July 18, 1975

To the Graduate Council:

I am submitting herewith a thesis written by Francis John Goodman entitled "Electrochemical Reduction of Ethylene Trithiocarbonate in N,N-Dimethylformamide." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

James Q. Chambers
Major Professor

We have read this thesis and recommend its acceptance:

William E Bull

Accepted for the Council:

Vice Chancellor for
Graduate Studies and Research

ELECTROCHEMICAL REDUCTION OF ETHYLENE TRITHIOCARBONATE IN N,N-DIMETHYLFORMAMIDE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

Francis John Goodman

August 1975

1035930

ACKNOWLEDGEMENTS

I would like to thank Norm Canfield, presently at Ohio State, and Chi-Sheng Liao for helping me to get started in electrochemistry. It was not easy. Norm was most appreciated for passing out his gingersnap cookies and sassafras tea when the going got rough. Chi-Sheng gave me all the spiritual help I needed.

I would like to thank Rick Moses, University of North Carolina, for the ^{13}C NMR spectrum and the NMR spectrum with added shift reagent. Thanks also go to Dr. Carol Anderson, University of Connecticut, for some mass spectra.

Many thanks go to the Chemistry Department of the University of Tennessee for financial support in the form of a Teaching Assistantship from September 1973 to August 1975, and especially for the Teaching Assistant Award for the Summer of 1975.

I would also like to thank Mrs. Maxine Hopson for numerous favors and for withstanding my quips. Thanks also go to Miss Linda Torbett for typing the final copy of this thesis.

And last, but not least, thanks (x 10^{21}) go to the Chief, Dr. James Q. Chambers, for directing me through this research and thesis.

ABSTRACT

The electrochemical reduction of ethylene trithiocarbonate was carried out in N,N-dimethylformamide. The integrated electrolysis current gave a value of 0.98 Faradays of electricity per mole of ethylene trithiocarbonate. After alkylation of the electrolysis solution, products were isolated and characterized.

Alkylation with methyl iodide produced 1,2-ethane bis(methyl trithiocarbonate) as the major product and a small amount of dimethyl trithiocarbonate.

Alkylation with ethyl iodide produced 1,2-ethane bis(ethyl trithiocarbonate) as the only isolated product.

Alkylation with either 1,2-dibromoethane or 1,2-diiodoethane produced 1,4,6,9-tetrathiaspiro[4.4]nonane as the major product and smaller amounts of a yellow insoluble material and ethylene trithiocarbonate.

A mechanism is proposed based on the formation of the above compounds and other experimental facts.

The Appendix contains the synthesis of tetra-n-butylammonium bis(4,5-dimercapto-1,3-dithiolen-2-thione)nickelate(II) by the electrochemical reduction of carbon disulfide in N,N-dimethylformamide followed by the addition of either nickel perchlorate hexahydrate or nickel chloride hexahydrate to the electrolysis solution. Copious amounts of a black precipitate formed and from this, two distinct nickel complexes were isolated and characterized.

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CHAPTER I

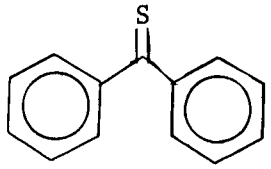
INTRODUCTION

I. Background

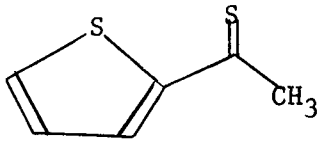
The research presented in this thesis is based upon the ease of electrochemical reduction of the carbon-sulfur double bond. The thiocarbonyl bond can usually be reduced in a potential range ca. -0.5 volts (V) to -1.5V vs. a saturated calomel electrode (SCE), a range somewhat lower than the carbon-oxygen analogues.[1] In a study of substituted benzophenones vs. thiobenzophenones in acetonitrile conducted by Loutfy and Loutfy,[2] the thiobenzophenones were reduced in a range from -1.17V to -1.51V vs. Ag/AgCl, 0.1 M tetraethylammonium perchlorate (TEAP), by polarographic means, while the corresponding benzophenones were reduced at potentials on the average of 0.7V more negative.

This difference in reactivity has been attributed to the longer carbon-sulfur bond in thiocarbonyls due to poor overlap between the 3p orbitals of sulfur and the 2p orbitals of carbon compared to the overlap of 2p orbitals on oxygen with those on carbon in carbonyl compounds.[3] This longer bond length can lead to steric stabilization of sulfur radicals over oxygen radicals in the reduction process.[4,5]

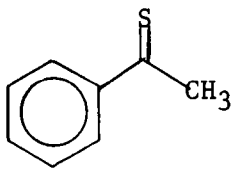
The carbon-sulfur double bond can be reduced electrochemically under a variety of conditions in both aqueous and nonaqueous solvents. Melhorn, et al.,[6] reported the reduction of a number of thiones (I-IV) and trithiocarbonates (V,VI) polarographically with a dropping mercury electrode using an aqueous 40% isopropanol solution with a phosphate buffer (pH=7.2).



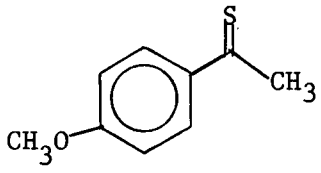
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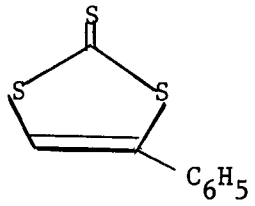
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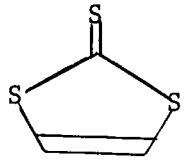
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IV

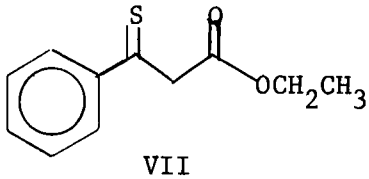


V



VI

Compounds I-VI were reduced to the corresponding thiols at the following respective potentials vs. SCE: -0.95V, -1.13V, -1.19V, -1.24V, -1.35V, -1.52V. In aqueous ethanol using an acetate buffer, Reyes and Silverstein[7] reported the reduction of ethyl thiobenzoylacetate (VII) at -0.85V vs. SCE with a dropping mercury electrode. The initial product formed was

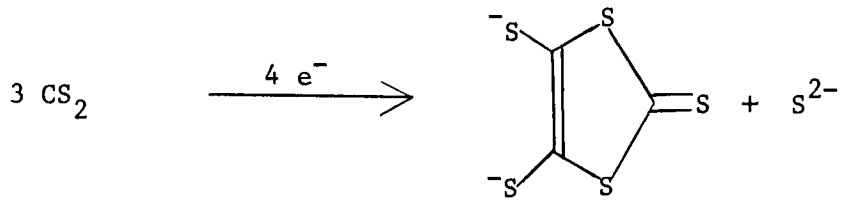


VII

the thiol of VII. Mayer and coworkers[8] also reported the reduction of VII at -1.60V vs. SCE with a dropping mercury electrode in methanol containing an acetate buffer. Loutfy and Loutfy,[2] as previously mentioned, reported the thiobenzophenone reductions in acetonitrile which was 0.05 M in tetra-n-butylammonium bromide (TBABr). Many more examples of reductions can be found in a recent review on the electrochemistry of sulfur compounds.[1]

Not only can the reduction of the carbon-sulfur double bond be easily achieved, but cathodic electrolysis may prove useful in syntheses. Wawzonek and Heilmann[9] reduced carbon disulfide in N,N-dimethylformamide

(DMF), which was 0.2 M in TBABr, at potentials from -1.4V to -1.9V vs. SCE using a mercury electrode. The overall scheme of the reaction is presented.

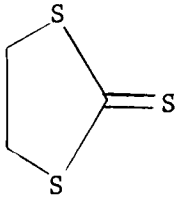


VIII

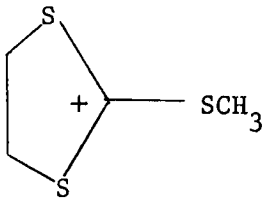
The dianion VIII was isolated by alkylation with methyl iodide. The procedure for the reaction has since been improved and used to make other interesting molecules[10] (see Appendix).

II. Proposed Problem

The electrochemical reduction of ethylene trithiocarbonate (IX) in nonaqueous solvents has not been previously studied with regard to product formation. However, the trithiocarbenium ion (X), resulting from the reac-

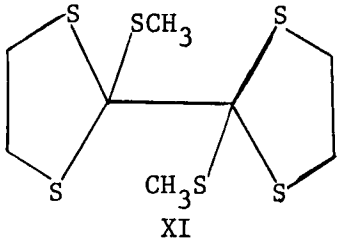


IX



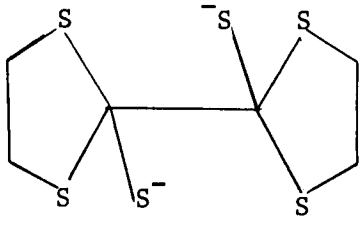
X

tion of IX with a Meerwein reagent (trimethyloxonium tetrafluoroborate), has been found to electrodimerize to XI via a radical coupling mechanism.[11]



XI

This analogy and the fact that IX initially forms a radical anion upon reduction,[11] suggests that the dianion XII is a possible electroreduction product of IX.



XII

In the following research presentation, the reduction of IX was carried out in DMF and the products were isolated. The predicted result was found not to be the case.

CHAPTER II

EXPERIMENTAL

I. Apparatus

Instruments

1. Bulk Electrolyses. The following instruments were used in all electrochemical reductions. The power supply was a Lambda C-280 regulated power supply. A Dynasciences Digital Multimeter Model 330 was used to monitor the potential of the working electrode vs. the saturated calomel reference electrode. To integrate the electrolysis current, an electronic integrator was employed which utilized a chopper stabilized operational amplifier. The integrator output was displayed on a Fairchild Model 7050 digital voltmeter. A diagram showing the electrical connections among the above instruments and electrolysis cell is given in Figure 1.

2. Cyclic Voltammetry. Cyclic voltammograms were obtained with a three electrode potentiostat designed utilizing solid state components.[12] Experimental curves were recorded on a Hewlett-Packard 136 AM X-Y-Y' recorder.

3. Spectrometers. Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian A-60 Analytical Spectrometer or a Varian T-60A Spectrometer to observe proton chemical shifts. A ^{13}C NMR spectrum was recorded on a Varian XL-100 Spectrometer. Samples were run as concentrated as possible in either deuteriochloroform, deuterioacetonitrile, or carbon tetrachloride. Tetramethylsilane (TMS) was added as an internal standard with all samples.

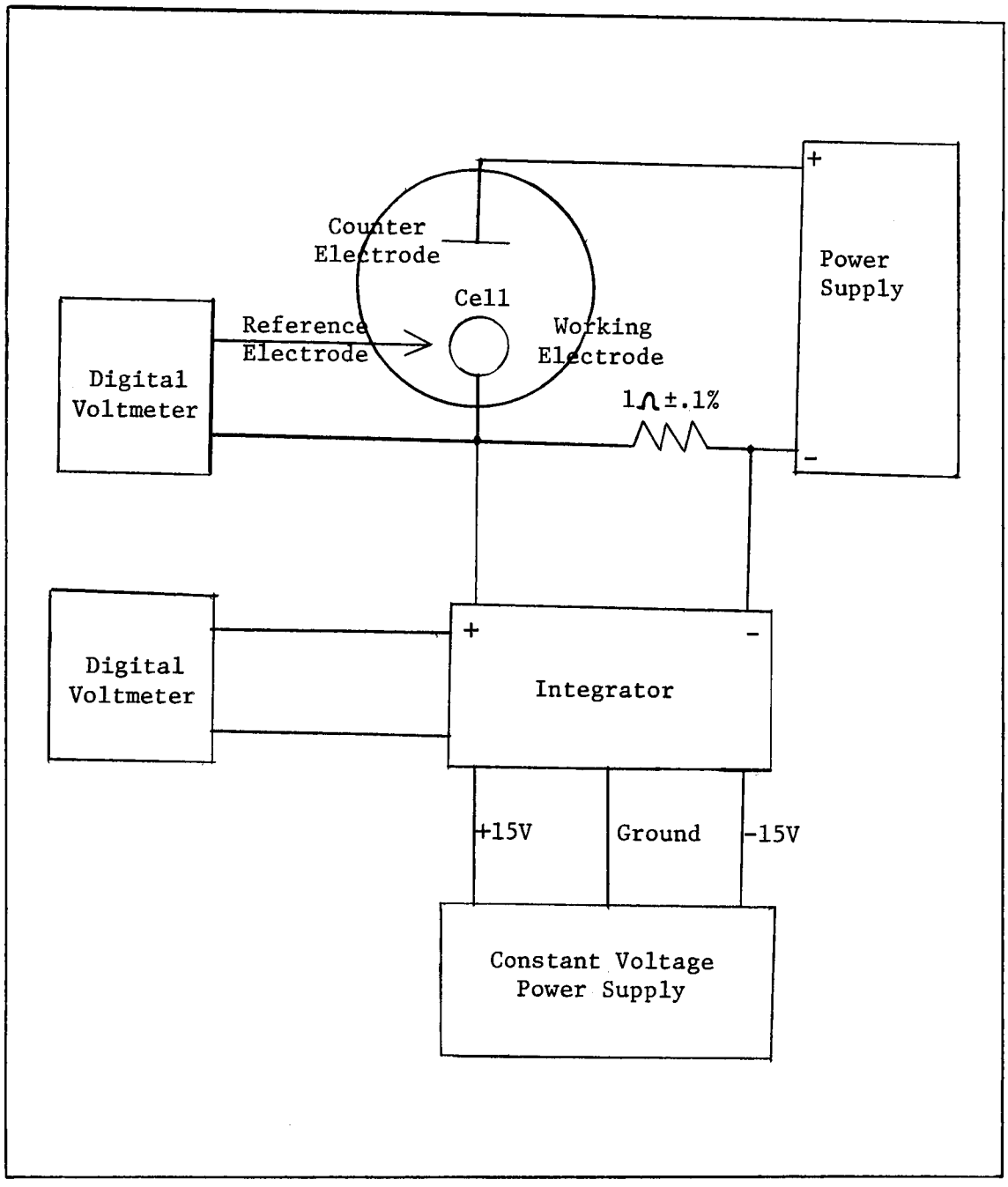


Figure 1. Wiring diagram for bulk electrolysis.

Infrared (IR) spectra were recorded on either a Beckman IR5A or a Perkin Elmer 727 Spectrophotometer. For solid phase spectra, potassium bromide pellets were made on a Blackhawk pellet press. For liquid phase spectra, a liquid cell (Barnes Engineering Co.) was used with carbon disulfide as the solvent. Spectra were calibrated vs. polystyrene.

Ultraviolet and visible spectra were acquired by use of a Cary Instruments Model 17I Spectrophotometer. The solvents used were chloroform, methylene chloride, or DMF.

Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E Mass Spectrometer. Mass to charge (m/e) ratios were determined by comparison to a perfluoroalkane standard.

4. Miscellaneous. Melting points of samples were obtained on a Mel-Temp melting point detector and were uncorrected.

Elemental analyses were done by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

Cells

1. Bulk Electrolyses. For bulk electrolyses the cell used exclusively was of a three compartment design (see Figure 2). Glass tubing connected the bottom of the working compartment below the glass frit to the top of the cell via a three-way stopcock. By manipulation of the stopcock, nitrogen gas could pass through the solution for deaeration or stirring, or across the solution to prohibit reabsorption of oxygen and water vapor. The working compartment had a 30 mm coarse frit in the bottom and an extra stopcock in the lower tubing so that electrolyzed solutions could be easily drained from the cell for workup. The middle

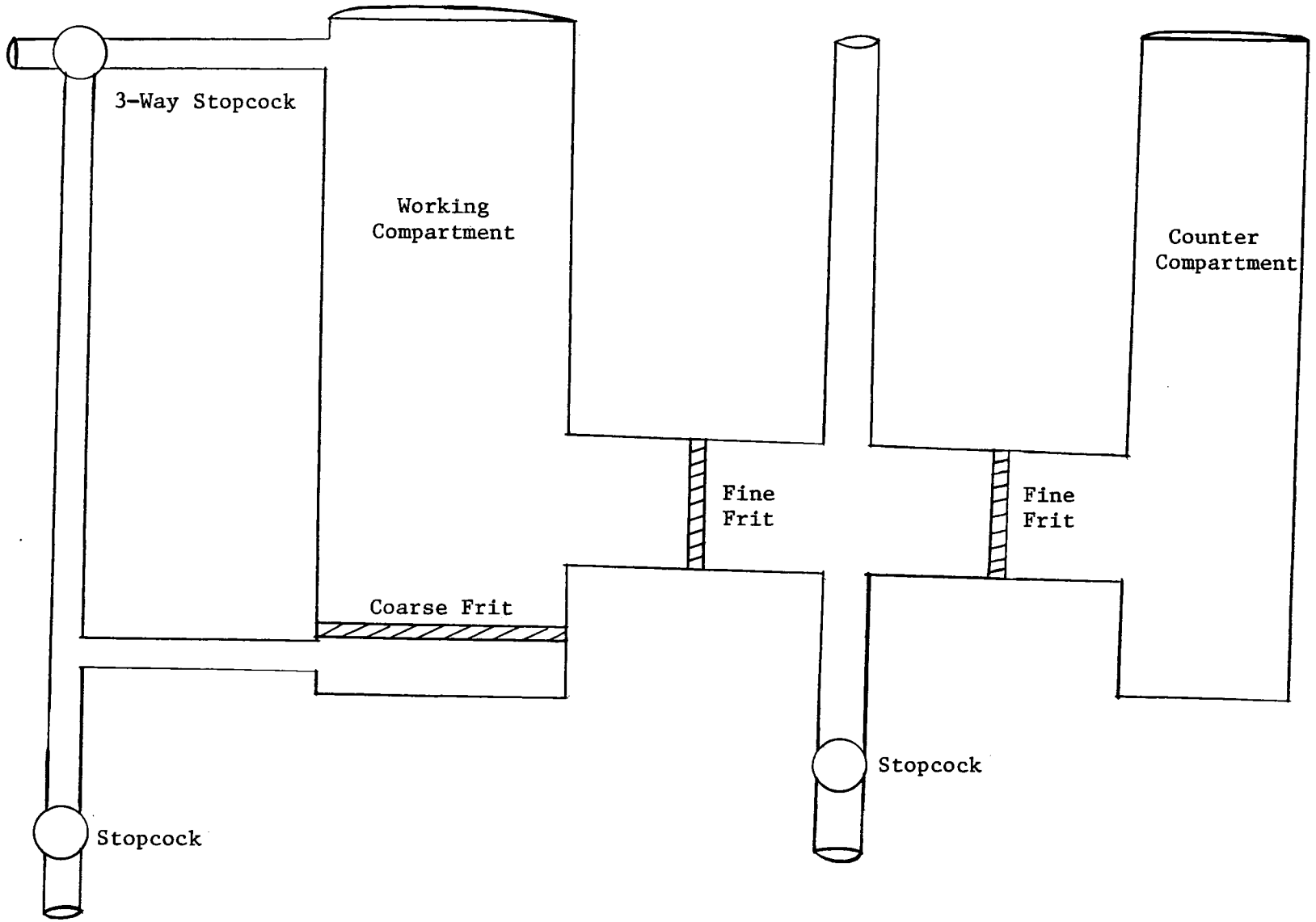


Figure 2. Electrolysis cell (actual size).

compartment had a stopcock for draining and replacing spent electrolyte, thus reducing working compartment contamination from counter compartment product migration. The middle compartment was separated from both the working and counter compartments by 20 mm fine frits. A Teflon cover with holes drilled through it to allow electrodes to make contact with the solution fitted snugly over the working compartment. During normal electrolyses, the cell contained approximately 100 ml of solution, 40 ml in the working compartment.

2. Cyclic Voltammetry. The cell used for cyclic voltammetry was a single compartment cell with a 30 mm medium frit in the bottom. Glass tubing directed nitrogen gas either through the solution for stirring and deaeration or across the top to prohibit reabsorption of oxygen and water vapor. A Teflon cover with holes drilled through it for the electrodes fitted snugly over the top of the cell.

Electrodes

Platinum gauze electrodes with areas of ca. 30 cm^2 were used as working electrodes in bulk electrolyses or as counter electrodes in cyclic voltammetry experiments.

A Beckman platinum inlay electrode was used as a working electrode in cyclic voltammetry experiments. The electrode had an area of 0.214 cm^2. It was polished after each scan with lapping compound (Buehler Gamma micropolish) of 1.0 micron size particles.

A hanging mercury drop electrode was also employed as a working electrode for cyclic voltammetry experiments. This consisted of a 20 cm length of glass tubing closed on one end with platinum metal to which the

mercury drop adhered. The tube was filled with mercury to assure electrical connection to the mercury drop from a length of copper wire which extended out of the glass tubing. The mercury drop was changed after each scan.

Saturated calomel electrodes, constructed from a design described by Adams,[13] were used exclusively as reference electrodes in all electrochemical experiments.

A carbon rod was used as the counter electrode in all bulk electrolyses.

Solvent Towers

Solvent towers were used to saturate nitrogen gas with solvent vapor before the gas entered the electrolysis cell. Glass tubing directed nitrogen gas to the bottom of the glass tower where the gas would pass through a coarse frit which capped the tubing and bubble through the solvent. The gas then left the tower at the top and was directed with Tygon tubing to the electrolysis cell.

II. Chemicals

Solvents

1. N,N-Dimethylformamide. DMF was the primary solvent used in this investigation. It was purified by a procedure of Faulkner and Bard.[14] Ten grams of reagent grade anhydrous copper sulfate was added to 800 ml of reagent grade DMF (Fisher Scientific Co.). After stirring at room temperature for two days in a glass-stoppered flask, the solvent was vacuum distilled and the middle 500 ml fraction was collected. This was stored in brown reagent bottles.

2. Acetonitrile. Acetonitrile was used in cyclic voltammetry

experiments. Practical grade acetonitrile (Matheson, Coleman, and Bell or Fisher Scientific Co.) was purified by a procedure derived from Mann, et al.,[15] and Wallace and Ramely.[16] To approximately 1.5 l of acetonitrile in a 2 liter single-necked flask was added 20 g of potassium permanganate and 15 g of lithium carbonate. The acetonitrile was rapidly distilled, usually discarding the first 50 ml and the last 100 ml of distillate. The acetonitrile was next acidified with 6 drops of concentrated sulfuric acid and allowed to stand overnight to precipitate amines and other basic impurities. The acetonitrile was next filtered through a fine frit at aspirator pressure, collected, and distilled slowly from calcium hydride, again discarding the first 50 ml and last 100 ml of distillate. The acetonitrile was then stored in a sealed glass flask.

3. Methylene Chloride. Methylene chloride (Fisher Scientific Co.) was used as a solvent in obtaining ultraviolet-visible spectra, as a solvent in column chromatography separations, and as a solvent for Meerwein reagents. It was distilled neat or from calcium hydride if dry solvent was required.

4. Hexane (Isomers). Hexane (Fisher Scientific Co.) was used as a solvent in column chromatography separations. It was purified by distillation neat.

5. Spectrophotometric Solvents. Reagent grade carbon disulfide (Allied Chemical Co.) was used in the liquid IR cell or as a reagent in some experiments.

All deuterium solvents for NMR use were purchased from either Fisher Scientific Co. or Mallinckrodt Chemical Works. Reagent grade carbon tetrachloride was purchased from J. T. Baker Chemical Co.

Reagent grade chloroform was purchased from J. T. Baker Chemical Co. and used in obtaining ultraviolet-visible spectra.

Supporting Electrolytes

1. Tetra-n-butylammonium Bromide. TBABr (Eastman Kodak Co.) was used in all bulk electrolyses of ethylene trithiocarbonate. The electrolyte was not purified further.

2. Tetra-n-butylammonium Iodide. Tetra-n-butylammonium iodide (TBAI) (Eastman Kodak Co.) was used in bulk electrolyses of carbon disulfide (see Appendix). The electrolyte was not purified further.

3. Tetraethylammonium Perchlorate. TEAP was used in all cyclic voltammograms. TEAP was made by a procedure from House, et al.,[17] or purchased from Eastman Kodak Co. It was recrystallized from water three times and then dried in a vacuum oven for one week at 60°C.

Reagents

1. Ethylene Trithiocarbonate. Practical grade ethylene trithiocarbonate, 1,3-dithiolane-2-thione, (Aldrich Chemical Co.) was recrystallized twice from acetonitrile.

2. Alkylating Reagents. Methyl iodide and ethyl iodide were purchased from Eastman Kodak Co., 1,2-dibromoethane from Fisher Scientific Co., and 1,2-diiodoethane from Aldrich Chemical Co. All alkylating reagents were used without further purification.

3. Meerwin Reagents. Triethyloxonium and trimethyloxonium hexafluorophosphate (Aldrich Chemical Co.) were used without further purification.

4. Miscellaneous. Potassium trithiocarbonate was purchased from Alpha Inorganics and was used without further purification.

Sodium trithiocarbonate was synthesized by dissolving 0.23 g of reagent grade anhydrous sodium sulfide in 10 ml of DMF and adding 0.25 g of carbon disulfide. This solution was then used in subsequent reactions.

All other chemicals used were of reagent grade.

III. Techniques

Bulk Electrolyses

The electrical apparatus was set up according to Figure 1, page 6. The three compartment cell (Figure 2, page 8) was set up last and wrapped in Tygon tubing through which tap water flowed to avoid excessive heating of the electrolysis solution. The cell was filled with 1 M TBABr in DMF and at the same time nitrogen gas was directed first through a solvent tower partially filled with DMF and then through the solution in the working compartment of the cell. The nitrogen gas continued to bubble through the solution throughout the electrolysis. After ten minutes of deaeration, between 0.5 g and 1.5 g of ethylene trithiocarbonate was added to the working compartment. The electrodes were then placed in the cell and the electrolysis was initiated. The voltage across the cell was kept between -1.40V and -1.60V vs. SCE by manual adjustment of the power supply and the current averaged 175 milliamperes (mA) throughout most of the electrolysis. The color of the working compartment solution became light brown and the solution temperature stabilized at 30°C. After an hour, when the electrolysis current had decreased to less than 5 mA, the electrolysis was terminated.

Product isolation was as follows. An excess of alkylating reagent

was added to the working compartment causing a color change to yellow. The working compartment solution was collected and poured into 500 ml of water to remove DMF and all products were then extracted with ether. The ether was dried with anhydrous magnesium sulfate, filtered, and evaporated on a roto-evaporator. Products remained as an oil. Recrystallization of the oil with acetonitrile gave the main product and any residue left after recrystallization was separated by column chromatography.

Column Chromatography

The intial conditions for column chromatography separations were determined by thin layer chromatography (TLC). TLC plates were made by dipping glass microscope slides into a slurry of methylene chloride and silica gel G. The plates were activated when needed by placing in a drying oven at 110°C for ten mintues.

Two columns were used in the separations. For separating small amounts of material, a column 11 mm in diameter was used. A column 25 mm in diameter was used for larger amounts of material. Both columns were packed to a depth of 15 cm with silica gel.

The solvent system used was a mixture of methylene chloride and hexane (isomers). To separate products formed from the addition of methyl iodide to the electrolysis solution, a 90% hexane-10% methylene chloride solution was employed. To separate products formed from the addition of either 1,2-dibromoethane or 1,2-diiodoethane to the electrolysis solution, a 66% hexane-33% methylene chloride solution was used.

Cyclic Voltammetry

The cell used was previously described (see page 9). To the cell

was added 25 ml of 0.1 M TEAP in acetonitrile and the solution was then deaerated for ten minutes with nitrogen gas which flowed first through a solvent tower partially filled with acetonitrile. The nitrogen gas was then directed over the solution in order to prohibit reabsorption of oxygen and water vapor. The background of the solution was tested. The solution was then made 0.001 M in the product of interest and cyclic voltammograms were recorded.

Ethylene Trap

The electrolysis cell was tightly sealed with rubber stoppers through which holes were drilled to fit the electrodes snugly. One hole in the stopper sealing the working compartment was fitted with glass tubing through which nitrogen gas could escape from the cell. The nitrogen gas was directed with Tygon tubing through a Dry Ice-acetone cold trap to remove solvent vapors and then into a solvent tower partially filled with bromine dissolved in methylene chloride. At the end of the electrolysis, the bromine solution was evaporated on a roto-evaporator and the residue was subjected to spectral analyses.

Alternate Syntheses

Potassium trithiocarbonate (0.56 g) or sodium trithiocarbonate (0.45 g) were treated with ethylene trithiocarbonate (0.40 g) in 15 ml of DMF at room temperature in a glass-stoppered flask from several minutes to two days. Methyl iodide was then added in excess and workup of the solution proceeded as described for electrolysis solutions (see page 13). Workup produced an oil which was subjected to NMR spectral analysis.

Sodium (0.10 g) was treated with excess ethylene trithiocarbonate

(0.60 g) in 10 ml of DMF at room temperature in a glass-stoppered flask for one hour. Methyl iodide was then added in excess and workup of the solution proceeded as described above. Workup produced an oil which was subjected to NMR spectral analysis.

Dimethyl trithiocarbonate was synthesized by dissolving 0.5 g of potassium trithiocarbonate in 10 ml of DMF and adding excess methyl iodide. Workup proceeded as described above and the product was recovered as an oil.

Reaction with Meerwein Reagents

1,2-Ethane bis(methyl trithiocarbonate) (0.045 g) and excess triethyloxonium or trimethyloxonium hexafluorophosphate were dissolved in 5 ml of dry methylene chloride and acetonitrile respectively and allowed to react in a glass-stoppered flask overnight at room temperature. Both solutions turned orange in color and a white precipitate formed. The solutions were evaporated and residues were subjected to NMR spectral analyses. The white solid was found to be insoluble in all available NMR solvents and was examined no further.

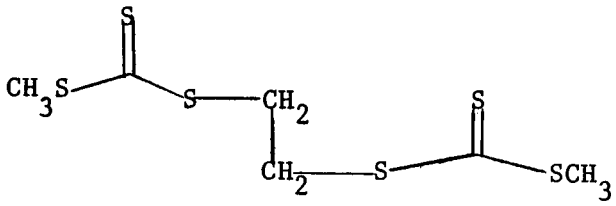
CHAPTER III

RESULTS

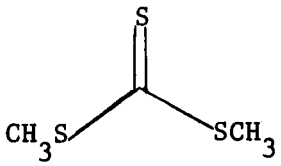
I. Electrochemical Reduction of Ethylene Trithiocarbonate

Alkylation with Methyl Iodide

The electrochemical reduction of ethylene trithiocarbonate followed by alkylation with methyl iodide yielded two isolated products: 1,2-ethane bis(methyl trithiocarbonate) (XIII) and dimethyl trithiocarbonate (XIV).



XIII



XIV

1. 1,2-Ethane Bis(methyl trithiocarbonate). The product XIII was isolated in better than 50% current yield after two recrystallizations from acetonitrile and formed yellow needles which melted between 59.0°C and 59.8°C. The current yield calculated was based on 1.0 Faradays per mole of ethylene trithiocarbonate. The addition of 0.50 g of IX (page 3) to the working compartment followed by reduction consumed 360 coulombs.

The NMR spectrum of XIII in deuteriochloroform showed two singlets in a ratio of 2 to 3. A singlet at 3.67 parts per million (ppm) from TMS was assigned to the ethylenic protons. A singlet at 2.78 ppm was assigned to the methyl protons and this agreed with a value of 2.73 ppm in carbon tetrachloride assigned to the methyl protons of XIV.[18] Addition of a shift reagent, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octane-

dionate)europium(III), produced no resolution of the singlet peaks in deuteriobenzene. A ^{13}C NMR spectrum of the methyl and ethylene carbon atoms exhibited two singlets in a 1 to 1 ratio at 34.84 ppm and 20.29 ppm from TMS.

The IR spectrum is given in Figure 3. The most intense peak at 1050 cm^{-1} agreed with values for the thiocarbonyl stretch of various trithiocarbonates reported by Mecke, et al.[19]

The ultraviolet-visible spectrum of XIII in chloroform yielded wavelength maxima at 431 nm and 309 nm. The corresponding molar absorptivities ($\underline{M}^{-1}$ cm^{-1}) were 85 and 30,000. The wavelength maxima agreed with values for various trithiocarbonates reported by Muller and Krebs.[20] The molar absorptivities for XIII were approximately twice those reported which is consistent with its bifunctionality. In accordance with Muller and Krebs, the absorption at 431 nm was assigned to the n-pi* transition, and the absorption at 309 nm was assigned to the pi-pi* transition.

The mass spectrum at 20 eV gave the following major m/e peaks and assigned fragments: 274(parent mass, M^+), 183($CH_3SCSSCH_2CH_2S^+$), 138($CH_3SCSSCH_3^+$), 136($CH_3SCSSCH^+$), 91($SCSCH_3^+$), 76(SCS^+, base peak), 60($SCH_2CH_2^+$), 59($SCHCH_2^+$), 47(SCH_3^+), and 45(SCH^+).

The calculated elemental composition for XIII is 26.25% C, 3.67% H, and 70.07% S. The elemental composition found was 26.30% C, 3.66% H, and 69.99% S. This gave an empirical formula of $C_6H_{10}S_6$.

Cyclic voltammograms showed two irreversible reduction waves. The first wave gave the following parameters: peak potential (Ep)= -1.58V vs. SCE, Ep- potential at half peak height ($Ep_{1/2}$)= -49 mV, current function (CF)= 1.39 A cm^{-2} $\underline{M}^{-1}$ $(V/sec)^{-1/2}$. The second wave gave these parameters: Ep= -1.76V vs. SCE, $Ep-Ep_{1/2}$= -64 mV, CF= 1.34 A cm^{-2} $\underline{M}^{-1}$ $(V/sec)^{-1/2}$. The

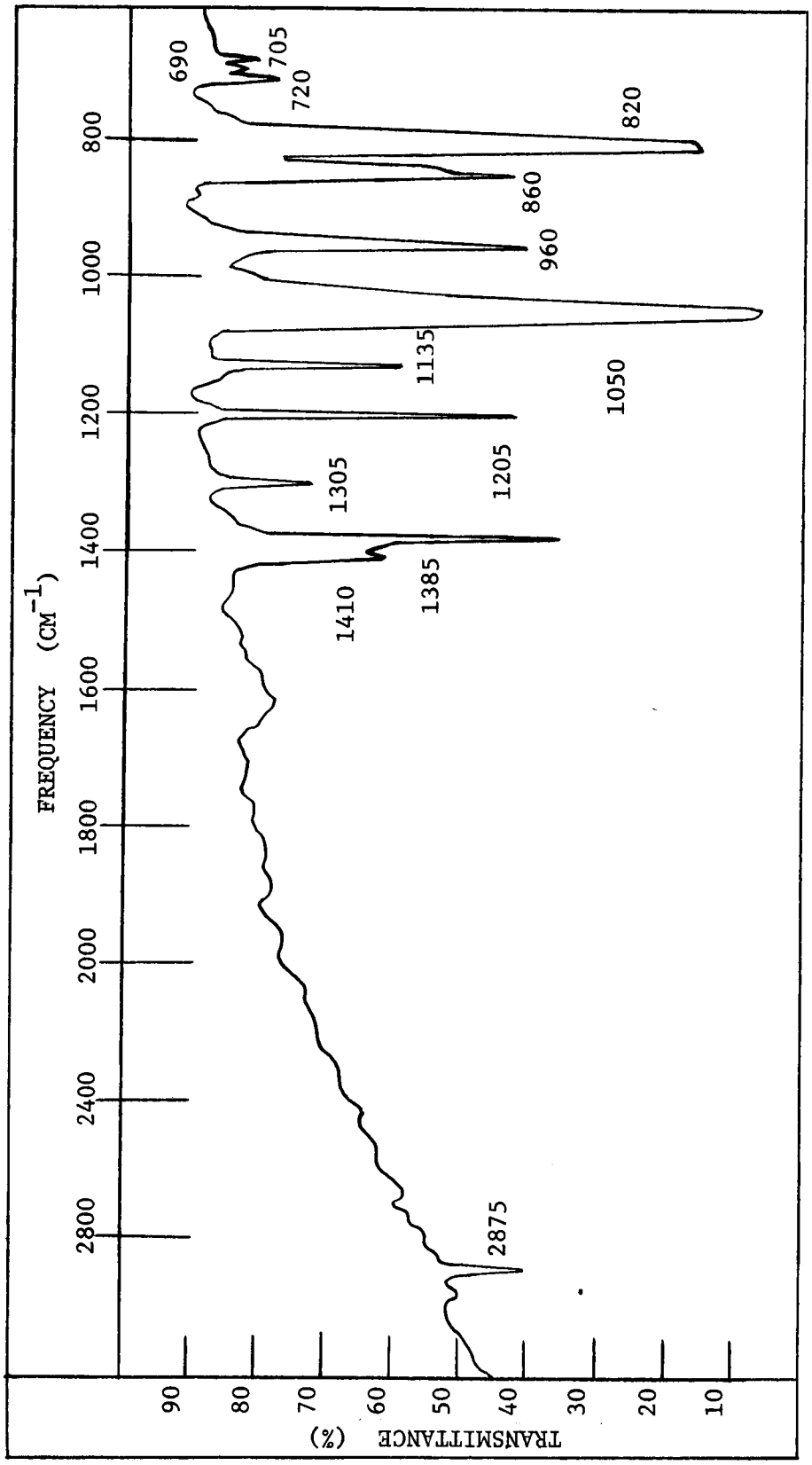
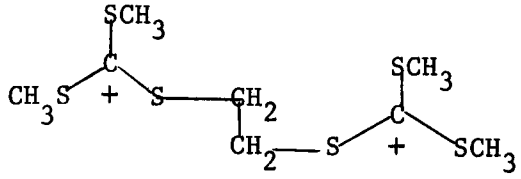


Figure 3. IR spectrum of XIII in KBr.

electrochemical data are consistent with successive reduction of the thiocarbonyl groups in XIII.[11] No significant oxidation waves were observable.

Methylation of XIII with trimethyloxonium hexafluorophosphate in acetonitrile produced the doubly-charged cation XV. The NMR spectrum



XV

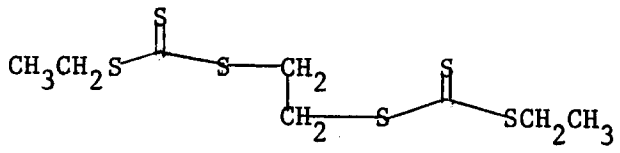
gave two singlets in a ratio of 1 to 3 at 4.05 ppm and 3.10 ppm respectively.

In one experiment carbon disulfide was added to the electrolysis mixture prior to alkylation. After addition of methyl iodide, the product was isolated in the usual manner and found to be orange in color and not the expected yellow color of XIII. However, the melting points, the NMR spectra, the IR spectra, the ultraviolet-visible spectra, and the mass spectra were found to be identical for XIII and the orange compound.

2. Dimethyl Trithiocarbonate. The product XIV was found to be 40% of the concentration of XIII by NMR spectral analysis of the crude reaction mixture (prior to recrystallization). The compound was identified by comparison of its NMR and IR spectra to that of an authentic sample and published spectra.[18,21]

Alkylation with Ethyl Iodide

The reduction of ethylene trithiocarbonate followed by alkylation with ethyl iodide yielded 1,2-ethane bis(ethyl trithiocarbonate) (XVI).



XVI

Recrystallization of XVI twice from acetonitrile yielded yellow crystalline flakes which melted between 34.5°C and 35.5°C. Neither percent yield nor byproducts were determined.

The NMR spectrum of XVI in deuteriochloroform showed a singlet at 3.75 ppm assigned to the ethylenic protons, a quartet centered at 3.38 ppm assigned to the methylene protons, and a triplet centered at 1.38 ppm assigned to the methyl protons. Integration of peak areas yielded a ratio of 2 to 2 to 3 respectively.

The IR spectrum is given in Figure 4.

The ultraviolet-visible spectrum in chloroform yielded wavelength maxima at 434 nm and 310 nm. The corresponding molar absorptivities ($\underline{M}^{-1}$ cm^{-1}) were 105 and 40,000.

The mass spectrum at 10 eV gave the following major m/e peaks and assigned fragments: 302(M^+), 197($CH_3CH_2SCSSCH_2CH_2S^+$, base peak), 168($SCSSCH_2CH_2S^+$), 136($SCSSCH_2CH_2^+$), 105($SCSCH_2CH_3^+$), 76(SCS^+), and 61($SCH_2CH_3^+$).

Cyclic voltammograms of XVI showed two irreversible reduction waves. The first wave gave the following parameters: Ep= -1.58V vs. SCE, $Ep-Ep_{1/2}$= -61 mV, CF= 1.83 A cm^{-2} $\underline{M}^{-1}$ $(V/sec)^{-1/2}$. The second wave was partially obscured by the first wave and only one parameter was determined, Ep= -1.73V vs. SCE. No significant oxidation waves were observable.

Alkylation with 1,2-Dibromoethane and 1,2-Diiodoethane

The reduction of ethylene trithiocarbonate followed by alkylation

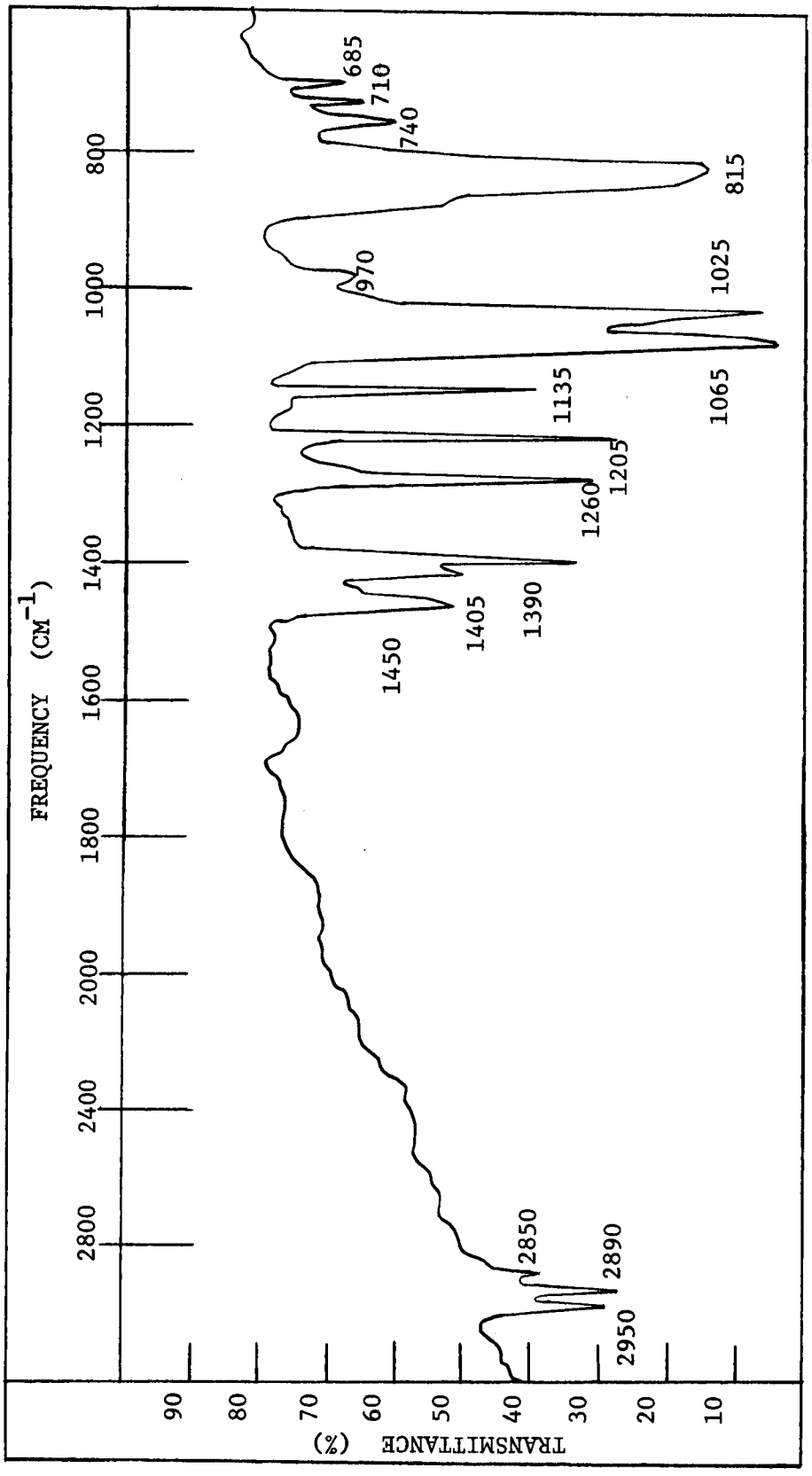
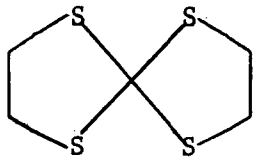


Figure 4. IR spectrum of XVI in KBr.

with either 1,2-dibromoethane or 1,2-diiodoethane produced three isolated compounds: a yellow insoluble material (0.16 g per 0.75 g ethylene trithiocarbonate reduced), 1,4,6,9-tetrathiaspiro[4.4]nonane (XVIII), and ethylene trithiocarbonate. The yield of the spiro compound XVIII was not determined,



XVIII

but XVIII appeared to be the major product of the reduction. By NMR spectral analysis, XVIII was twice the concentration of ethylene trithiocarbonate.

1. Yellow Material. The yellow material precipitated from solution soon after the addition of the alkylating reagent. It was found to be slightly soluble in hot DMF, but otherwise insoluble at all temperatures in 14 solvents that encompassed a wide range of polarity. Upon heating, the color gradually turned brown beginning at 90°C and the substance turned tar-like at 140°C.

The IR spectrum of the yellow material is given in Figure 5.

The ultraviolet-visible spectrum in DMF yielded wavelength maxima at 430 nm and 312 nm.

Cyclic voltammograms in DMF showed one cathodic wave with the following parameters: Ep= -1.71V vs. SCE, $Ep-Ep_{\frac{1}{2}}$= -76 mV. There were no significant oxidation waves.

An elemental analysis gave the following results: 21.57% C, 2.47% H, 71.71% S.

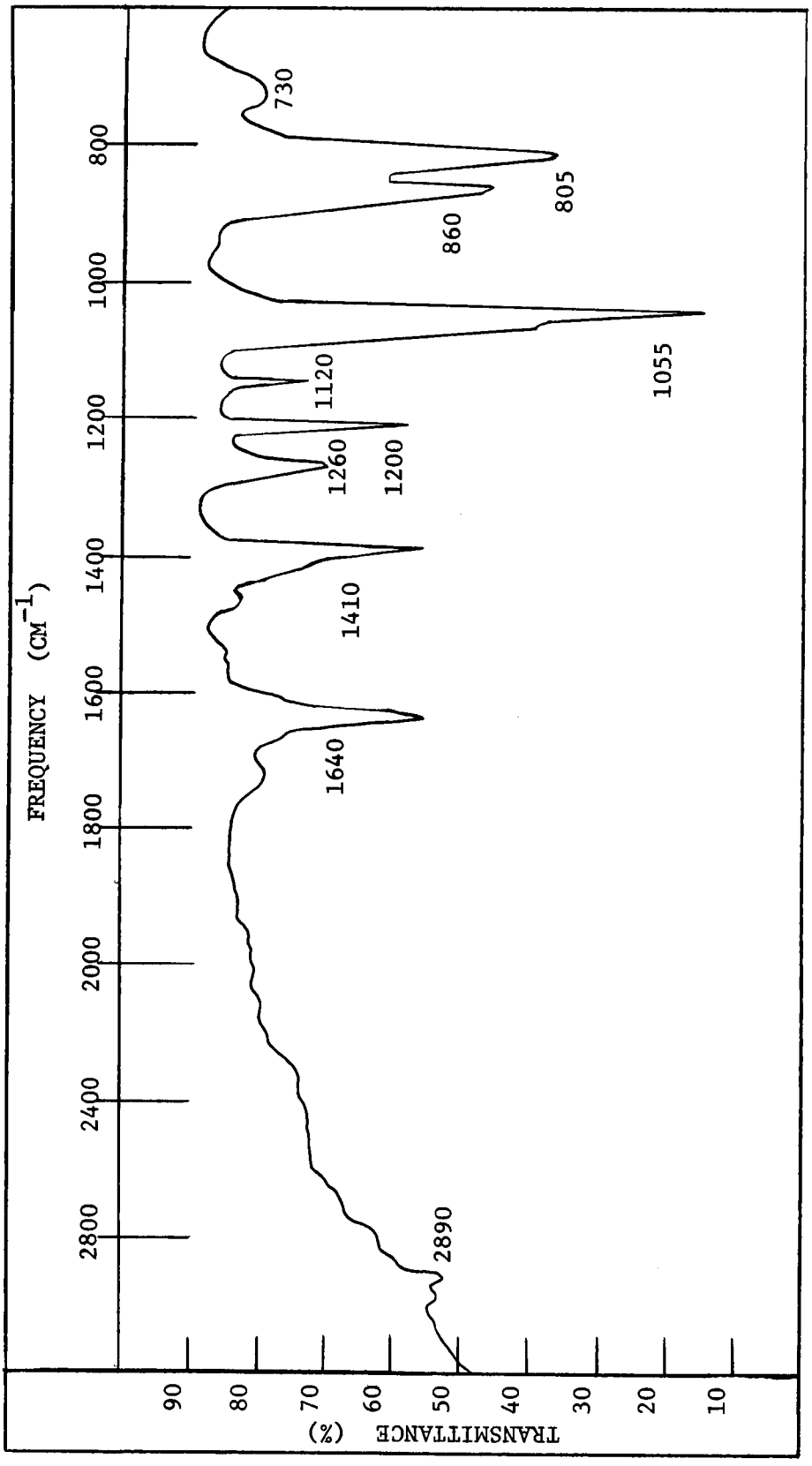


Figure 5. IR spectrum of yellow material in KBr.

The compound may be a polymer of the following structure: $-SCSSCH_2-CH_2SCSSCH_2CH_2-$. The color, decomposition point, and IR spectrum were similar to pentamethylene and hexamethylene polytrithiocarbonates reported by Braun and Kiessel.[22]

2. 1,4,6,9-Tetrathiaspiro[4.4]nonane. The spiro compound XVIII was recrystallized from acetonitrile and gave a white fluffy powder which melted between 139°C and 140°C. The NMR spectrum in deuteriochloroform gave a singlet at 3.40 ppm. The IR spectrum in KBr gave the following major bands (cm^{-1}): 1410(m), 1270(s), 965(m), 945(s), 845(m), 795(vs), and 755(s). A mass spectrum of XVIII gave a parent mass of 196 m/e. The compound was identified by comparison of the above data with that first reported by D'Amico and Campbell.[23]

Cyclic voltammograms, which have never been reported for XVIII, gave no reduction waves. Oxidation yielded two irreversible waves with the following parameters: Ep= 0.99V vs. SCE, $Ep-Ep_{1/2}$= 186 mV, CF= 0.60 A cm^{-2} $\underline{M}^{-1}$ $(V/sec)^{-1/2}$; Ep= 1.53V vs. SCE, $Ep-Ep_{1/2}$= 95 mV, CF= 0.65 A cm^{-2} $\underline{M}^{-1}$ $(V/sec)^{-1/2}$.

3. Ethylene Trithiocarbonate. Ethylene trithiocarbonate was isolated as yellow needles which melted between 32°C and 34°C. It was identified by comparison of its melting point, IR spectrum, and NMR spectrum to those of an original sample.

II. Ethylene Trap

Ethylene bromide, 1,2-dibromoethane, was identified as a product in the residue of the ethylene trap experiment by comparison of the NMR and IR spectra of the residue to those of an actual sample of ethylene bromide and to those reported in the literature for ethylene bromide.[24,25]

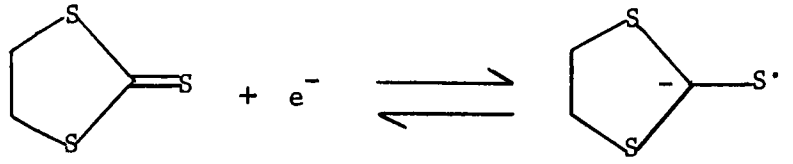
CHAPTER IV

DISCUSSION

I. Proposed Mechanism for the Reduction of Ethylene Trithiocarbonate

The intent of this study was not to provide a detailed mechanism for the electrochemical reduction process, but to isolate and characterize final products of the reduction. However, based on product distribution and other experimental facts, the following mechanism is proposed.

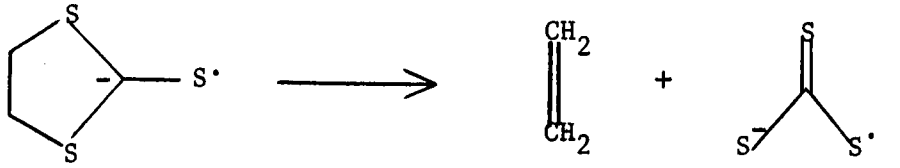
Step 1 is the addition of an electron to the carbon-sulfur pi system. The formation of the radical anion was shown by Moses, et al.,[11] to



IX XIX (Step 1)

be the initial step in the reduction of IX. Cyclic voltammograms at fast sweep rates (ca. 200 V/sec) gave a reversible one-electron wave, while slow sweep rates (ca. 0.06 V/sec) gave an irreversible two-electron wave, indicative of an ECE-type mechanism. Electron spin resonance (ESR) experiments also supported radical formation in the reduction. Thiocarbonyl radicals in other compounds have also been detected by ESR methods.[26]

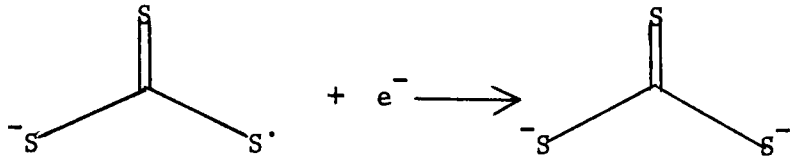
Step 2 involves the elimination of ethylene to form the radical



XIX XX (Step 2)

trithiocarbonate anion (XX). There is precedence in the literature for this type of anionic elimination involving similar oxygen compounds.[27]

Step 3 may involve two pathways in which XX can react. In Step 3A XX can gain an electron to form the trithiocarbonate dianion (XXI).



(Step 3A)

XX XXI

This step completes the ECE mechanism and would yield a two-electron voltammetric wave. However, three results argue against the importance of this step in the bulk electrolysis. First, the dimethyl or ethylene esters of XXI were only isolated in small amounts. Second, formation of XXI would result in a two-electron reduction, but an average of current integrations for the reduction yielded a value of 0.98 Faradays transferred per mole of IX. Third, experiments in which potassium or sodium trithiocarbonate and excess IX were dissolved in DMF and allowed to react showed that no reaction had occurred. This result is partial evidence for the lack of nucleophilic attack on IX by XXI.

Step 3B may then be the preferred path for the reaction under the conditions of the bulk electrolyses. Step 3B involves a radical recombi-



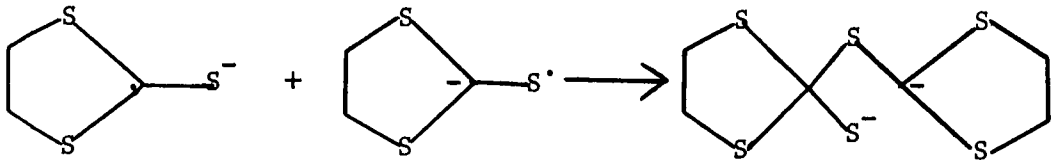
(Step 3B)

XIX XX XXII

nation of XIX and XX to form the dianion XXII. The integrated electrolysis current would yield a one-electron reduction. This step is also

favored by the high concentration of IX and low current density in the bulk electrolysis solution. Under these conditions the electrode potential is maintained at the foot of the voltammetric wave where the addition of the second electron (Step 3A) is likely to be slow. This is contrasted to the sodium metal reduction of IX which produced twice as much of XIV (page 17) as XIII (page 17) as determined by NMR spectral analysis. At the higher potential of sodium (-2.95V vs. SCE) the second electron transfer is fast and Step 3A becomes the favored pathway.

A competitive step to Step 3B is Step 3C. Here dimerization to

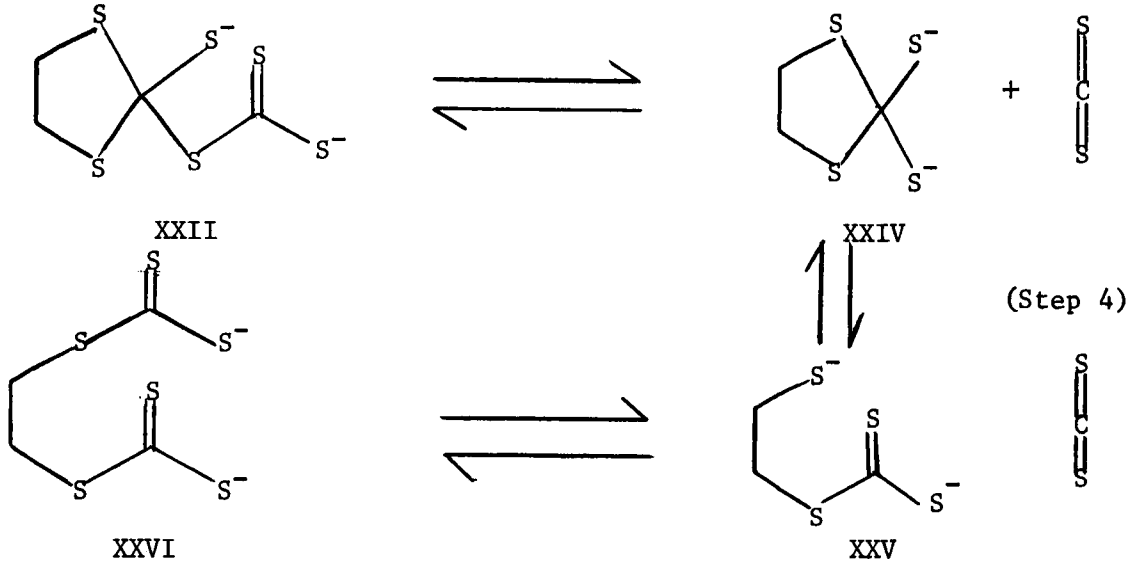


(Step 3C)

XX XX XXIII

form XXIII could occur prior to elimination of ethylene. Elimination of ethylene from XXIII then could yield XXII. Results of the electrolyses cannot distinguish between these two steps.

Step 4 encompasses a series of equilibria. The dianion XXII could



XXII XXIV

(Step 4)

XXVI XXV

eliminate carbon disulfide to form XXIV followed by rearrangement to XXV and addition of carbon disulfide to yield XXVI, the dianion isolated as XIII (page 17) or XVI (page 20). The dianion XXVI will be favored by virtue of resonance stabilization of both negative charges in the trithiocarbonate anions. Dianions XXII and XXV were never isolated in an alkylated form. However, XXIV was isolated as XVIII (page 23) when 1,2-diiodoethane or 1,2-dibromoethane was used as the alkylating reagent.

There is some evidence for carbon disulfide participation in Step 4. After reduction was complete, addition of small amounts of carbon disulfide to the electrolysis solution before alkylation produced a color change from brown to red. Cyclic voltammograms of the electrolysis solution showed the disappearance of a significant irreversible anodic wave at -0.06 V vs. SCE at slow sweep rates (ca. 0.2 V/sec) after addition of carbon disulfide. Carbon disulfide addition would be expected to increase the concentration of XXVI if the equilibria in Step 4 were occurring. However, no detectable change in the amount of product isolated was found. It may be that the equilibria of Step 4 are in favor of XXVI in the absence of added carbon disulfide and that the amount of alkylated product lost in the workup procedure determines the experimental yield.

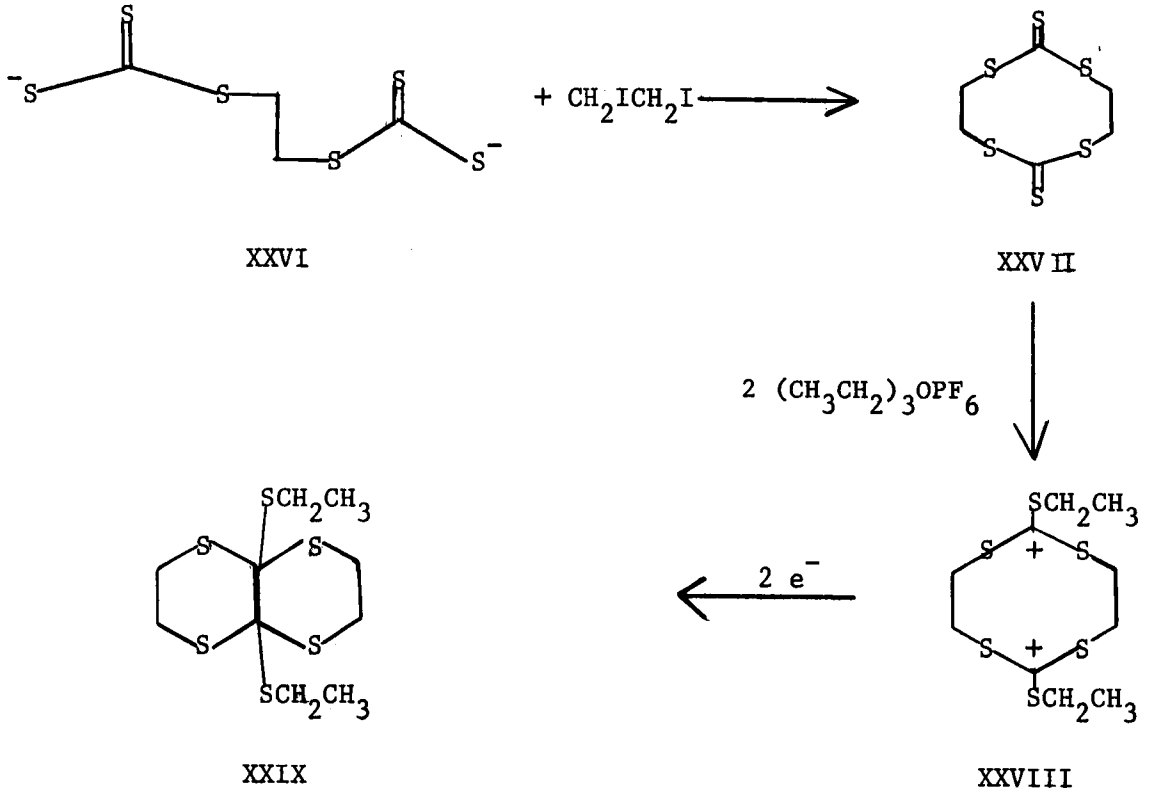
II. Synthetic Utility

The electrochemical reduction of ethylene trithiocarbonate proceeds in good synthetic yield. This fact makes the reduction an attractive procedure for synthesizing numerous derivatives with two trithiocarbonate functional groups in the molecule by variation of the alkylating reagent. Molecules with two or more trithiocarbonate functional groups have not been extensively reported in the literature.[22,28,29]

III. Uses of the Reduction Product

Derivatives of trithiocarbonates have been used for several functions. They have been used as oil additives,[30,31] curing agents for neoprene and butyl rubber,[32] bird repellants,[33] and most importantly as insecticides and fungicides.[34-37] Derivatives formed from XXVI may perform equal to or better than those compounds presently employed in the above uses.

The reduction product may also find use in the synthesis of larger novel molecules by taking advantage of one or both trithiocarbonate groups. An example for the synthesis of 1,6-ethylthio-bicyclo[4.4.0]-2,5,7,10-tetrathiadecane (XXIX) is given.[10] The molecule has not been previously isolated.



XXVI XXVII XXVIII XXIX

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LIST OF REFERENCES

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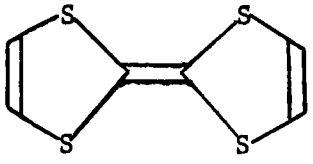
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APPENDIX

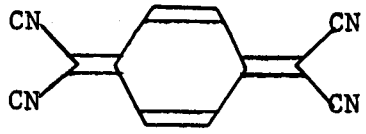
SYNTHESIS OF TETRA-N-BUTYLAMMONIUM BIS(4,5-DIMERCAPTO-1,3-DITHIOLEN-2-THIONE)NICKELATE(II)

I. Introduction

Recently reports on electrically conducting charge transfer complexes have been appearing in the literature.[38-45] The best studied example is the crystalline charge transfer complex of tetrathiofulvalenium tetracyano-p-quinodimethanide, commonly called (TTF)(TCNQ). This complex

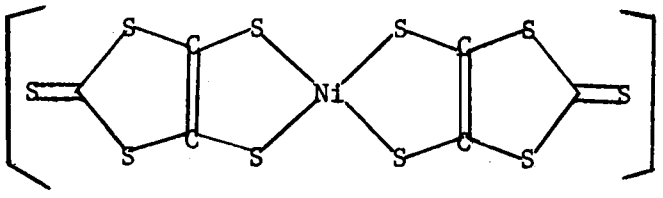


TTF



TCNQ

has the highest electronic conductivity of any known organic compound. Its conductivity at 66°K is 1.47×10^4 ohm^{-1} cm^{-1}, whereas copper has a conductivity of 6×10^5 ohm^{-1} cm^{-1} at 298°K.[41] The current interest is to synthesize derivatives of TTF which, when treated with TCNQ, may be as good or better electronic conductors than (TTF) (TCNQ). It was for this reason that the synthesis of XXX had been undertaken.

$(TBA^+)_x$  (x=0,1,2)

XXX

The tetra-n-butylammonium 4,5-dimercapto-1,3-dithiolen-2-thionide salt has been previously synthesized by the electrochemical reduction of

carbon disulfide.[9,10] The salt is unstable and must be alkylated with reagents such as methyl iodide prior to isolation. Using the 4,5-dimercapto-1,3-dithiolen-2-thione dianion to chelate metal ions had not been previously reported in the literature at the start of this project. Thus, the synthesis of XXX seemed a simple and promising experiment.

II. Experimental

Apparatus

All equipment used was described in the Apparatus Section on pages 5 to 10.

Chemicals

All chemicals and purification procedures have been previously described on pages 10 to 12.

Techniques

1. Bulk Electrolyses. The instruments and cell were set up as previously described on page 13. The cell was filled with 0.4 M TBAI in DMF and deaerated for ten minutes with nitrogen gas saturated with solvent vapor. To the working compartment was added 2 g of carbon disulfide and the electrolysis was initiated at -1.4V vs. SCE. The color of the working compartment solution became dark red. Reduction continued for about seven hours. Each hour the solution in the middle compartment was changed to prevent clogging of the frits from generated byproducts. Extra 1 ml portions of carbon disulfide were added from time to time to replace that lost by evaporation.

After complete reduction had occurred, either nickel perchlorate hexahydrate (Alpha Inorganics) or nickel chloride hexahydrate (Fisher Scientific Co.) was added in excess to the working compartment solution to complex all anions. This caused a color change in the solution to dark green. The working compartment solution was then poured into 800 ml of water, whereupon copious amounts of a black precipitate formed which were collected by filtration.

2. Column Chromatography. Column separation methods were the only methods found to separate the precipitated material. Columns were packed as described on page 14 with silica gel. A 10% hexane-90% methylene chloride mixture was used as the mobile phase.

3. Other Techniques. All other techniques including cyclic voltammetry and spectral analyses were described on pages 5 and 14.

III. Results

Two distinct complexes have been isolated, one green-colored, one brown-colored.

1. Brown-Colored Complex. The brown-colored complex was recrystallized from acetonitrile yielding crystalline flakes that decomposed slowly ca. 250°C. The infrared spectrum is given in Figure 6. The ultraviolet-visible spectrum, using methylene chloride, yielded the following wavelength maxima (nm): 510, 455, 381, 318, and 285. The corresponding absorptivities (1 g^{-1} cm^{-1}) were: 11.4, 15.5, 56.9, 30.1, and 36.9. Cyclic voltammograms of the brown-colored complex yielded two reversible reduction waves (Figure 7) and massive irreversible oxidation waves (Figure 8).

2. Green-Colored Complex. The isolated green-colored complex was

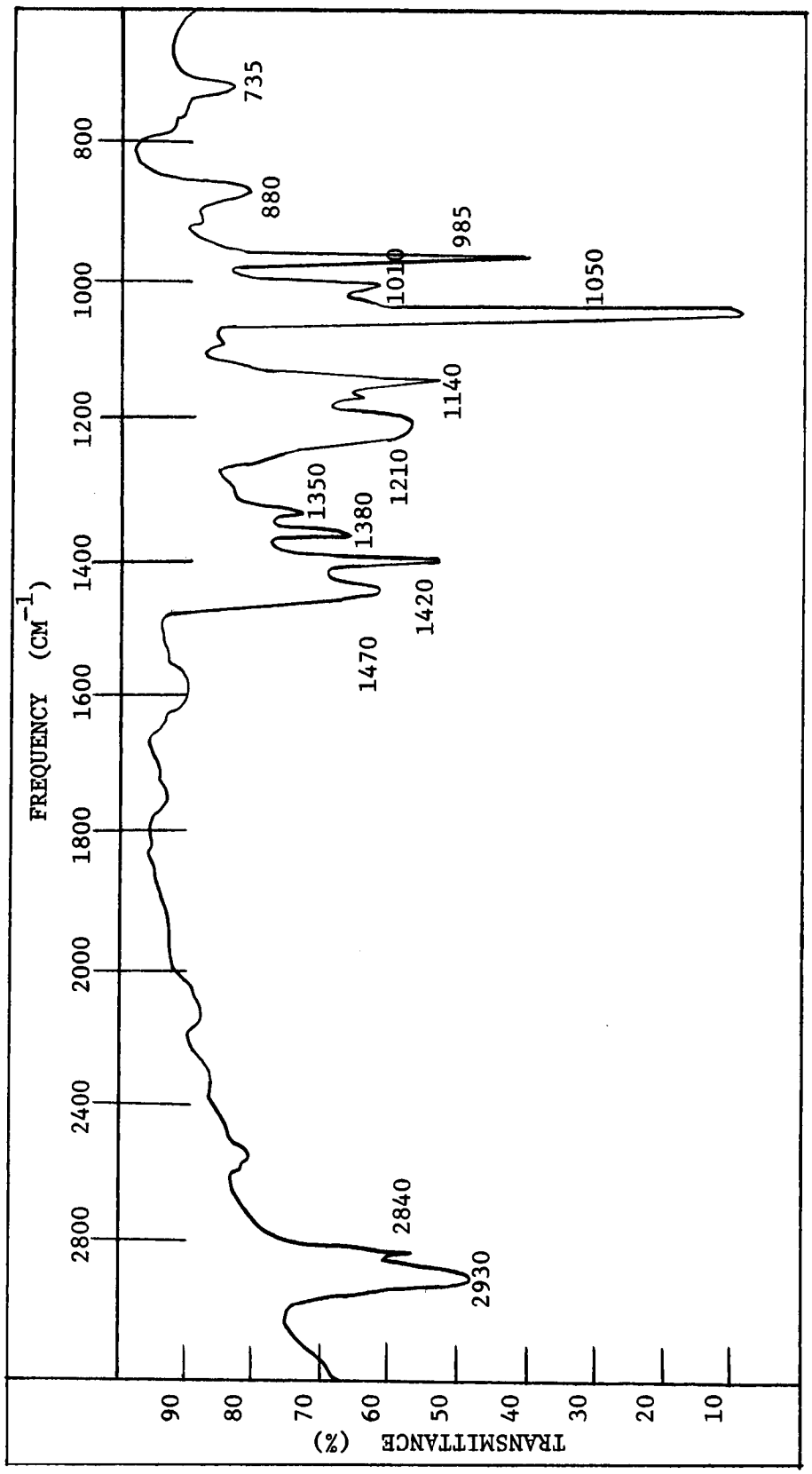


Figure 6. IR spectrum of brown-colored complex in KBr.

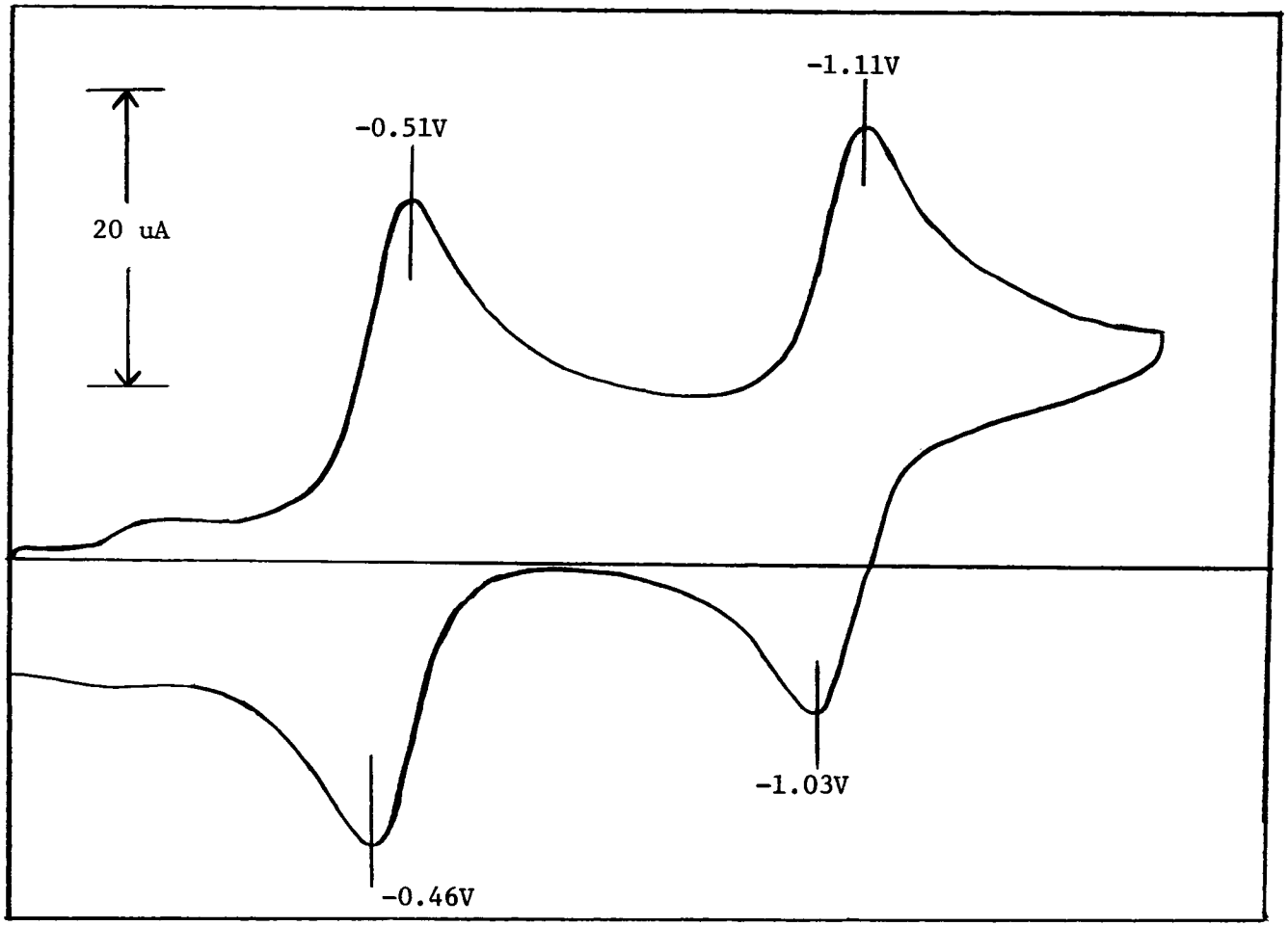


Figure 7. Cyclic voltammogram of reduction of brown-colored complex at 200 mV/sec. Platinum; Concentration 0.40 g/l; vs. SCE.

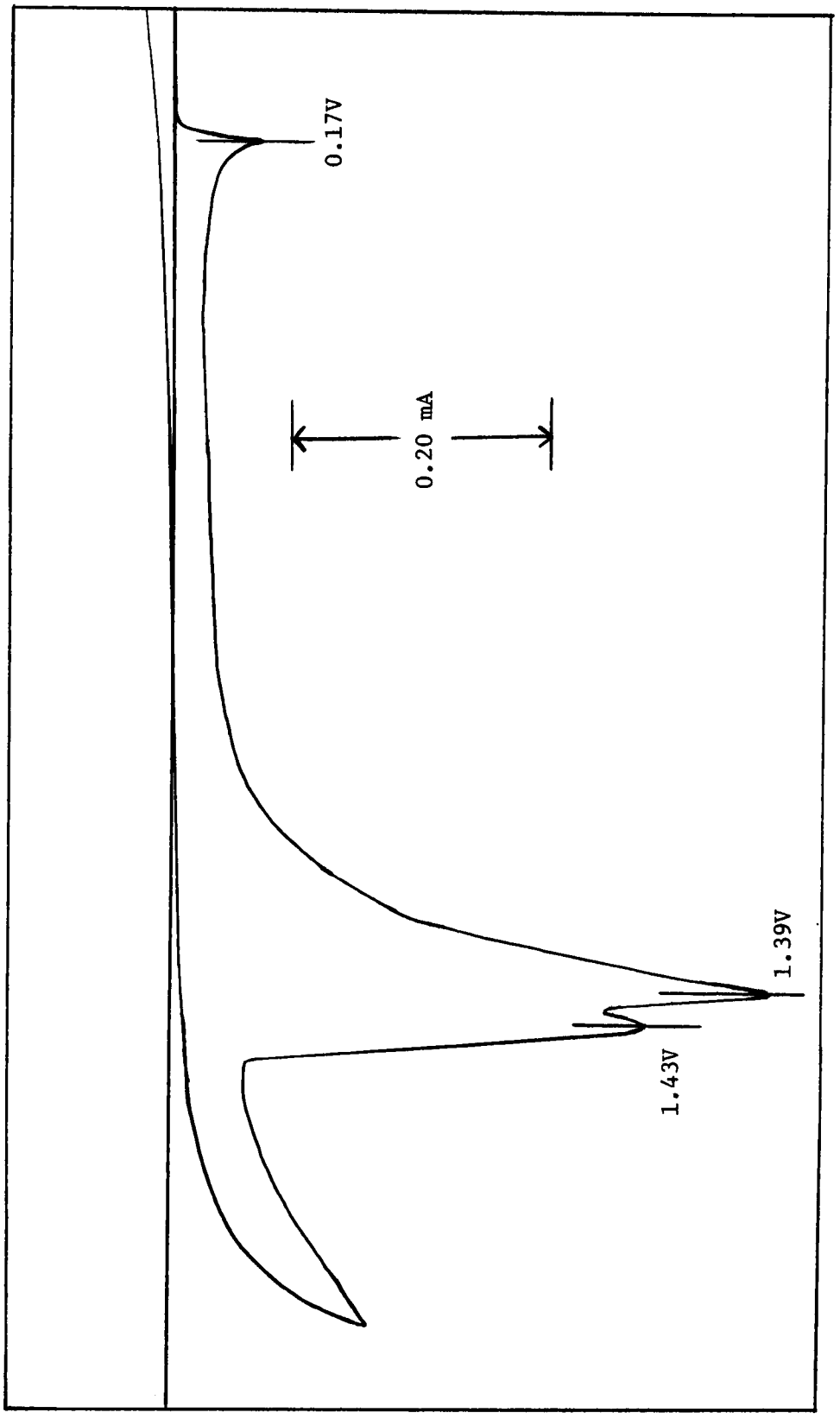


Figure 8. Cyclic voltammogram of oxidation of brown-colored complex at 200 mV/sec.

Platinum; Concentration 0.40 g/l; vs. SCE.

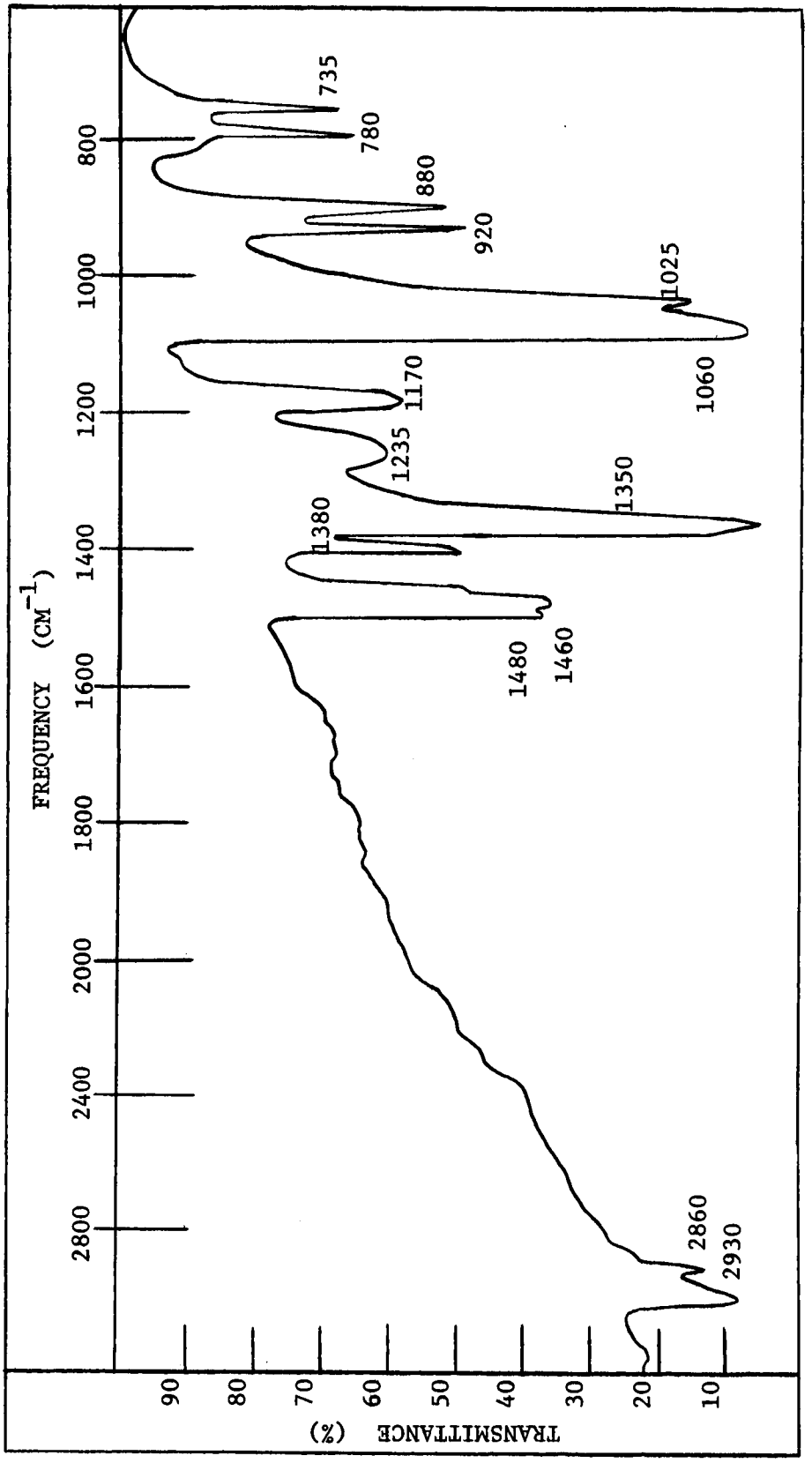


Figure 9. IR spectrum of green-colored complex in KBr.

recrystallized from acetonitrile yielding needle-like crystals that decomposed sharply at 185°C. The infrared spectrum is given in Figure 9. The ultraviolet-visible spectrum, using methylene chloride, yielded the following wavelength maxima (nm): 627, 590, 445, 395, 345, 314, and 278. The corresponding absorptivities ($1\ g^{-1}\ cm^{-1}$) were: 5.0, 4.3, 23.0, 27.0, 27.1, 31.3, and 28.1. Cyclic voltammograms of the green-colored complex yielded a reversible reduction wave (Figure 10) and an irreversible wave at -1.77V vs. SCE that was partially obscured by background current. Oxidation yielded massive irreversible waves at 0.18V, 1.40V, and 1.44V vs. SCE which were identical in shape to those of Figure 8 under the same conditions. Mass spectra of the complex at 70 and 20 eV showed the following m/e peak values and assigned fragments: 196(4,5-dimercapto-1,3-dithiolen-2-thione ligand$^+$), 76(SCS^+), 44(CS^+), and numerous peaks attributable to the fragmentation of the TBA^+ cation.

3. Qualitative Test for Sulfur and Nickel. Both complexes were decomposed separately in concentrated nitric acid which yielded yellow precipitates of elemental sulfur. The acid solutions were then diluted, neutralized with 6 M ammonium hydroxide, and a solution of dimethylglyoxime in ethanol was added in excess to both. This yielded cherry-red precipitates indicating the presence of Ni^{2+}.

IV. Discussion

Steimecke, et al.,[46] have recently synthesized and isolated sodium 4,5-dimercapto-1,3-dithiolen-2-thionide formed from the sodium reduction of carbon disulfide. The salt was then treated with metal ions and the corresponding complexes, including the nickel complex XXX, were isolated.

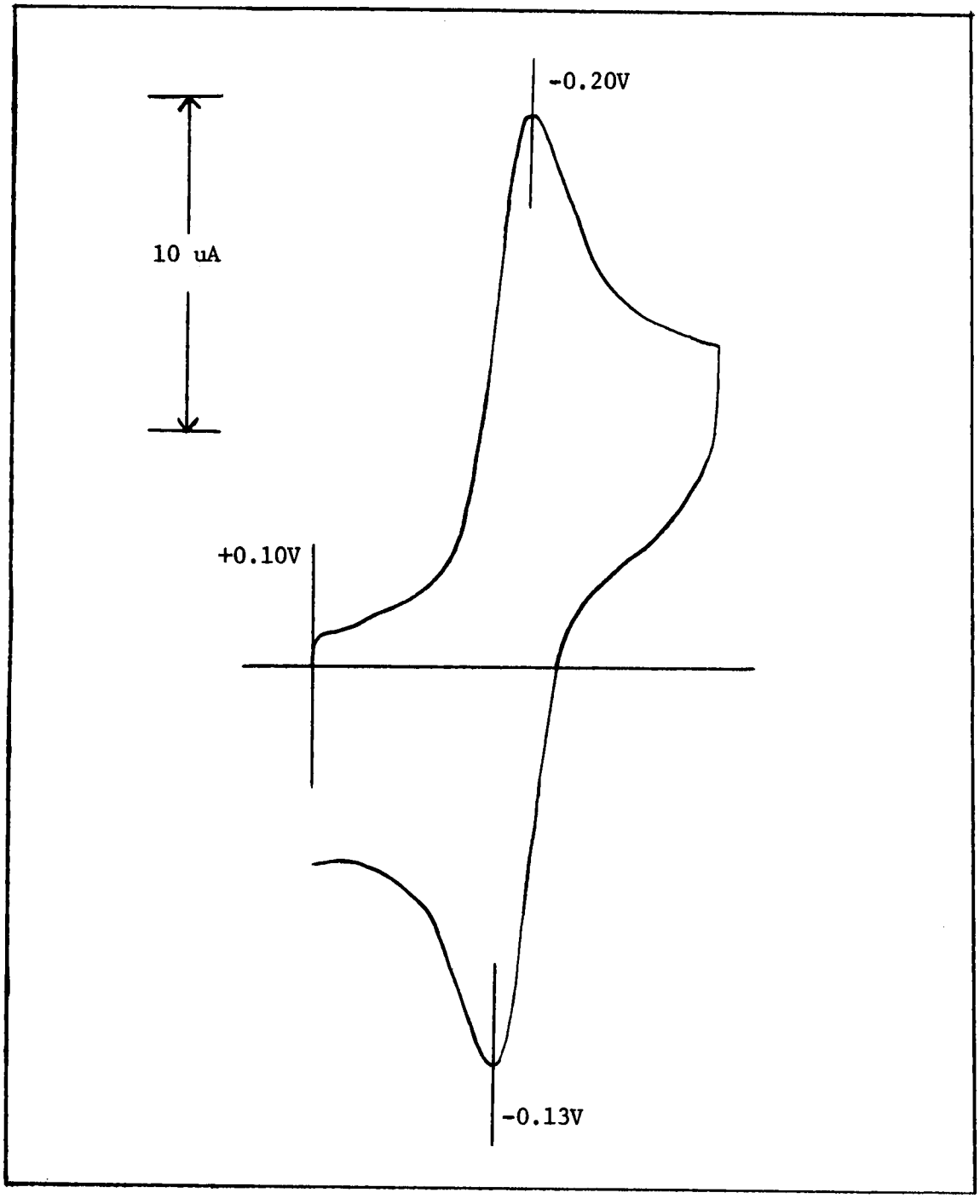


Figure 10. Cyclic voltammogram of reduction of green-colored complex at 200 mV/sec.

Platinum;Concentration 0.20 g/1; vs. SCE

The nickel complex was reported as green in color and decomposed between 197°C and 199°C.

The green-colored complex as reported in this thesis may be the nickel complex XXX reported by Steimecke et al. The color was correct, the decomposition point was close to that reported, the mass spectrum showed expected fragments, and the IR spectrum contained a peak at 1350 cm^{-1}, a peak characteristic of compounds with a dithiolene structure.[47,48] A peak had also appeared at 1060 cm^{-1} which is characteristic of the thiocarbonyl bond in trithiocarbonates.[9,19]

The brown-colored complex also had a characteristic thiocarbonyl bond stretch at 1050 cm^{-1} in the IR spectrum. No other data were obtained which could yield detailed structural information on this complex.

By TLC analysis, there were at least two more complexes to be isolated from the crude product mixture. Better separation techniques or an alternate synthetic route are needed to obtain increased yields of complexes for further characterizations.

In structural determinations x-ray crystallography may be the most useful technique to employ in future studies.

VITA

Francis John Goodman was born in the town of Derby, Connecticut, on April 9, 1951. He soon moved to neighboring Shelton and made that town his permanent residence.

After completing his elementary education in Shelton, he commuted to nearby Trumbull beginning in the Fall of 1965 to further his education at St. Joseph High School.

In the Fall of 1969 he accepted a Headmaster's Scholarship at Fairfield University in Fairfield, Connecticut, and later graduated magna cum laude with a Bachelor of Science degree in Chemistry in the Spring of 1973.

At the urging of a good friend and Chemistry professor at Fairfield, Dr. Salvatore Carrano, Mr. Goodman applied to and was accepted at the University of Tennessee, Knoxville. Two years of ardous study and experimentation earned him a Master of Science degree in Chemistry in August of 1975.

Mr. Goodman is still happily single despite having been a teaching assistant in Chemistry for Home Economics and Nursing majors during part of his years at Tennessee.

As for the future, having now mastered the precise skills required for doing sulfur electrochemistry, he looks forward to less demanding studies beginning in the Fall of 1975 at the University of Connecticut School of Medicine.