Electrochemistry of Four-co-ordinate Quadrivalent Organosulphur(IV) Compounds

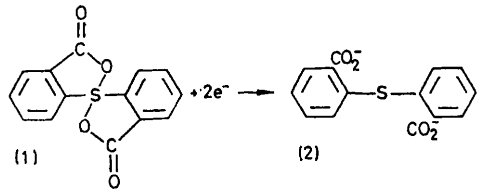
By CHI-SHENG LIAO and JAMES Q. CHAMBERS*
(*Department of Chemistry, University of Tennessee, Knoxville, Tennessee* 37916)
and ISTVAN KAPOVITS and JOZSEF RABAI
(*Institute of Organic Chemistry, L. Eötvös University, Budapest, Hungary*)

Summary The irreversible two-electron electrochemical reductions of several quadrivalent sulphur(IV) dilactones to dianions of 2,2′-thiodibenzoic acid derivatives and the anodic oxidations of the latter species in acetonitrile are reported.

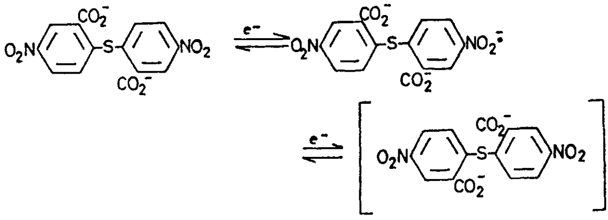
THIS communication reports the first electrochemical study of sulphuranes, a class of molecules which has attracted interest recently. The molecules studied were the dilactone (**1**)[1d,e] and its 4,4′-dinitro- and 4,4′-dimethoxy-derivatives.[1f]

Cyclic voltammograms of (**1**) in acetonitrile solution (see Figure, A) exhibit a single two-electron reduction wave (R1) and three peaks (Ox1, Ox2, and Ox3) due to oxidation of reduction products formed at R1. Peak potential data for (**1**), its 4,4′-dinitro- and 4,4′-dimethoxy-derivatives, and related compounds are given in the Table. Only the dimethoxy-derivative of the three sulphur(IV) dilactones studied could be oxidized in the potential range accessible at a platinum electrode in acetonitrile. Voltammograms of this derivative in MeCN–CH_2Cl_2 mixtures exhibit a large peak at 1·66 V *vs.* Ag/Ag+ (0·01 M) which is characteristic of methoxy-group oxidation.[2]

Coulometry [$n = 1{\cdot}98$ F per mol (**1**)] at −2·0 V and current function data indicate that the R1 wave is a two-electron process. The current functions of R1 remain



(1)



(2)

TABLE. Voltammetric peak potentials of four-co-ordinate sulphur(IV) and related compounds in acetonitrile

Compound	R1	R2	R3	Ox1	Ox2	Ox3
	E_p (V *vs.* Ag/Ag+)[a]					
(**1**)[b]	−1·87	—	—	0·42[e]	0·58[e]	1·20[e]
(**1**)[c]	−1·99	—	—	0·44[e]	0·62[e]	1·25[e]
4,4′-Dinitro-(**1**)[b]	−0·99	−1·48	−1·65	0·83[e]	1·01[e]	1·71[e]
4,4′-Dimethoxy-(**1**)[b,d]	−1·89	—	—	0·29[e]	0·55[e]	1·15[e]
2,2′-Thiodibenzoic acid[b]	−1·16	−1·70	—	—	0·57[e]	1·23[f]
2,2′-Thiodibenzoate (**2**)[b]	−1·92[e]	—	—	0·45	0·69	1·26
2,2′-Thiodibenzoate (**2**)[c]	−1·98[e]	—	—	0·47	0·74	1·30
2,2′-Thiodibenzoic acid sulphoxide[e]	−1·12	−1·75	—	—	0·96[e]	1·57

[a] Reference electrode: Ag/Ag+ (0·01 M-$AgNO_3$, 0·10 M-tetraethylammonium perchlorate, TEAP). [b] 0·10 M-TEAP. [c] 0·10 M-Tetraethylammonium tetrafluoroborate. [d] MeCN–CH_2Cl_2 mixture (2 : 1). [e] Potentials of product waves which appear on reverse and subsequent scans. [f] In addition a wave is observed at 1·46 V in the initial anodic scan.

constant as the sweep rate is increased and no evidence of an electroactive intermediate in this reduction was obtained at sweep rates up to *ca.* 100 V/s. The identity of the reduction product was firmly established by comparison[3] of the u.v. spectra and cyclic voltammograms of authentic 2,2′-dithiobenzoic acid[3] (or its tetra-alkylammonium salt) with those of the electrolysis solutions. Thus the reduction is written as an irreversible two-electron process [equation (1)].

The cyclic voltammogram of the dinitro-derivative (see Figure, B) shows that the initial reduction has shifted to a potential region characteristic of the nitro-group but has retained its irreversible two-electron nature. Apparently both dilactone rings are also rapidly opened in this case to give a dianion species which undergoes two successive one-electron additions [equation (2)] which are characteristic of dinitro-compounds.[4] Although care was taken to exclude trace amounts of water and oxygen from the electrolysis cell, the tetra-anion formed in the reduction may exist in a protonated form under the experimental conditions.

During coulometric reduction of (**1**), wave Ox1 grows more rapidly and becomes more prominent than waves Ox2 and Ox3. The peak potentials of waves Ox1 and Ox2 are concentration dependent and shift to more positive values as the electrolysis proceeds. Careful neutralization of the acid form of (**2**) with Bu_4NOH, followed by evaporation to dryness, and dissolution in MeCN yielded a solution which gave cyclic voltammograms almost identical to those of the electrolysis solution of (**1**). Double potential step chronoamperometry[5] between −2·10 V and +0·80 V *vs.* Ag/Ag^+ (0·01 M) indicated that the same number of electrons (two) was involved in wave R1 and the sum of Ox1 and Ox2. At fast sweep rates (84 V/s), wave Ox2 is relatively large compared with wave Ox1 although the total current function for waves Ox1 and Ox2 remains approximately constant. Thus, both Ox1 and Ox2 are viewed as due to oxidation of (**2**). Wave Ox3 is assigned to the oxidation of protonated (**2**) on the basis of its peak potential (Table) and wave shape.

In order to determine if the sulphurane could be generated by anodic oxidation, electrolysis of (**2**) was carried out at potentials between waves Ox2 and Ox3. However, oxidation at platinum electrodes did not go smoothly and only partial regeneration of (**1**) occurred as shown by cyclic voltammograms and u.v. spectra of the electrolysis solutions. The overall *n*-value for the oxidation was 1·8 F per mole of (**2**) and a current yield of 80% was calculated from the peak current of generated (**1**). In this case double potential step chronoamperometry and the u.v. spectra also suggested the formation of side products other than (**1**). These experiments indicate that anodic oxidation is a possible alternative to chemical oxidation as a synthetic entry into four-co-ordinate sulphur(IV) compounds.

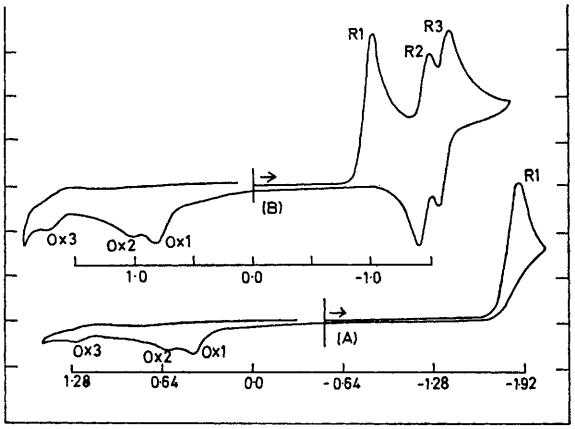


FIGURE. Cyclic voltammograms of (A) 1·0 × 10^{-3} M-(**1**) and (B) 0·97 × 10^{-3} M-4,4′dinitro-(**1**) in acetonitrile, 0·1 M-TEAP, at a platinum disc electrode (area = 0·214 cm^2). (A) 0·120 V/s, 40 μA/div.; (B) 0·200 V/s, 50 μA/div. Reference electrode: see Table.

We thank the National Science Foundation for financial support and Professor J. I. Musher for helpful discussions.

(*Received, 12th November* 1973; *Com.* 1554.)

---

[1] (a) J. I. Musher, 'Advances in Chemistry Series,' No. 10, American Chemical Society, 1972, p. 44; (b) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, 1972, **94**, 4997; (c) L. J. Kaplan and J. C. Martin, *ibid.*, 1973, **95**, 793; (d) I. Kapovits and A. Kalman, *Chem. Comm.*, 1971, 649; (e) A. Kalman, K. Sasvari, and I. Kapovits, *Acta Cryst.*, 1973, **B29**, 355; (f) I. Kapovits and J. Rabai, unpublished results.

[2] A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, 1967, **32**, 1322.

[3] A. Kucsman and I. Kapovits, *Acta Chim. Acad. Sci. Hung.*, 1962, **34**, 7.

[4] J. E. Harriman and A. E. Maki, *J. Chem. Phys.*, 1953, **39**, 778; J. Q. Chambers and R. N. Adams, *J. Electroanalyt. Chem.*, 1965 **9**, 400.

[5] T. Kambara, *Bull. Chem. Soc. Japan*, 1954, **27**, 523; W. M. Schwartz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.