though experimental conditions and data were not given by Fisher et al., we attempted to repeat their spectrophotometric determination as follows. Extinction coefficients for pyruvic oxime and acid at neutral pH were measured each at 230 and 240 nm, and the ratio $\epsilon^{230}/\epsilon^{240}$ was as follows: oxime, 1650/1220; acid, 680/290. Sodium pyruvate (1.26×10^{-4} M) was then mixed with hydroxylamine (2.39×10^{-4} M) at pH 6.33, and after equilibrium had been achieved (6 h at room temperature), it was found that the pyruvate had been converted quantitatively to oxime as indicated by absorbance at 230 and 240 nm. A K_B value of 2.2×10^4 M^{-1} would have required that only 63% of the pyruvate be converted to oxime.

Biochemical Significance. The large equilibrium constant for pyruvic oxime formation and the small rate constant for its hydrolysis at neutral pH indicate that pyruvic oxime is extremely stable toward hydrolytic cleavage. Thus, in order for an organism to grow aerobically on pyruvic oxime and produce nitrite from oxime nitrogen,[2-5] it would need either to catalyze oxime hydrolysis or to carry out direct oxidative attack without prior C–N bond cleavage. There is some evidence to suggest that an *Alcaligines* sp. from soil does the latter.[5] In addition, we have been unable to detect pyruvic oxime hydrolase activity in cell-free extracts of the bacterium.[22]

Experimental Section

The sodium salt of pyruvic oxime was synthesized by the method of Quastel et al.[23] Hydroxylammonium chloride was recrystallized before use. Reagent grade (Fisher) 8-quinolinol, sodium pyruvate, and inorganic salts were used without further purification. Solutions of pyruvic oxime, hydroxylammonium chloride, and sodium pyruvate were freshly prepared each day. 8-Quinolinol was dissolved in ethanol. Spectrophotometric measurements were made on either a Zeiss PM6 or a Cary 188 spectrophotometer. pH measurements were made with an Orion Model 701A meter with a Markson V445 combination electrode. Hydroxylamine released from pyruvic oxime was assayed by the following general procedure. A 1-mL sample (concentrations given in Results and Discussion) was heated at 100 °C with an equal volume of dilute acid or phosphate buffer in a stoppered tube for varying lengths of time and then allowed to cool to room temperature. This solution (1 mL) was mixed with water (1 mL) and a 1% (w/v) solution of 8-quinolinol in ethanol (1 mL). Finally a suitable Na_2CO_3 solution (1 mL) was added to give a pH of 10.9, and the absorbance at 710 nm, due to indooxine, was read after having allowed the color to develop for 1 h. Resynthesis of pyruvic oxime between the hydrolysis step and the addition of 8-quinolinol was negligible. At 100 °C, hydrolysis of pyruvic oxime was conveniently rapid. Because pK_a values and the pH values of buffered solutions vary with temperature, it was necessary to make corrections to values obtained at 25 °C in order that they may apply to solutions at 100 °C. Lumme et al.[24] have developed an empirical equation relating hydroxylammonium ion pK_a to temperature from which we estimate a value of 4.90 at 100 °C. A value of $\delta pH/\delta T = -0.025$ for phosphate buffers[21] indicates that the pH of a solution, found to be 6.43 at 25 °C, would be 4.55 at 100 °C. Values of $\delta pK_a/\delta T$ for carboxylic acids are typically small[21] and are taken as zero for the purposes of this paper.

Acknowledgment. We thank D. Castignetti for his interest and advice.

Registry No. Pyruvic oxime, 2211-14-5; pyruvic oxime anion, 20230-94-8.

---

(22) Unpublished results.

(23) Quastel, J. H.; Scholefield, P. G.; Stevenson, J. W. *Biochem. J.* **1952**, *51*, 278.

(24) Lumme, P.; Lahermo, P.; Tummavouri, J. *Acta Chem. Scand.* **1965**, *19*, 2175.

Oxidative Electrodimerization of 1,3-Dithioles to Tetrathiafulvalenes

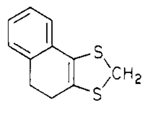
Franklin D. Saeva,* Bradley P. Morgan,
Michael W. Fichtner, and Neil F. Haley

*Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650*

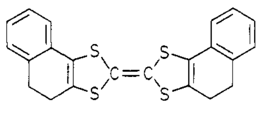
Received July 6, 1983

Molecular charge-transfer complexes of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSeF) with tetracyanoquinodimethane (TCNQ) behave optically and electrically like one-dimensional metals at room temperature.[1]

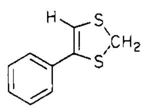
General interest in one-dimensional conductors has led to the synthesis of new electron donors of the TTF type.[2] Electrochemical synthesis of TTF derivatives has been limited thus far to reductive dimerization reactions requiring a thermal elimination step.[3,4] We report an alternative synthesis of TTF derivatives via an electrochemical oxidative dimerization of 1,3-dithioles. 4,5-Dihydronaphtho[1,2-*d*]-1,3-dithiole (**1**) and 4-phenyl-1,3-dithiole (**2**) undergo oxidative dimerization to the tetrathiafulvalenes **3** and **4**, respectively.



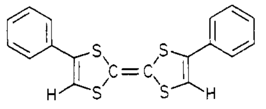
1



3



2



4

Results and Discussion

1,3-Dithioles **1** and **2** were synthesized by the method of Takamizawa and Hirai,[5] and the TTF derivatives **3** and **4** were prepared independently by the procedure of Schukat and Fanghaenel.[6] Cyclic voltammetry (CV) shows that the dithioles **1** and **2** exhibit an irreversible oxidation at $E_p = 1.38$ and 1.05 V, respectively. An anodic CV scan beyond the peak potential for **1** and **2** produces the TTF derivatives **3** and **4**, which can be detected on the following cathodic scan only in the presence of pyridine (see Figure 1). The figure shows a typical cyclic voltammogram of **1** and **3** in acetonitrile vs. SCE.

A bulk electrolysis of **1** ($c = 1.7 \times 10^{-3}$ M) and **2** ($c = 2.5 \times 10^{-3}$ M) in acetonitrile containing 5 mol % pyridine at constant potential (peak values) produced **3** and **4**, respectively. The yield of the TTF derivative is dependent on the number of electron equivalents removed. In theory the reaction requires the removal of 2 electron equiv (2 Faradays/mol) and two protons; however, the TTF product of the reaction can be oxidized at the anodic potential applied and assist in the oxidation of the dithiole. A coulometric study showed that the yield of the TTF de-

---

(1) Epstein, A. J.; Miller, J. S. *Sci. Am.* **1979**, *242*, 52.

(2) Narita, M.; Pittman, C. U. Jr. *Synthesis* **1976**, 489.

(3) Braun, R. D.; Green, D. C. *J. Electroanal. Chem.* **1977**, *79*, 381.

(4) Moses, P. R.; Chambers, J. Q.; Sutherland, J. O.; Williams, D. R. *J. Electroanal. Chem.* **1975**, *122*, 608.

(5) Takamizawa, A.; Hirai, K. *Chem. Pharm. Bull.* **1981**, *17*, 1931.

(6) Schukat, G.; Fanghaenel, E. *J. Prakt. Chem.* **1979**, *321*, 675.

0022-3263/84/1949-0390$01.50/0

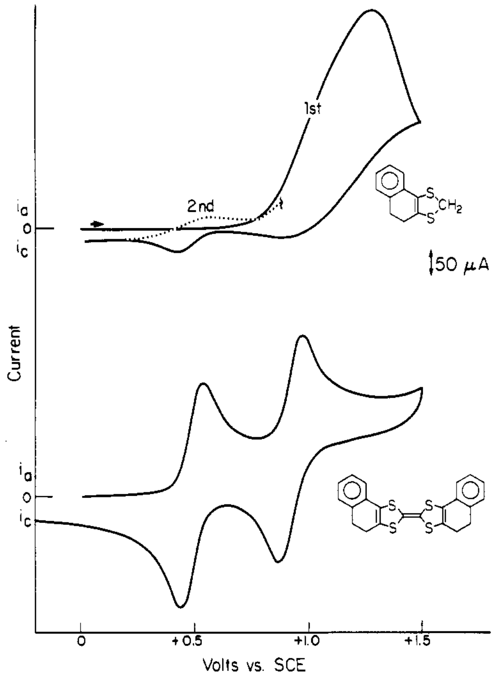


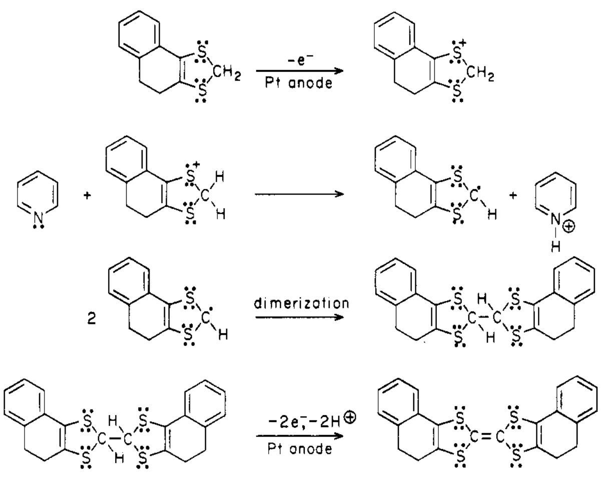
Figure 1. Cyclic voltammogram of 4,5-dihydronaphtho[1,2-*d*]-1,3-dithiole (1; $c = 1.0 \times 10^{-3}$ M in CH_3CN containing 5 mol % pyridine and 0.1 M TBAF; 50 mV/s scan rate), and dihydronaphthotetrathiafulvalene **3** ($c = 1.0 \times 10^{-4}$ M in CH_3CN containing 0.1 M TBAF).

rivative reached a maximum, e.g., 40% for **3** and 13% for **4**, after removal of 3.5 and 3.2 electron equiv, respectively. Further removal of electrons results in lower yields.

We favor a mechanism for the oxidative electrodimerization reaction that involves the initial formation of a cation–radical intermediate. The cation–radical is deprotonated by pyridine to a radical that can dimerize. Further oxidation of the dimer and proton loss provides the product as shown in Scheme I. We did not include the dimerization of the cation–radical to produce a dication in the mechanistic scheme because it is expected that such a process would be reversible or lead to the same intermediates under the reaction conditions.[7]

In summary, electrochemical oxidation of 1,3-dithioles **1** and **2** provides the corresponding TTF derivatives in moderate to low yields. Pyridine is required to deprotonate the cation–radical species produced by anodic oxidation before dimerization and product formation can occur.

Scheme I. Mechanism



Experimental Section

Electrochemistry Equipment. For cyclic voltammetry, a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer were used in the standard three-electrode configuration (platinum inlay electrode as the working electrode, a platinum auxiliary electrode, and a standard calomel electrode). The electrolyte was 0.1 M tetrabutylammonium fluoroborate (TBAF) recrystallized from ethyl acetate/pentane in dry acetonitrile freshly distilled from CaH_2 under argon. For coulometry, a Princeton Applied Research Model 179 digital coulometer with a Model 377A coulometry cell system was used.

Bis(4,5-dihydronaphtho)tetrathiafulvalene 3. A solution of 17.5 mg of 4,5-dihydronaphtho[1,2-*d*]-1,3-dithiole (**1**) in 50 mL of electrolyte solution containing 0.20 g of pyridine was purged with argon and electrolyzed at 1.40 V (vs. SCE) in the coulometry cell system consisting of a platinum-gauze working electrode, a platinum counterelectrode, and a standard calomel reference electrode. We determined the yield of **3** by periodically monitoring the cyclic voltammetry and comparing signal intensities with those of standard solutions of **3** synthesized independently. The TTF derivative formed electrochemically was identical in every respect with samples prepared by the method of Schukat and Fanghaenel.[6] After 3.5 electron equiv was removed, the yield of **3** was 40%. Further oxidation gave a lower yield of **3**.

Diphenyltetrathiafulvalene 4. A solution of 22.5 mg of 4-phenyl-1,3-dithiole (**2**) in 50 mL of electrolyte solution containing 0.20 g of pyridine was purged with argon and electrolyzed at 1.05 V. When 3.2 electron equiv was removed, the yield of **4** reached 13%. Further oxidation again gave a lower yield.

Registry No. **1**, 88130-95-4; **2**, 15112-40-0; **3**, 71938-96-0; **4**, 5152-94-3.

---

[7] Musker, W. K.; Roush, P. B. *J. Am. Chem. Soc.* **1976**, *98*, 6745.