

CATHODIC BEHAVIOR OF AROMATIC POLYTHIOETHERS: MOLECULAR ASTERISKS CONTAINING SULFUR AS REDOX MEDIATORS

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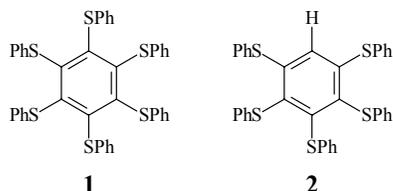
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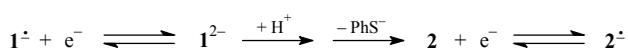
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Although aromatic thioethers are well known in organic synthesis, comparatively little is known about their reductive electrochemistry (1,2). Recently, however, a series of poly(arylthio)arenes was reduced at platinum cathodes, which prompted us to begin an electrochemical study of this new class of π -acceptors (3). In this report, we examine the reduction of hexakis(thiophenyl)benzene (**1**) and pentakis(thiophenyl)benzene (**2**) at glassy carbon electrodes in dimethylformamide (DMF) containing tetraalkylammonium salts.



Shown in Figure 1 are cyclic voltammograms for the reduction of compound **1** in DMF containing 0.10 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) (4). These curves demonstrate that, although formation of **1**^{•-} is reversible (peaks Ic and Ia), reduction of **1**^{•-} to **1**²⁻ (peak IIc) is irreversible. Because peaks IIIc and IIIa are easily assigned to the reversible reduction of compound **2**, we postulate that **1**²⁻ is rapidly protonated by the medium and eliminates thiophenolate to yield **2**, which is subsequently reduced:



EPR spectra acquired at room temperature *in situ* establish that the unpaired electron of **1**^{•-} remains located on the central benzene ring, whereas the signal for **2**^{•-} exhibits weak coupling with a single proton. We estimate that the lifetimes of **1**^{•-} and **2**^{•-} are 60 and 15 s, respectively.

Figures 2 and 3 reveal that both **1**^{•-} and **2**^{•-} catalyze the reduction of alkyl halides. However, peaks IVc and VIc indicate that alkylation and cleavage reactions accompany these processes. Bulk electrolysis of a solution of **1** with excess 1-iodoalkane at a potential corresponding to peak Ic consumes more than the expected 2 F mol⁻¹ and results in the appearance of monoalkylated product(s), along with a corresponding amount of thiophenolate. No dialkylated materials were detected.

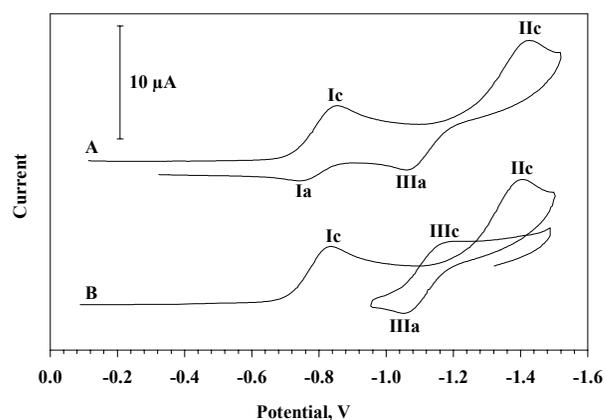


Figure 1. Cyclic voltammograms recorded at 50 mV s⁻¹ at a glassy carbon electrode in DMF containing 0.10 M TBABF₄ and 1.2 mM **1**.

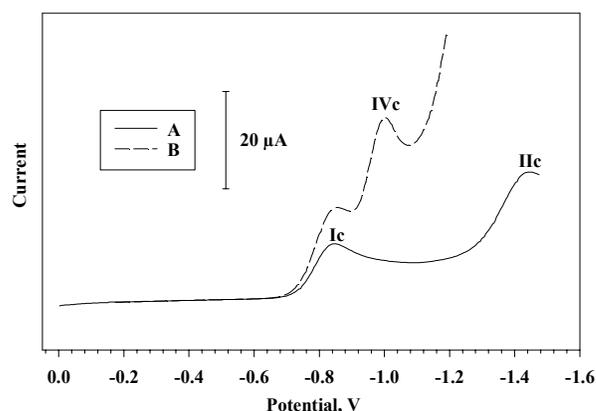


Figure 2. Linear-sweep voltammograms recorded at 100 mV s⁻¹ at a glassy carbon electrode in DMF containing 0.10 M TBABF₄ and (A) 1.1 mM **1**, (B) 1.1 mM **1** with 22 mM 1-iodopentane.

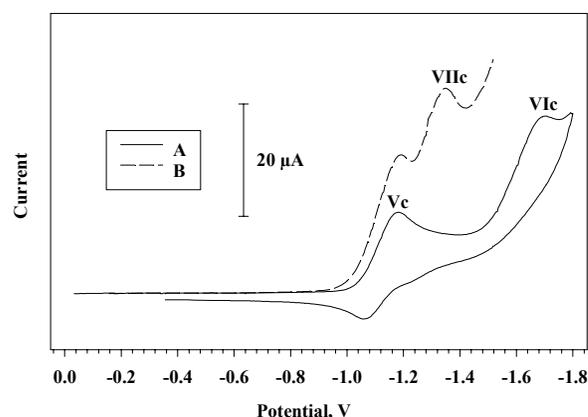


Figure 3. Voltammograms recorded at 100 mV s⁻¹ at a glassy carbon electrode in DMF containing 0.10 M TBABF₄ and (A) 3.7 mM **2**, (B) 3.7 mM **2** with 190 mM 1-bromobutane.

1. S. Oae, ed., *Organic Chemistry of Sulfur*, Plenum Press: New York, 1977.
2. J. Simonet in *Chemistry of Sulfur-Containing Functional Groups*, S. Patai and Z. Rappoport, eds., John Wiley & Sons: Chichester, 1993, pp. 439–493.
3. J. H. R. Tucker, M. Gingras, H. Brand, and J.-M. Lehn, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1303.
4. All potentials are quoted with respect to a saturated cadmium amalgam in contact with DMF saturated with both CdCl₂ and NaCl; its potential is -0.76 V vs. SCE.