



Electrochemical reduction of dihalothiophenes at silver cathodes in dimethylformamide: Evidence for a halogen dance



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ARTICLE INFO

Keywords:

Electrochemical reduction
Silver cathodes
Carbon–halogen bond cleavage
Dihalogenated thiophenes
Halogen dance

ABSTRACT

Cyclic voltammetry and controlled-potential (bulk) electrolysis have been used, along with gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS), to investigate the electrochemical reductions of 2-bromo-5-chlorothiophene (**1**), 3-bromo-2-chlorothiophene (**2**), and 2,5-dibromothiophene (**3**) at silver cathodes in dimethylformamide (DMF) containing 0.050 M tetramethylammonium perchlorate (TMAP) as the supporting electrolyte. Cyclic voltammograms for each compound exhibit two irreversible cathodic peaks that correspond to successive cleavage of the relevant carbon–halogen bonds. Controlled-potential electrolyses of 2-bromo-5-chlorothiophene revealed a two-electron cleavage of the carbon–bromine bond to afford 2-chlorothiophene as the major product along with traces of 3-bromo-2-chlorothiophene and 4-bromo-2-chlorothiophene, each arising from occurrence of a halogen dance. Bulk electrolysis of 3-bromo-2-chlorothiophene produces only 2-chlorothiophene in a two-electron process. Controlled-potential electrolysis of 2,5-dibromothiophene yields only 2-bromothiophene, via a process that involves a carbanion intermediate. A mechanistic scheme for the two-electron reduction of 2-bromo-5-chlorothiophene (**1**) is proposed that accounts for the formation of 2-chlorothiophene as well as two minor products that arise via a halogen dance.

1. Introduction

In a paper [1] published in 1996 from our laboratory, the electrochemistry of a number of mono- and dihalogenated thiophenes at glassy carbon electrodes in dimethylformamide (DMF) containing 0.10 M tetramethylammonium perchlorate (TMAP) was examined, and it was found that cyclic voltammograms for reduction of 2,5-dibromothiophene, 2,3-dibromothiophene, 2,4-dibromothiophene, and 2-bromo-5-chlorothiophene exhibit two irreversible cathodic peaks. Controlled-potential (bulk) electrolyses of each dihalothiophene at a potential corresponding to its first stage of reduction led to a mixture of products that included species in which the positions of the halogen atoms on the thiophene ring differed from those of the starting material—affording the first and unexpected examples of an electrolytically induced “halogen dance” that was encountered again in an investigation of the electrochemical reduction of 1,2,4,5-tetrabromobenzene at reticulated carbon cathodes in DMF–0.10 M TMAP [2]. Within the last decade or so, at least five review articles [3–7] have dealt with use of the “halogen dance” for purposes of organic synthesis; these articles provide a starting point toward broader aspects of this topic.

In parallel with renewed interest in the halogen dance have been

studies of the ability of silver cathodes to promote electrocatalytic cleavage of carbon–halogen bonds. Notable is a recent short overview of this topic [8], which emphasizes fundamental work by the groups of Gennaro, Isse, and Rondinini to discern whether reduction of organic halides at silver involves a concerted or a stepwise process. More specific toward the subject of the present report is a publication by Arnaboldi et al. [9] which dealt with the electrocatalytic reduction of bromothiophenes at gold, silver, and glassy carbon cathodes in acetonitrile containing tetraethylammonium tetrafluoroborate. Prompted by the preceding reference as well as by our continuing interest in the possible involvement of the halogen dance in the electrochemical reduction of halogenated thiophenes, we have undertaken the present study of the reductions of 2-bromo-5-chlorothiophene, 3-bromo-2-chlorothiophene, and 2,5-dibromothiophene at silver cathodes in dimethylformamide (DMF) containing 0.050 M tetramethylammonium perchlorate (TMAP).

An early discovery of the halogen dance was made by Vaitiekunas and Nord [10], who attempted to synthesize 2-ethynylthiophene from 2-bromothiophene and sodium acetylide in liquid ammonia. However, these workers obtained tetrabromothiophene in 35–45% yield, along with a mixture of di- and tribromothiophenes. Further research

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revealed that, under the same experimental conditions, 2-iodothiophene formed tetraiodothiophene in 50% yield, along with small amounts of di- and triiodothiophene. It has been established [7] that the classic halogen dance involves a series of deprotonation (metal–hydrogen exchange) and metal–halogen exchange reactions. A base has to be present in stoichiometric amounts and has to be strong enough to deprotonate the substrate irreversibly.

In recent years, silver electrodes have attracted much attention due to their catalytic ability as cathodes for the reduction of carbon–halogen bonds. In particular, the electrochemical cleavage of carbon–halogen bonds at silver occurs at much less negative potentials than reductive cleavage of carbon–halogen bonds at classic electrodes such as carbon or mercury. In the present study, we have investigated the reduction of three dihalothiophenes (2-bromo-5-chlorothiophene, 3-bromo-2-chlorothiophene, and 2,5-dibromothiophene) at silver electrodes with the aid of cyclic voltammetry and controlled-potential (bulk) electrolysis to search for whether the halogen dance occurs in the same manner as it does at glassy carbon electrodes. To the best of our knowledge, no previous study of this kind has appeared in the literature. Cyclic voltammetry and controlled-potential electrolysis were used to examine the direct reduction of 2-bromo-5-chlorothiophene (**1**), 3-bromo-2-chlorothiophene (**2**), and 2,5-dibromothiophene (**3**) in dimethylformamide (DMF) containing 0.050 M tetramethylammonium perchlorate (TMAP) as the supporting electrolyte. Products arising from the reduction of the three different halogenated thiophenes have been separated, identified, and quantitated with the aid of gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Reagents

Each of the following chemicals (with purity in parentheses) was obtained from Sigma Aldrich, or from another source when indicated, and was used as received without further purification unless stated otherwise: 2-bromo-5-chlorothiophene (98%), 3-bromo-2-chlorothiophene (98%), 2,5-dibromothiophene (95%), 4-bromo-2-chlorothiophene (95%, Merck), 2-chlorothiophene (96%), 2-bromothiophene (98%), 3-bromothiophene (97%), *n*-hexadecane (99%), deuterium oxide (D₂O, 99.9 atom % D), and diethyl ether (absolute, anhydrous, EMD). Dimethylformamide (DMF, 99.99%, Omnisolv) was used as the solvent for all electrochemical experiments. A few controlled-potential electrolyses were done in dimethylformamide-*d*₇ (≥ 99.9 atom % D, Sigma Aldrich). Tetramethylammonium perchlorate (TMAP, 98% min., GFS Chemicals, reagent grade) served as the supporting electrolyte; it was recrystallized twice from an ethanol–water mixture and stored in a vacuum oven at 80 °C to ensure the removal of residual water. Before the start of electrochemical experiments, solutions were deoxygenated with zero-grade argon (Air Products) for at least 20 min.

2.2. Cells, electrodes, instrumentation, and procedures

Cyclic voltammetry experiments were carried out in a specially designed one-compartment, three-electrode cell [11] with a silver working electrode (having a circular planar area of 0.071 cm²) that we fabricated by press fitting a short length of 3.0-mm diameter silver wire (Alfa Aesar, 99.9% purity) into one end of a machined Teflon tube; electrical contact to this electrode was achieved with a stainless-steel rod that was inserted into the opposite end of the Teflon tube. This working electrode was polished with an aqueous suspension of 0.05- μ m alumina paste on a rotary Master-Tex polishing pad (Buehler) and then washed with DMF in an ultrasonic bath. A coil of thin platinum wire served as the auxiliary (counter) electrode. As reference electrode for both cyclic voltammetry and controlled-potential (bulk) electrolyses, we employed a cadmium-saturated mercury amalgam in contact with

DMF that was saturated with both sodium chloride and cadmium chloride, the potential of which is -0.76 V vs. the aqueous saturated calomel electrode (SCE) at 25 °C [12–14]. To generate wave forms and to collect data for cyclic voltammetry, a Princeton Applied Research Corporation (PARC) model 2273 or 273A potentiostat with a PowerSuite® software package was used, and processing of data was done with OriginPro 2015 software.

Controlled-potential (bulk) electrolyses were performed in a two-compartment (divided) cell that is described in an earlier publication [15]. A silver gauze electrode constructed from commercially available mesh (99.9%, Alfa Aesar) that was woven from 0.356-mm-diameter wire served as a working cathode with an approximate surface area of 45 cm²; a single silver wire extending from the mesh provided an electrical connection. Before each bulk electrolysis, the silver gauze electrode was cleaned by ultrasonication in an aqueous sodium bicarbonate paste for approximately 30 min, washed thoroughly in distilled water, and dried in an oven at 180 °C for 20 min. A sintered-glass disk along with a methyl cellulose plug consisting of solvent and electrolyte was used to separate the anode and cathode compartments of the cell, and a carbon rod auxiliary electrode was immersed in solvent–electrolyte in the anode compartment. A PARC model 173 potentiostat was used for the electrolyses, and data were collected with the aid of a locally written LabView program before being processed through the use of OriginPro 2015 software.

2.3. Separation, identification, and quantitation of products

Gas chromatography–mass spectrometry (GC–MS) was used to identify electrolysis products. We employed an Agilent 6890N gas chromatograph, fitted with a 30 m \times 0.25 mm capillary column with a 0.25- μ m DB-5 stationary phase of 5% phenylpolysiloxane and 95% methylpolysiloxane (J & W Scientific), in tandem with an Agilent 5973 inert mass-selective detector operating in electron ionization mode (70 eV). By appropriate inclusion of D₂O or DMF-*d*₇ in the solvent–electrolyte, we detected the intermediacy of carbanion or radical intermediates by measuring deuterium incorporation in targeted products. We determined the degree of deuterium incorporation in the targeted products according to a procedure described in the literature [16]. A product (4-bromo-2-chlorothiophene) arising from an electrolytically induced halogen dance was identified unambiguously from its characteristic gas chromatographic retention time and mass spectrum.

In our procedure for the quantitation of products, a fixed amount of an internal standard (10 μ L of *n*-hexadecane) was injected into a known volume of solvent–supporting electrolyte in the cathode compartment of the cell at the start of each experiment. At the end of an electrolysis, the catholyte was partitioned between diethyl ether and NaCl-saturated distilled water; then the organic layer was separated and washed twice with distilled water, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation. Finally, the electrolysis products were separated and quantitated by use of an Agilent 7890A gas chromatograph fitted with a DB-5 capillary column (described above) and a flame ionization detector. Product yields were determined from experimentally determined gas chromatographic response factors and measured with the aid of Agilent ChemStation software as previously described [17].

3. Results and discussion

3.1. Cyclic voltammetric behavior of 2-bromo-5-chlorothiophene (**1**), 3-bromo-2-chlorothiophene (**2**), and 2,5-dibromothiophene (**3**)

Depicted in Fig. 1 are cyclic voltammograms recorded at 100 mV s⁻¹ for the reduction of separate 2.0 mM solutions of 2-bromo-5-chlorothiophene (**1**, black curve), 3-bromo-2-chlorothiophene (**2**, red curve), and 2,5-dibromothiophene (**3**, green curve), each with a freshly polished silver electrode in oxygen-free DMF containing 0.050 M TMAP

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