform and the effective potential is therefore not the same over the whole electrode. It is thus difficult to reduce selectively one of two electroactive groups when the difference in reduction potential between the groups is less than 0.15 V. Other advantages are that complications with inhibitions occurring during macroelectrolysis may be overcome, lower electrode potentials may be employed, and higher current densities may be used especially towards the end of the experiment, compared to direct electrolysis.

In the present investigation a comparison is made with regard to the selectivity of direct and indirect electrochemical reduction of some compounds XRY where the difference in peak potential between the groups X and Y is 0.1–0.15 V; X and Y are here both benzenesulfonyl groups, X being allylic, whereas Y is not activated. The following compounds were included: 2-Methyl-1,5-bis(benzenesulfonyl)pent-2-ene (1), 2-ethyl-1,5-bis(benzenesulfonyl)pent-2-ene (2), and 2,6-dimethyl-5,9-bis(benzenesulfonyl)-nona-2,6-diene (3).



- 1, R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = H; 2, R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = H;  
3, R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = CH<sub>2</sub>CH = C(CH<sub>3</sub>)<sub>2</sub>.

In 1, 2, and 3 the two electrophores ( $C_6H_5SO_2CHR^2CR^1=CH-$  and  $C_6H_5SO_2^-$ ) are separated by two  $sp^3$ -hybridized C-atoms, so the molecule can to a first approximation be regarded as having two isolated electrophores. In the scheme below A is a compound forming a stable anion radical, whereas XRY is the disulphone.  $A^{\cdot-}$  transfers electrons to XRY in a homogeneous reaction.



The peak potentials of 1 and 2 in dimethylformamide (DMF) containing tetrabutylammonium perchlorate (TBAP) are  $-2.05$  and  $-2.20$  V vs. SCE for the first and second peak, respectively; for 3 the corresponding values are  $-2.09$  and  $-2.22$  V. In DMF containing phenol the peak potentials are shifted less than  $0.02$  V, but the peak currents are higher than in aprotic medium due to the fact that in aprotic medium the disulfones themselves act as proton donors and their anions are not electroactive.

It has previously been shown<sup>12</sup> that allylic benzenesulfonyl groups are cleaved preferentially to unactivated ones, so  $K_x k_x \gg K_y k_y$ . The A-compound should thus be chosen in such a way that it has a suitable reduction potential;  $K_x k_x$  should have a reasonable magnitude whereas  $K_y k_y$  should be negligible. As the X and Y are practically isolated electrophores the A compounds can be screened by using suitable allylic and unactivated benzenesulfonyl groups as RX and RY compounds.

9,10-Diphenylanthracene ( $E_p = -1.83$  V vs. SCE) is reduced at too positive a potential for the present systems, as the rate of reaction with the disulfones is too low. Pyrene ( $E_p = -2.04$  V) has too negative a reduction potential as it exchanges electrons both with allylic and unactivated benzenesulfonyl groups. Anthracene (4) ( $E_p = -1.92$  V) is a suitable choice, which is illustrated in Fig. 1 where the  $i-E$  curves of 4 in the presence of increasing concentrations of 2 is shown. Fig. 1 shows that the second reduction peak of XRY behaves normally and gives no indication of a fast electron transfer from  $A^{\cdot-}$ .

It has furthermore previously been found<sup>3</sup> that allylic and benzylic radicals do not couple with  $4^{\cdot-}$ , but are reduced by electron transfer from  $4^{\cdot-}$ . The indirect reduction of the disulfones is thus not complicated by removal of the electron transfer reagent in a coupling reaction.

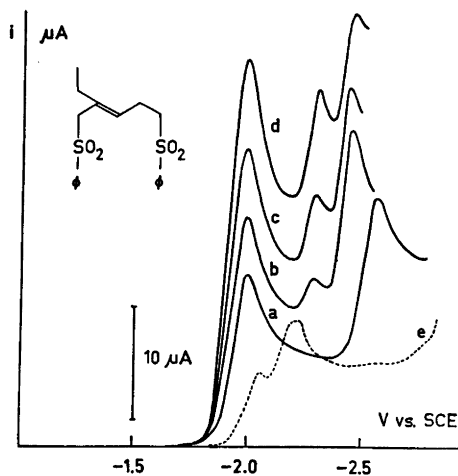


Fig. 1. Voltammetric curves at a stationary mercury electrode of anthracene in the presence of 2. a: Anthracene ( $6.5 \times 10^{-3}$  M); b, c, and d: a+2 ( $2.3$ ,  $5.1$ , and  $7.6 \times 10^{-3}$  M, respectively). e: 2 without anthracene. Medium, DMF/ $1.4 \times 10^{-1}$  M TBAP. Sweep-rate  $10$  mV  $s^{-1}$ .

In coulometric experiments, using direct electrolysis with the potential of the mercury pool electrode close to the first peak potential of the disulfone ( $-2.10$  V),  $n$  values from  $2.35$  to  $2.7$  were found, and voltammetric curves obtained before and after electrolysis showed a decrease of the height of the second peak. In contrast to that indirect electrolysis, using 4 as A-compound at a cathode potential of  $-1.95$  V, gave  $n = 2.0 \pm 0.1$  F  $mol^{-1}$ ; the electrolysis was stopped when the blue colour of  $4^{\cdot-}$  appeared, and a negligible decrease of the peak-height of the second peak was observed.

The differences in selectivity was furthermore tested by preparative experiments. Direct electrolysis of 1, 2, and 3 at  $-2.10$  V vs. SCE consumed  $3.4-3.8$  F  $mol^{-1}$ ; analytical determination of  $C_6H_5SO_2^-$  by anodic polarography showed that both benzenesulfonyl groups had been cleaved.

Indirect preparative electrolysis of 1, 2, and 3 using 4 as electron transferring agent permitted a selective cleavage of the allylic benzenesulfonyl group. In the reduction of 2 and 3 this was proved by polarography of the product which was shown to be an unactivated benzenesulfonyl compound without any vinylic or allylic benzenesulfonyl groups. From the indirect reduction of 1 2-methyl-5-benzenesulfonyl-2-pentene (5) and a small amount of 2-methyl-5-benzenesulfonyl-1-pentene (6) was isolated in good yield. Both isomers (5 and 6) would be expected as the allylic anion formed

in (4) could accept a proton at either C-1 or C-3.

The experiments thus show that in certain cases by suitable choice of electron-transferring agent a higher selectivity may be obtained using indirect rather than direct electrolysis, at least when the cell geometry is not perfect.

*Experimental.* For the coulometric measurements was used a Tacussel cell (RMO5 vessel) with a 10 cm<sup>2</sup> mercury pool electrode. The cell for macroelectrolysis was that used previously.<sup>1,2</sup>

*Chemicals.* The disulfones were a gift from Professor M. Julia, Paris. DMF was obtained from Merck and distilled once *in vacuo*; tetrabutylammonium perchlorate (TBAP) was delivered by Fluka.

*Coulometry.* In the direct electrolysis the disulfones (*C* ~ 3 mM) were reduced at a mercury pool electrode in DMF/0.15 M TBAP at the potential of the first voltammetric peak, *E* = -2.1 V *vs* SCE. Voltammograms were measured with the microelectrode directly in the catholyte before and after the electrolysis; the decrease of the second peak was taken as a measure of the extent of cleavage of the second sulfone group. In the coulometric experiment using indirect electrolysis the concentration of anthracene was about 0.5 mM; the experiment was stopped when the blue colour of *4*<sup>-</sup> appeared.

*Preparative electrolysis.* *1* (0.5 g) was reduced in 70 ml DMF/0.1 M tetrabutylammonium iodide (TBAI) at -2.0 V *vs* SCE in the presence of *4* (0.2 g). The blue colour of *4*<sup>-</sup> appeared after 2.0 F mol<sup>-1</sup>, and the electrolysis was stopped. The catholyte was worked up by diluting the catholyte with water and extracting the products with diethyl ether; evaporation of the solvent left a residue which was separated into hydrocarbons and sulfones on a column of silica using a 9:1 mixture of light petroleum and ethyl acetate as eluent. Isolated were 2-methyl-5-benzenesulfonyl-2-pentene *5* (60 % yield) and minor amounts of the 1-pentene isomer *6*.

*2* and *3* (0.2 g) were reduced similarly in the presence of *4* (0.05 g). After a similar work-up the fractions containing the benzenesulfones were analyzed by polarography. The voltammograms showed only one peak at -2.20 V *vs* SCE indicating the presence of an unactivated benzenesulfonyl group and the absence of vinylic and allylic benzenesulfonyl groups.<sup>13</sup>

When *1* was reduced electrolytically at -2.10 V *vs* SCE in DMF/0.1 M TBAP the reduction consumed 2.6 F mol<sup>-1</sup>, and a complex mixture of starting material and products was obtained; in the mixture the presence of *5* and *6* (about 10 %) was detected by <sup>1</sup>H NMR spectroscopic analysis.

*2* and *3* were reduced similarly and after consumption of 3.4–3.8 F mol<sup>-1</sup> the catholyte was analyzed for C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub><sup>-</sup> by anodic voltammetry.

*Acknowledgement.* We thank Professor M. Julia, Paris for providing samples of the disulfones.

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Received August 31, 1977.