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Electrochemical Reduction of Mono- and Dihalothiophenes at Carbon Cathodes in Dimethylformamide. First Example of an Electrolytically Induced Halogen Dance

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Cyclic voltammetry and controlled-potential electrolysis have been employed to probe the electrochemical reduction of a number of mono- and dihalothiophenes at carbon cathodes in dimethylformamide containing tetramethylammonium perchlorate. Reduction of 2-bromo-, 3-bromo-, 2-chloro-, 3-chloro-, and 2-iodothiophene gives rise to a single irreversible cyclic voltammetric wave for each compound that corresponds to the two-electron cleavage of the carbon−halogen bond, and thiophene is obtained as the only product. Cyclic voltammograms for the reduction of 2,3-dibromo-, 2,4-dibromo-, 2,5-dibromo-, 3,4-dibromo-, 2-bromo-5-chloro-, and 3-bromo-2-chlorothiophene each exhibit a pair of irreversible two-electron waves. Electrolyses of either 2,3-dibromo- or 2,4-dibromothiophene at potentials corresponding to the first voltammetric wave yield a two-to-one mixture of 3-bromo- and 3,4-dibromothiophene; under similar conditions, electrolyses of 2,5-dibromothiophene give a mixture of 2-bromo-, 3-bromo-, and 3,4-dibromothiophene, electrolyses of 2-bromo-5-chlorothiophene afford a mixture of 3-bromo-, 3,4-dibromo-, 3-bromo-2-chloro-, 4-bromo-2-chloro-, and 2-chlorothiophene, and electrolyses of 3-bromo-2-chlorothiophene yield 2-chlorothiophene. Aside from the last result, these product distributions appear to arise from an electrolytically induced halogen dance. When electrolyses of the dibromothiophenes and of 2-bromo-5-chloro- and 3-bromo-2-chlorothiophene are performed at potentials that correspond to the second voltammetric wave, thiophene is the only product obtained.

Introduction

Several publications dealing with the electrochemical reduction of halogenated thiophenes have appeared in the literature. In 1963, Brown and Krupski[1] examined the polarographic behavior of eight mono-, di-, tri-, and tetraiodothiophenes in both dimethylformamide and 2-ethoxyethane containing tetra-*n*-butylammonium iodide, and they tabulated the half-wave potentials for the reduction of the various carbon−iodine bonds. Shortly thereafter, Mairanovskii, Barashkova, and Vol'kenshtein[2] reported the results of a polarographic study of the entire nine-member family of mono-, di-, tri-, and tetrabromothiophenes as well as 2-iodothiophene in aqueous ethanol solutions; for each of these compounds, a diffusion-controlled reduction wave was observed for the two-electron cleavage of each carbon−halogen bond, but no definitive information was provided concerning the products of these reductions. Cyclic voltammetry was employed by Feldmann and Koberstein[3] to probe the three-step reduction of 2,3,5-tribromothiophene at mercury in methanol, and Pletcher and Razaq[4] have demonstrated that 3-bromothiophene can be prepared in good yield via the controlled-potential electrolytic reduction of 2,3,5-tribromothiophene at lead, mercury, zinc, and graphite cathodes in dioxane−water containing sodium bromide as electrolyte. A paper by Gedye, Sadana, and Leger[5] describes the electrochemical reduction of tetrabromothiophene, tetraiodothiophene, 2,3,4-tribromothiophene, and 3,4-dibromothiophene at mercury, copper, and lead cathodes in dimethylformamide containing tetraethylammonium bromide; typical of the behavior of these compounds is the electrolysis of tetrabromothiophene which, depending on the choice of potential, could be converted sequentially into 2,3,4-tribromo-, 3,4-dibromo-, and 3-bromothiophene. Most recently, procedures for the selective electrolytic debromination of thiophene derivatives at graphite cathodes have been devised by Dappenheld and co-workers;[6] these investigators were able to prepare 3-bromo- or 3,4-dibromothiophene from 2,3,4,5-tetrabromothiophene, 3,4-dibromo-2-chlorothiophene from 2,3,4-tribromo-5-chlorothiophene, and 3-bromo-4-chlorothiophene from 2,3,5-tribromo-4-chlorothiophene in good yield.

There has been considerable interest in base-catalyzed halogen migrations that involve various halogen-substituted thiophenes.[7−9] An investigation of the use of potassium amide in liquid ammonia to promote halogen migrations in 2-bromo-, 2,3-dibromo-, 2,4-dibromo-, and 2,5-dibromothiophene was reported by van der Plas and co-workers,[7] and Gronowitz and colleagues[8] have examined the reaction of methoxide ion with several bromo-

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[1] Brown, L. W.; Krupski, E. *J. Pharm. Sci.* **1963**, *52,* 55−58.

[2] Mairanovskii, S. G.; Barashkova, N. V.; Vol'kenshtein, Y. B. *Sov. Electrochem.* **1965**, *1,* 60−64.

[3] Feldmann, M.; Koberstein, E. *Chem.-Tech. (Heidelberg)* **1977**, *6,* 517−521.

[4] Pletcher, D.; Razaq, M. *J. Appl. Electrochem.* **1980**, *10,* 575−582.

[5] Gedye, R. N.; Sadana, Y. N.; Leger, R. *Can. J. Chem.* **1985**, *63,* 2669−2672.

[6] Dapperheld, S.; Feldhues, M.; Litterer, H.; Sistig, F.; Wegener, P. *Synthesis* **1990**, 403−405.

[7] van der Plas, H. C.; de Bie, D. A.; Geurtsen, G.; Reinecke, M. G.; Adickes, H. W. *Recl. Trav. Chim. Pays-Bas* **1974**, *93,* 33−36.

[8] Gronowitz, S.; Hallberg, A.; Glennow, C. *J. Heterocycl. Chem.* **1980**, *17,* 171−174.

[9] Reinecke, M. G. *Tetrahedron* **1982**, *38,* 427−498.

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iodothiophenes. A review article by Reinecke[9] presents a further discussion of these so-called base-catalyzed halogen dances of halogenated thiophenes.

Despite all of the earlier electrochemical work, there appear to have been no previous reports that the halogen dance can occur when halogenated thiophenes are subjected to electrolytic reduction. In this paper we describe the electrochemical reduction of a number of mono- and dihalothiophenes at glassy carbon cathodes in dimethylformamide containing tetramethylammonium perchlorate. Using cyclic voltammetry and controlled-potential electrolysis, and employing gas chromatography for the identification and quantitation of products, we have found that each of the monohalogenated starting materials (2-bromo-, 3-bromo-, 2-chloro-, 3-chloro-, and 2-iodothiophene) undergoes a one-step, two-electron reduction to form thiophene exclusively. On the other hand, dihalothiophenes (2,3-dibromo-, 2,4-dibromo-, 2,5-dibromo-, 3,4-dibromo-, 2-bromo-5-chloro-, and 3-bromo-2-chlorothiophene) are reduced in a stepwise fashion; the first stage of reduction entails two-electron cleavage of one carbon−halogen bond (accompanied by an electrolytically induced halogen dance) to yield mixtures of mono- and dihalothiophenes, whereas the second stage of reduction of a dihalothiophene corresponds to an overall four-electron process to give thiophene.

Experimental Section

Reagents. Burdick and Jackson "distilled in glass" dimethylformamide (DMF) was used as received as the solvent, and tetramethylammonium perchlorate (TMAP) from GFS Chemicals, Inc., was employed without further purification as supporting electrolyte. Each of the following halogenated thiophenes was used as obtained from the Aldrich Chemical Co.: 2-bromothiophene (98%), 3-bromothiophene (97%), 2-chlorothiophene (96%), 3-chlorothiophene (98%), 2-iodothiophene (98+%), 2,3-dibromothiophene (98%), 2,5-dibromothiophene (95%), 3,4-dibromothiophene (99%), and 2-bromo-5-chlorothiophene (95%). Thiophene (Eastman Kodak Co., 99%), 2,4-dibromothiophene (Lancaster, 97%), 3-bromo-2-chlorothiophene (Acros Organics USA, 97%), and 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich, 99+%) were used as received. Deaeration procedures were carried out with Air Products zero-grade argon.

Cells, Electrodes, Instrumentation, and Procedures. Details of the cells, instrumentation, and procedures for cyclic voltammetry[10] and controlled-potential electrolysis[11,12] are presented in earlier papers. A short length of 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Co., Tokyo, Japan) was press-fitted into Teflon to give a circular, planar working electrode with an area of 0.077 cm^2 for cyclic voltammetry. Reticulated vitreous carbon disks (RVC 2X1−100S, Energy Research and Generation, Inc., Oakland, CA) were used for controlled-potential electrolyses; these electrodes (having surface areas estimated to be 200 cm^2) were fabricated, cleaned, and handled according to procedures given elsewhere.[11] All potentials are quoted with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam which is in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V vs the aqueous saturated calomel electrode at 25 °C.[13,14]

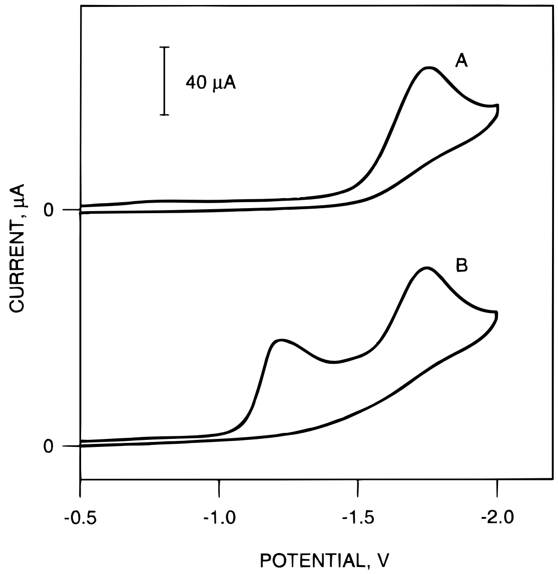

Figure 1. Cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} with a circular, planar glassy carbon electrode (area = 0.077 cm^2) in DMF containing 0.10 M TMAP and (A) 2 mM 3-bromothiophene and (B) 2 mM 2,3-dibromothiophene.

Thiophene, 2-bromothiophene, 3-bromothiophene, 3,4-dibromothiophene, 4-bromo-2-chlorothiophene, 3-bromo-2-chlorothiophene, and 2-chlorothiophene were identified by means of gas chromatography from a comparison of retention times of suspected products with those of commercially available authentic compounds. One product of the electrolytic reduction of 2-bromo-5-chlorothiophene was found to have a chromatographic retention time just slightly shorter than that of 3-bromo-2-chlorothiophene; believing that this unknown product was most likely to be 4-bromo-2-chlorothiophene, we acquired mass spectral data at 70 eV for authentic 3-bromo-2-chlorothiophene and for suspected 4-bromo-2-chlorothiophene. (a) For 3-bromo-2-chlorothiophene: m/z 200 M$^+$ (30); 198 M$^+$ (100); 196 M$^+$ (73); 163 [M − Cl]$^+$ (9); 161 [M − Cl]$^+$ (9%); 119 [M − Br]$^+$ (11); 117, [M − Br]$^+$ (26); 82 [M − Br − Cl]$^+$ (14). (b) For 4-bromo-2-chlorothiophene: m/z 200 M$^+$ (30); 198 M$^+$ (100); 196 M$^+$ (75); 163 [M − Cl]$^+$ (27); 161 [M − Cl]$^+$ (26); 119 [M − Br]$^+$ (10); 117 [M − Br]$^+$ (21); 82 [M − Br − Cl]$^+$ (19). This agreement seems to be adequate to confirm the identity of 4-bromo-2-chlorothiophene. Quantitation of all electrolysis products was accomplished with the aid of gas chromatography, as outlined in a previous publication.[12] A 30 m × 0.53 mm capillary column (AT-35, Alltech Associates) with a stationary phase of poly(phenylmethylsiloxane) was used. All product yields reported in this paper are based on gas chromatographic measurements (with *n*-octane being added as an electroinactive internal standard to each solution prior to the start of an electrolysis) and reflect the absolute percentage of starting material incorporated into a particular species.

Results and Discussion

Cyclic Voltammetric Behavior of Mono- and Dihalothiophenes. Figure 1A shows a cyclic voltammogram for the reduction of 3-bromothiophene at a glassy carbon electrode in DMF containing 0.10 M TMAP. A single, irreversible wave is observed that corresponds to the two-electron scission of the carbon−bromine bond to yield thiophene; this process is proposed on the basis of the results of controlled-potential electrolyses and on the identification of thiophene as the only electrolysis product, as discussed later. Other monohalogenated thiophenes exhibit the same kind of behavior as 3-bromothiophene, and peak potentials for all of the compounds investigated are listed in Table 1.

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[10] Vieira, K. L.; Peters, D. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *196*, 93−104.

[11] Cleary, J. A.; Mubarak, M. S.; Vieira, K. L.; Anderson, M. R.; Peters, D. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *198*, 107−124.

[12] Mubarak, M. S.; Nguyen, D. D.; Peters, D. G. *J. Org. Chem.* **1990**, *55*, 2648−2652.

[13] Marple, L. W. *Anal. Chem.* **1967**, *39*, 844−846.

[14] Manning, C. W.; Purdy, W. C. *Anal. Chim. Acta* **1970**, *51*, 124−126.

Table 1. Cyclic Voltammetry Data for Reduction of Mono- and Dihalothiophenes at Glassy Carbon[a]

compd	E_{p1}, V	E_{p2}, V
2-bromothiophene	−1.57	
3-bromothiophene	−1.76	
2-chlorothiophene	−1.75	
3-chlorothiophene	−1.84	
2-iodothiophene	−0.97	
2,3-dibromothiophene	−1.23	−1.75
2,4-dibromothiophene	−1.28	−1.69
2,5-dibromothiophene	−1.31	−1.58
3,4-dibromothiophene	−1.52	−1.74
2-bromo-5-chlorothiophene	−1.34	−1.78
3-bromo-2-chlorothiophene	−1.25	−1.72

[a] A 2.0 mM concentration of each compound in DMF containing 0.10 M TMAP was used, and the scan rate was 100 mV s^{-1}.

Table 2. Coulometric Data and Product Distributions for Electrolytic Reduction of 5.0 mM Solutions of Monohalothiophenes at Reticulated Vitreous Carbon in DMF Containing 0.10 M TMAP

compd	*E, V*	*n*	thiophene, %
2-bromothiophene	−1.60	1.99	97
3-bromothiophene	−1.80	2.05	101
2-chlorothiophene	−1.80	1.95	95
3-chlorothiophene	−1.90	2.03	102
2-iodothiophene	−1.20	1.97	103

When a cyclic voltammogram for the reduction of 2,3-dibromothiophene is recorded (Figure 1B), under conditions that are identical with those of Figure 1A, two irreversible cathodic waves are seen. We attribute the first wave to reductive cleavage of the carbon−bromine bond at the 2-position (to give the 3-bromo-2-thienyl carbanion that is more stable than the 2-bromo-3-thienyl carbanion),[7,15,16] whereas the second wave corresponds formally to reduction of the carbon-bromine bond at the 3-position. As revealed in Table 1, it is not surprising that the peak potential for the second stage of reduction of 2,3-dibromothiophene (−1.75 V) is very close to the peak potential for reduction of 3-bromothiophene (−1.76 V). Moreover, owing to the inductive effect of the 3-bromo substituent of 2,3-dibromothiophene, reduction of the carbon−bromine bond at the 2-position of 2,3-dibromothiophene is considerably easier than reduction of the carbon−bromine bond of 2-bromothiophene. Peak potentials for five other dihalothiophenes are included in Table 1, allowing one to make additional comparisons among the mono- and dihalothiophenes.

Controlled-Potential Electrolyses of Mono- and Dihalothiophenes. Compiled in Table 2 are coulometric data and product distributions for duplicate controlled-potential electrolyses of each of the five monohalothiophenes at reticulated vitreous carbon cathodes in DMF containing 0.10 M TMAP. Coulometric *n* values are reproducible to ±0.05, and product yields agree to within ±3% absolute. Clearly, the electrolytic reduction of each monohalogenated compound is a two-electron process, and thiophene is the only product.

Table 3. Coulometric Data and Product Distributions for Electrolytic Reduction of 5.0 mM Solutions of Dihalothiophenes at Reticulated Vitreous Carbon in DMF Containing 0.10 M TMAP

			Product Distribution, [a]%						
compd	*E*, V	*n*	**1**	**2**	**3**	**4**	**5**	**6**	**7**
2,5-dibromothiophene	−1.60	4.04	103						
	−1.20	1.33		63	24	16			
	−1.20[b]	1.96	2	92	5				
	−1.20[c]	1.99	1	95	2				
3,4-dibromothiophene	−1.80	3.98	101						
2,3-dibromothiophene	−1.80	3.91	96						
	−1.25	1.32			65	36			
2,4-dibromothiophene	−1.80	3.81	103						
	−1.25	1.26			66	32			
2-bromo-5-chlorothiophene	−1.80	3.92	99						
	−1.30	1.63			6	3	8	6	79
	−1.30[b]	1.76[d]							104
	−1.30[c]	1.93							100
3-bromo-2-chlorothiophene	−1.80	4.04	102						
	−1.30	1.99							100

[a] **1** = thiophene, **2** = 2-bromothiophene, **3** = 3-bromothiophene, **4** = 3,4-dibromothiophene, **5** = 4-bromo-2-chlorothiophene, **6** = 3-bromo-2-chlorothiophene, **7** = 2-chlorothiophene. [b] 50 mM 1,1,1,3,3,3-hexafluoro-2-propanol was present. [c] 1 M H_2O was present. [d] This *n* value appears to be artifically low due to an excessively large background correction.

Table 3 lists coulometric data and product distributions for electrolytic reductions of the six dihalothiophenes at potentials corresponding to either their first or second voltammetric waves; the reproducibilities of the *n* values and product distributions were comparable with those mentioned in the preceding paragraph. Each dihalothiophene, when electrolyzed at a potential corresponding to its second voltammetric wave, undergoes an overall four-electron reduction to give thiophene as the only product. However, intriguing results are obtained when these compounds are electrolyzed in the absence of a proton donor at potentials that correspond to their first voltammetric waves. For each compound, except 3-bromo-2-chlorothiophene, the coulometric *n* value is significantly lower than 2, because some of the starting material is consumed via nonelectrochemical processes (namely, the halogen dance). When 2,5-dibromothiophene is electrolyzed at −1.20 V, three products (2-bromo-, 3-bromo-, and 3,4-dibromothiophene) are obtained. Electrolyses of 2,3- and 2,4-dibromothiophene at −1.25 V afford a two-to-one mixture of 3-bromo- and 3,4-dibromothiophene, and electrochemical reduction of 2-bromo-5-chlorothiophene at −1.30 V gives rise to five products (2-chloro-, 3-bromo-, 3,4-dibromo-, 4-bromo-2-chloro-, and 3-bromo-2-chlorothiophene). When 3-bromo-2-chlorothiophene is reduced at −1.30 V, the coulometric *n* value is 2 and the only product is 2-chlorothiophene, because the carbon−chlorine bond cannot undergo direct reductive cleavage at this potential (Table 1). Electrolyses of 3,4-dibromothiophene at potentials corresponding to its first voltammetric wave could not be done successfully; because the two voltammetric waves associated with stepwise reduction of this compound are not adequately separated (Table 1), one cannot prevent the occurrence of the second stage of reduction.

Electrolyses of 2,5-dibromo- and 2-bromo-5-chlorothiophene were conducted at potentials corresponding to their respective first voltammetric waves and in the presence of an excess of a proton donor (50 mM 1,1,1,3,3,3-hexafluoro-2-propanol or 1 M water). As revealed in Table 3, addition of a proton donor causes the *n* value to become essentially 2 and the halogen dance that occurs in the absence of a proton donor is largely blocked. For 2-bromo-5-chlorothiophene, only one product (2-chlorothiophene) is obtained; however, for 2,5-dibromothiophene the principal product is the expected 2-bromothiophene,

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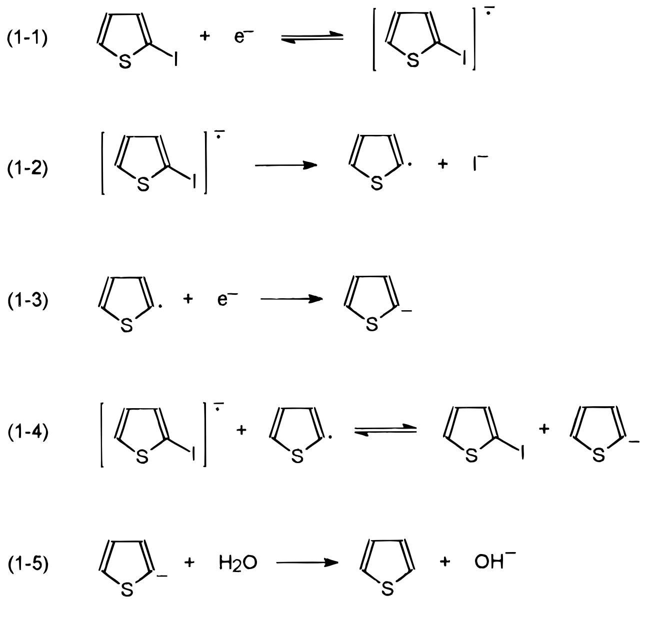
(15) Reinecke, M. G.; Hollingworth, T. A. *J. Org. Chem.* **1972**, *37*, 4257−4259.

(16) de Bie, D. A.; van der Plas, H. C.; Geurtsen, G.; Nijdam, K. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 245−252.

Scheme 1

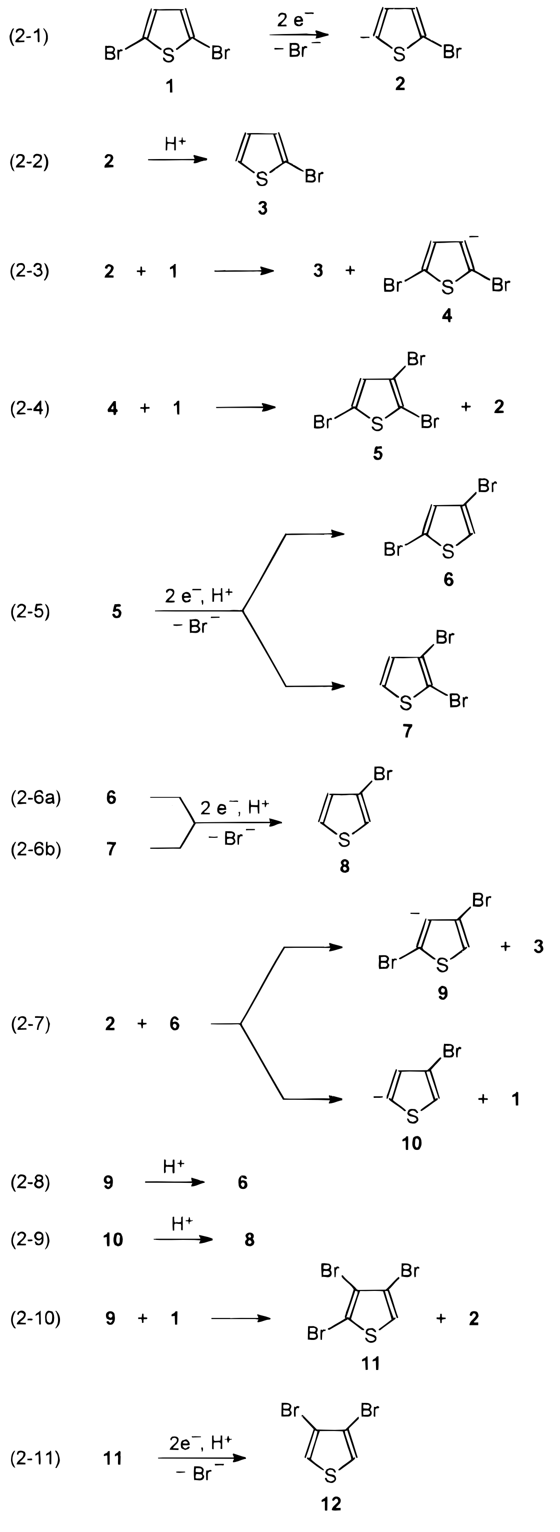


but thiophene and 3-bromothiophene are formed in very small amounts.

Mechanistic Features of the Reduction of Mono- and Dihalothiophenes. To rationalize the electrochemical behavior of the monohalothiophenes, we propose a mechanistic picture, depicted in Scheme 1, that is analogous to the well-established set of reactions[17] involved in the electrolytic reduction of aryl monohalides. Using 2-iodothiophene as a representative compound, we suggest that there is reversible uptake of one electron to yield a radical-anion intermediate (reaction 1-1), which subsequently undergoes carbon−halogen bond cleavage to give a 2-thienyl radical and iodide ion (reaction 1-2). Once formed, the 2-thienyl radical can accept a second electron in two ways: it can undergo (a) direct irreversible reduction at the surface of the cathode (reaction 1-3) or (b) a reversible solution electron-transfer reaction with an electrogenerated radical-anion intermediate near the electrode surface (reaction 1-4). In either case, the resulting 2-thienyl carbanion is protonated, most probably by water (present in the solvent-supporting electrolyte) but possibly by the tetramethylammonium cation.[18]

Attempts were made to employ fast-scan cyclic voltammetry[19] and double-potential-step chronoamperometry[19] to measure the rate constant for cleavage of the electrogenerated 2-iodothiophene radical-anion intermediate (reaction 1-2) and to determine whether the resulting 2-thienyl radical prefers to accept a second electron from the electrode (reaction 1-3; ECE$_{\mathrm{irr}}$ process) or from the electrogenerated radical-anion intermediate (reaction 1-4; DISP1 process). Unfortunately, our studies revealed that 2-iodothiophene (as well as other monohalogenated thiophenes) or the electrogenerated radical-anion intermediate is adsorbed onto glassy carbon (as well as mercury) electrodes, so that quantitative results were unattainable. However, we did find that, at cyclic voltammetric scan rates as slow as 5 to 10 V s^{-1}, a small anodic current for oxidation of the radical anion of 2-iodothiophene was observable, which indicates that the lifetime of the radical-anion is in the realm of 100 ms.

Scheme 2



To explain the electrolytically induced halogen dance that takes place when a dihalothiophene is reduced at potentials corresponding to its first voltammetric wave, we have constructed Scheme 2, showing a sequence of reactions pertaining to 2,5-dibromothiophene; analogous schemes can be written for other dihalothiophenes. Scheme 2 includes several deprotonation-transbromination reactions, of the kind invoked by earlier workers,[7−9] in which the initially electrogenerated 2-bromo-5-thienyl

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[17] Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431−3441.

[18] Vieira, K. L.; Mubarak, M. S.; Peters, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5372−5373.

[19] Andrieux, C. P.; Savéant, J. M. In *Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; Vol. VI, pp 305−390.

anion plays a key role. As a first step (reaction 2-1), we have the overall two-electron reductive cleavage of 2,5-dibromothiophene (**1**) to give the 2-bromo-5-thienyl anion (**2**), which in reaction 2-2 accepts a proton from the medium to yield 2-bromothiophene (**3**) or in reaction 2-3 accepts a proton from **1** to give **3** and the 2,5-dibromo-3-thienyl anion (**4**). Next, in reaction 2-4, **4** and **1** interact to form 2,3,5-tribromothiophene (**5**) and **2**. Then **5** can undergo electrolytic reduction (reaction 2-5) to give either 2,4-dibromothiophene (**6**) or 2,3-dibromothiophene (**7**), and each of the last two compounds can be reduced (reactions 2-6a and 2-6b) to yield 3-bromothiophene (**8**). In addition, it is possible for **2** and **6** to interact (reaction 2-7) to give either the 2,4-dibromo-3-thienyl anion (**9**) and **3** or the 4-bromo-2-thienyl anion (**10**) and **1**. Protonation of **9** and **10** leads, respectively, to **6** and **8** (reactions 2-8 and 2-9). When **9** interacts with **1** (reaction 2-10), 2,3,4-tribromothiophene (**11**) and **2** are produced, and two-electron reduction of **11** leads in reaction 2-11 to the formation of 3,4-dibromothiophene (**12**). It should be emphasized that for Scheme 2 the source of protons in reactions 2-5, 2-6a, 2-6b, 2-8, 2-9, and 2-11 can be either the medium or the starting material itself. Scheme 2 provides a minimal set of reactions that can satisfactorily account for all of the products obtained from the electrochemical reduction of 2,5-dibromothiophene. However, one of the intermediate species, 2,3,5-tribromothiophene (**5**), might also be involved in the halogen dance. Deprotonation of **5** by **2** can give rise to the 2,3,5-tribromo-4-thienyl anion which can be transbrominated by **1** to yield 2,3,4,5-tetrabromothiophene. After it is formed, 2,3,4,5-tetrabromothiophene could undergo either two-electron reduction or debromination to yield the 2,3,4-tribromo-5-thienyl anion, each process being followed by protonation to afford **11** which is subsequently converted electrochemically into **12**.

As a separate test of the occurrence of an electrolytically induced halogen dance, an experiment was performed in which a solution containing 5 mM concentrations of both 2-iodothiophene and 2,5-dibromothiophene in DMF containing 0.10 M TMAP was electrolyzed at a potential (−1.00 V) at which only 2-iodothiophene is directly reducible; the particular aim of this experiment was to confirm that the 2-thienyl anion electrogenerated from 2-iodothiophene can induce a halogen dance for 2,5-dibromothiophene. We obtained an *n* value of 2.04 (indicating complete two-electron reduction of 2-iodothiophene—which correlated with the appearance of thiophene in 96% yield), and the species emanating from 2,5-dibromothiophene were 2-bromothiophene (48%), 3-bromothiophene (34%), 3,4-dibromothiophene (17%), 2,3-dibromothiophene (∼1%), and 2,4-dibromothiophene (∼1%), along with a remaining trace of 2,5-dibromothiophene (∼1%) itself.

In electrolyses in which either 1,1,1,3,3,3-hexafluoro-2-propanol or water is present during the reduction of 2,5-dibromothiophene (as well as 2-bromo-5-chlorothiophene) at potentials corresponding to its first voltammetric wave, it is reasonable to conclude that the electrogenerated 2-bromo-5-thienyl carbanion is quickly protonated by the medium (reaction 2-2) and that its interaction with the starting material (reaction 2-3) to initiate the halogen dance is almost completely blocked.

Although the behavior of tri- and tetrahalogenated thiophenes has not been examined in the present work, we believe that such compounds will also undergo an electrolytically induced halogen dance.

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