

Electrochemical Synthesis of Sulfinic Acids

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Thiolates, generated electrochemically from disulfides in dry *N,N*-dimethylformamide (DMF), react with oxygen to a mixture of the corresponding disulfide and sulfinate. If oxygen is present during the electrochemical reduction, the disulfide formed on reaction with oxygen is reduced again to thiolate, and the sulfinate is thus obtained in good yield.

Preparation of sulfides by *in situ* alkylation of electrochemically generated mercaptans has been reported.^{1,2} The reduction of sulfonyl chlorides¹ or disulfides² to the mercaptans is performed in the absence of oxygen in order to avoid reoxidation; below is reported that the electrochemical generation of thiolates in the presence of molecular oxygen leads to the formation of sulfinate in good yield.

Aromatic sulfinic acids are conveniently prepared by reduction of sulfonyl chlorides;³ zinc dust reduction of aliphatic sulfonyl chlorides also yields sulfinic acids.⁴ Other routes to aliphatic sulfinate include treatment of alkylmagnesium compounds with sulfur dioxide⁵ and alkylation of electrochemically generated anion radicals of sulfur dioxide.⁶ An old report⁷ mentions the reaction between dry sodium ethanethiolate and dry oxygen at 100–120 °C to sodium ethanesulfinate.

RESULTS AND DISCUSSION

Electrochemical reduction in *N,N*-dimethylformamide (DMF) or acetonitrile (AN) of disulfides RSSR (R = methyl, propyl, *t*-butyl and benzyl) to the thiolates RS⁻ under exclusion of oxygen, followed by alkylation with a suitable diphenylmethyl or benzyl halide gave the expected sulfide in almost quantitative yield.

In some cases the chloride reacted much more slowly than the bromide. If, however, the thiolate was allowed to react with oxygen, not only was the parent disulfide formed, but also the corresponding sulfinate, which was characterized as a sulfone after reaction with an alkylating agent. The yield of disulfide was generally higher in concentrated solutions of thiolate, whereas the formation of sulfinate was favoured by low thiolate concentrations.

Thus, addition of oxygen to a solution (5×10^{-3} M) of 1,1-dimethylethanethiolate (1) in DMF containing Bu₄NPF₆ gave a 50 % conversion of 1 after 5 min and practically complete oxidation of 1 after 20 min. Diphenylmethyl bromide (2) was then added to the solution and a yield of diphenylmethyl *t*-butyl sulfone (3) of 75 % and of di-*t*-butyl disulfide (4) (13 %) was obtained. If oxygen was bubbled through the solution of 1 for 2 h (rather than 20 min), the same yield was obtained, but longer reaction times at room temperature decreased the yield; after a reaction time of 2½–3 h the yield of 3 was decreased to 63 %. Addition of 2 to 1 before oxygen was admitted produced diphenylmethyl *t*-butyl sulfide (5) isolated in quantitative yield.

Preparation of sulfinate by electrochemical generation of thiolates from disulfides in the presence of oxygen is a convenient method; disulfides are readily available, the relatively low concentration of thiolate during the electrochemical generation favours the formation of sulfinate, and any disulfide formed during the oxidation is reduced again to thiolate at the electrode. Yields of 80–90 % of a mixed sulfone, formed on alkylation of the sulfinate, may be obtained.

Table 1. Voltammetric peak potentials of disulfides (reduction) and thiolates (oxidation) in DMF/0.1 M Bu₄NPF₆ vs. saturated calomel electrode (SCE) at a mercury and/or glassy carbon electrode.

Compound	Reduction or oxidation potentials/V vs. SCE	
	Mercury electrode	Glassy carbon electrode
(CH ₃ S-) ₂	-1.8 ^a	
(C ₂ H ₅ S-) ₂	-1.1; ^b -2.2	-2.5
(<i>t</i> -C ₄ H ₉ S-) ₂	-0.9; ^b -2.9	-2.8
(C ₆ H ₅ CH ₂ S-) ₂	-1.0; ^b -2.15	-2.5
C ₃ H ₇ S ⁻ Bu ₄ N ⁺	-0.95	-0.3
<i>t</i> -C ₄ H ₉ S ⁻ Bu ₄ N ⁺	-0.9	-0.15
C ₆ H ₅ CH ₂ S ⁻ Bu ₄ N ⁺	-1.05	

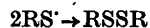
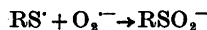
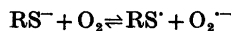
^a Polarographic $E_{1/2}$. ^b Due to complex formation with mercury.

Oxygen is reducible at the potential employed for the reduction of aliphatic disulfides (Table 1). This is not a serious complication, but the electron consumption is somewhat higher than required for the reduction of the disulfide and the completion of the reduction is not indicated by a nearly complete decrease of the current.

Another complication is that aliphatic sulfinate are not completely stable compounds, but decompose slowly, possibly due to further oxidation; by working at low temperatures and using a suitably designed cell to diminish reaction time the decomposition is not serious.

The reduction potential of oxygen is much less negative than the peak potentials of the disulfides employed here (Table 1), so an electron transfer from the thiolate ion to molecular oxygen is probably energetically favoured; furthermore, the fast coupling reaction would be a driving force for an electron transfer. The reaction also occurs without the current flowing, so the superoxide ions generated at the electrode by direct reduction is not essential for the reaction. The following reaction scheme is in accordance with that and it also explains the formation of disulfide and the concentration dependence of the yield. RS' and O₂⁻ are probably formed within a solvent cage; the pair may either collapse to the sulfinate or some

of the RS' radicals may diffuse out and dimerize to disulfide.



Electron transfer from anions or their equivalents to electron acceptors is well-known in substitution and addition reactions;⁸⁻¹³ only in a few cases¹³ are the reversible oxidation potentials of the anions known. The oxidation potentials of the thiolates have not been measured, but they must be between the peak potential of the disulfide ($E_p(S-S)$) and that of the thiolate ($E_p(S^-)$). If the reversible oxidation potentials of the aliphatic thiolates are not much more positive (> 0.6–0.7 V) than the mean value of $E_p(S-S)$ and $E_p(S^-)$, then the reaction would be able to proceed according to the scheme.

This investigation emphasizes the importance of excluding oxygen during the reduction of disulfides followed by reaction with an alkylating agent, if sulfides are the desired products. On the other hand, the reduction of disulfides in the presence of oxygen offers a convenient alternative to the known methods for the preparation of sulfinate or their alkylated derivatives. Mechanistically, the coupling between thiolate and oxygen seems to be another example of a synthetically useful reaction involving solution electron transfer from an anion.

EXPERIMENTAL

The electrochemical equipment has been described previously;¹⁴ the disulfides were commercially available or prepared by oxidation¹⁵ of commercially available mercaptans.

*Reduction of di-*t*-butyl disulfide (4) and ox-ygen.* 4 (0.5 g) was reduced in DMF/0.1 M Bu₄NI at -2.8 V (vs. SCE) with oxygen bubbling through the catholyte. After the passage of 2.2 F mol⁻¹ the electrolysis was stopped and diphenylmethyl bromide (2) (1.50 g) was added and allowed to react with 1 for 16 h; the catholyte was then diluted with water and the product extracted with diethyl ether; the ether was washed, dried and evaporated leaving a residue (1.4 g, 87%) which was recrystallized from chloroform/light petroleum. The product, m.p. 210 °C, was identified as diphenylmethyl *t*-butyl sulfone (3) from the IR- and ¹H NMR spectrum (CDCl₃): δ 1.27 (9 H, s), 5.45 (1 H, s), 7.25–7.50

(6 H, m), 7.60–7.90 (4 H, m). IR spectrum (KBr) cm^{-1} : 2920 (w), 1495 (m), 1450 (m), 1282 (s), 1107 (s), 837 (w), 777 (w), 752 (m), 707 (s), 689 (m), 678 (ms).

Similarly was reduced dipropyl disulfide (0.5 ml) at -2.3 V (SCE) with oxygen saturation; after the reduction 2 (1.73 g) was added to the catholyte. After work-up, the ^1H NMR spectrum of the crude product (1.40 g) indicated 68 % diphenylmethyl propyl sulfone (5) m.p. 116°C (111 – 113°C),¹⁶ 7 % diphenylmethyl propyl sulfide, 11 % benzhydrol and 14 % 1,1,2,2-tetraphenylethane.

Benzyl *t*-butyl sulfone (6), m.p. 122°C (126 – 127°C),¹⁷ benzyl propyl sulfone (7), m.p. 87°C (88 – 89.5°C),¹⁸ diphenylmethyl methyl sulfone (8), m.p. 130°C (128 – 134°C),¹⁹ benzyl methyl sulfone (9), m.p. 128°C (125 – 127°C)¹⁸ were obtained in yields of 85–95 % using a similar procedure.

Besides through their melting points, the sulfones were identified through their spectra. ^1H NMR spectra (CDCl_3), 5: δ 0.94 (3 H, tr, J 7 Hz), 1.5–2.2 (2 H, m); 2.83 (2 H, tr, J 7 Hz), 5.30 (1 H, s), 7.3–7.8 (10 H, m); 6: δ 1.43 (9 H, s), 4.22 (2 H, s); 7.42 (5 H, s); 7: δ 0.99 (3 H, tr, J 7 Hz), 1.4–2.2 (2 H, m), 2.78 (2 H, tr, J 7 Hz), 4.18 (2 H, s), 7.35 (5 H, s); 8: δ 2.72 (3 H, s), 5.32 (1 H, s), 7.2–7.8 (10 H, m); 9:¹⁹ δ 2.72 (3 H, s), 4.22 (2 H, s), 7.40 (5 H, s). All the compounds had two strong absorption bands at about 1300 and about 1100 cm^{-1} in the IR spectrum.

Reduction of *di-t-butyl*disulfide (4): 4 (0.12 g) was reduced as described above with argon bubbling through the catholyte, $n = 2.0\text{ F mol}^{-1}$. 2 (0.25 g) was added and the catholyte worked up as described for 3; the crude product (0.267 g, ~100 %) was identified as diphenylmethyl *t*-butyl sulfide, m.p. 45.7 – 46.7°C (light petroleum) from the ^1H NMR spectrum (CDCl_3): δ 1.25 (9 H, s), 5.21 (1 H, s), 7.1–7.6 (10 H, m). IR spectrum (KBr) cm^{-1} : 2900 (w), 1480 (w), 1435 (w), 1355 (w), 1150 (m), 1072 (w), 739 (s), 700 (s).

REFERENCES

- Gourcy, J.-G., Jeminet, G. and Simonet, J. *C. R. Acad. Sci.* 277 (1973) 1079.
- Iversen, P. E. and Lund, H. *Acta Chem. Scand. B* 28 (1974) 827.
- Muth, F. In Houben-Weyl, *Methoden der Organischen Chemie*, Thieme, Stuttgart 1955, Vol. 9, p. 303.
- Bazlen, M. *Ber. Dtsch. Chem. Ges.* 60 (1927) 1470, 1479.
- Allen, P. *J. Org. Chem.* 7 (1942) 23.
- Knittel, D. and Kastening, B. *Ber. Bunsenges.* 77 (1973) 833.
- Claessen, P. *J. Prakt. Chem.* [2] 15 (1877) 193, 222.
- Bunnett, J. F. *Acc. Chem. Res.* 11 (1978) 413.

- Kornblum, N. *Angew. Chem.* 87 (1975) 797.
- Russell, G. A. and Danen, W. C. *J. Am. Chem. Soc.* 88 (1966) 5663.
- House, H. O. *Acc. Chem. Res.* 9 (1976) 59.
- Holm, T., Crossland, I. and Madsen, J. *Acta Chem. Scand. B* 32 (1978) 754.
- Lund, H. and Kristensen, L. H. *Acta Chem. Scand. B* 33 (1979) 495.
- Degrad, C. and Lund, H. *Nouveau J. Chem.* 1 (1977) 35.
- Schöberl, A. and Wagner, A. In Houben-Weyl, *Methoden der Organischen Chemie*, Thieme, Stuttgart 1955, Vol. 9, p. 59.
- Klenk, M. M., Suter, C. M. and Archer, S. *J. Am. Chem. Soc.* 70 (1948) 3846.
- Bordwell, F. G. and Pitt, B. M. *J. Am. Chem. Soc.* 77 (1955) 572.
- Lewis, T. R. and Archer, S. *J. Am. Chem. Soc.* 73 (1951) 2109.
- Pettit, G. R., Douglass, I. B. and Hill, R. A. *Can. J. Chem.* 42 (1964) 2357.
- Doerffel, K. and Brunn, J. *J. Prakt. Chem.* 312 (1970) 701.

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