To the Graduate Council:

I am submitting herewith a thesis written by Joseph Carl Lodmell entitled "High Performance Liquid Chromatography Analysis of Electrolysis Solutions: A Study of the Reduction of Carbon Disulfide." 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:

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Charles A. Lane

Accepted for the Council:

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF ELECTROLYSIS SOLUTIONS: A STUDY OF THE REDUCTION OF CARBON DISULFIDE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Joseph Carl Lodmell

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ABSTRACT

Nonaqueous electrolysis solutions were analyzed using high performance liquid chromatography (HPLC). The electrochemical reduction of carbon disulfide in N,N-dimethylformamide was investigated in this manner.

Addition of methyl iodide to a sample of the electrolysis solution converted ionic multisulfur species to molecular species which were retained by an octadecylsilane (ODS) column operated in the reverse phase mode. A solution of 50:50 methanol and water was employed as the mobile phase. A spectrophotometric detector set at 330 or 412 nm was used.

The chromatograms of the reduction solution show evidence of six products. Two of the products were identified as 4,5-bis(methylthio)-1,3-dithiolen-2-thione, the major product of this reduction, and dimethyl trithiocarbonate. A third product is thought to be 4,5-bis(methylthio)-1,2,4-thithiolen-3-thione. These have all been reported in the literature. One major and two minor products were observed which are not yet identified and have not been reported in the literature. It is speculated that the major unidentified product, which is shown by chromatograms to decompose with time to give the trithiocarbonate as one of the decomposition products, is demethyl orthothiooxalate or a compound of similar structure. The HPLC analysis showed that there were only minor variations in the relative amounts of the major products as the carbon disulfide electrolysis proceeded.

The zinc(II) complex of the dianion of 4,5-dimercapto-1,3-dithiolen-2-thione ($C_3S_5^{2-}$) was prepared. It was used in the synthesis of gram quantities of ethylene-4,5-dimercapto-1,3-dithiolen-2-thione by the addition of 1,2-dibromoethane to a refluxing acetone solution of the complex.

HPLC analysis was employed to monitor the alkylation step and the ether extraction step used in purifying the thione.

The electrochemical reduction and the alkaline hydrolysis of ethylene-4,5-dimercapto-1,3-dithiolen-2-thione was studied in hopes of preparing a zinc(II) complex of the dianion, 1,4-dithia-2-cyclohexene-2,3-dithiolate. It was found that the dianion was not formed in the electrochemical reduction, at least not at synthetically useful concentrations.

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CHAPTER I

INTRODUCTION

The synthesis of new organic multisulfur electron donor compounds has been an active field of research in recent years. An important step in many of these syntheses involves either an electrochemical reduction or oxidation of a compound dissolved in nonaqueous media. A need exists for a rapid and accurate means of analyzing these electrolysis solutions, which are often complex mixtures of products, while the electrolysis is in progress.

Selection of the Method

Thin layer and gas chromatography (GC) methods have been used for these analyses, but these techniques require significant sample preparation and/or analysis time. A sample can be analyzed by thin layer chromatography with no preparation, but the analysis itself is slow. Gas chromatography provides for rapid analyses, but a lengthy sample preparation is required to dissolve the sample in a supporting electrolyte-free solvent suitable for injection into a GC column. A primary objective of this work is to develop a procedure in which high performance liquid chromatography (HPLC) could be used as the method of performing these analyses with minimal sample preparation and analysis time.

HPLC, in common with all forms of chromatography, finds its beginning with the works of Day, who used crude columns packed with clay or fuller's earth to separate fractions of crude oil samples,[1,2]

and Tswett, who separated plant pigments on a column packed with powdered chalk.[3] HPLC was first introduced, in theory, in a remarkable paper by Martin and Synge,[4] in 1941. In this paper they gave a theoretical treatment of the operating parameters in a column and described the efficiency of separation in terms of the height equivalent of one theortical plate (HETP). They also predicted that the mobile phase could be a gas instead of a liquid. A third point in the paper was a description of the new technique of liquid-liquid chromatography and, finally, a prediction that was not to be upheld for over twenty years, that for optimum separation, small particle size and operation with a high pressure difference across the column would be desirable.

It was not until the late 1960's that Huber,[5] Kirkland,[6] and Horvath, Preiss and Lipsky[7] built modern liquid chromatographic systems which employed columns packed with small particles and operated at high pressures.

In choosing a method for analyzing the electrolysis solutions, many factors concerning each chromatographic method were compared. These factors include analysis time, sample preparation, conditions encountered by the sample (e.g. temperature) as well as qualitative and quantitative data yielded.

A short analysis time was one of the primary considerations. Both GC and HPLC would probably require similar analysis times once the sample was injected in the column. The real time problem is in preparing the sample to be injected. For a GC analysis, it is necessary to remove the supporting electrolyte from the sample before injection

so as not to foul the column. The usual procedure is to draw the sample and then evaporate the solvent. This can be a time consuming step if the solvent is not very volatile, as is the case with N,N-dimethylformamide (DMF). Next the sample is taken up in a volatile solvent which will dissolve all but the supporting electrolyte. This sample is then injected into the GC. In HPLC analysis, by proper selection of the stationary phase, the supporting electrolyte would not be held by the column employed, and therefore, should not cause any interference or column degradation. This will usually be the case for the common reversed phase operation of HPLC methodology. Thus sample preparation would not involve an evaporation step and significantly shorter analysis times would be required for HPLC compared to a GC method.

Another factor that limits the necessary sample preparation for HPLC is the use of a precolumn to filter crude samples directly in the instrument. Thus the instrument does some of the required preparation.

A problem encountered in GC analysis is the high temperature to which a compound is exposed. Many of the sulfur compounds that are involved in these syntheses are known to be labile and could easily be destroyed within a GC. HPLC, on the other hand, is operated at, or only slightly above, room temperature. Thus the chance of altering or degrading the sample is much less under the conditions for HPLC analysis.

If quantitative results are desired, the HPLC technique would again appear to be superior. With GC the precision can vary from sample to sample because of decomposition or variations in the rate of

evaporation of the samples.[8] HPLC obviously does not suffer from these problems. Quantification with HPLC does have a problem with relation to the detector, which is often a single or variable wavelength UV-visible detector. This means that the absorbance signal will depend on the wavelength of the detector and the sample extinction coefficient at that wavelength. For the best quantitative results, it would be desirable to have the detector set at a wavelength of an absorbance maximum. Therefore, in a multicomponent sample, quantitation of more than one component can be a problem.

The dependence upon absorbance means that a component might never appear on the chromatogram if it has little or no absorbance at the detector wavelength. GC, with a flame ionization detector, or especially a thermal conductivity detector, does not usually have this problem. However, the capability of variation of the detector wavelength to mask a component from the chromatogram has an advantage if two inseparable compounds have differences in their absorbance spectra. Thus a spectrophotometric detector allows selectivity in the HPLC experiment.

This feature also aids in identification of components. Chromatograms obtained at different detector wavelength settings will give some information about the components in addition to the usual retention times.

Reduction of Carbon Disulfide

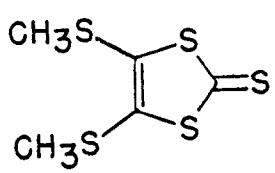
To study the applicability of HPLC to the analysis of electrolysis solutions, the reduction of carbon disulfide was chosen as a test case. The reduction of carbon disulfide in nonaqueous solvents is an important step in the synthesis of many of the multisulfur compounds.[9,10,11,12,13]

It is a complex reaction in which a variety of multisulfur compounds are formed. Some of these have been identified, so that it will be possible to evaluate the analysis method. It was also hoped that new compounds could be identified and that information could be gained about the mechanism of the reaction, since the complete mechanism and all intermediates are not known.

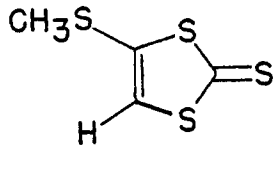
A brief review of the history of this reaction will illustrate the complexity of the reaction and will also introduce the intermediates that were to be identified in the HPLC analysis.

The reduction of carbon disulfide dates back to the work of Fetkenheuer[14] in 1927. Fetkenheuer reduced carbon disulfide by means of a sodium-mercury amalgam, but erronously reported the main product to be the dimeric thiooxalate entity.

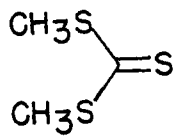
Nothing more was reported about the carbon disulfide reduction for almost fifty years, then in 1974, Wawzonek and Heilman[15] studied the reaction and, after addition of methyl iodide to the reaction solution, identified as the major produce, 4,5-bis(methylthio)-1,3-dithiolen-2-thione, 1. Two other identified products were 4-methylthio-1,3-dithiolen-2-thione, 2 and dimethyl thrithiocarbonate, 3. They proposed a mechanism,



1

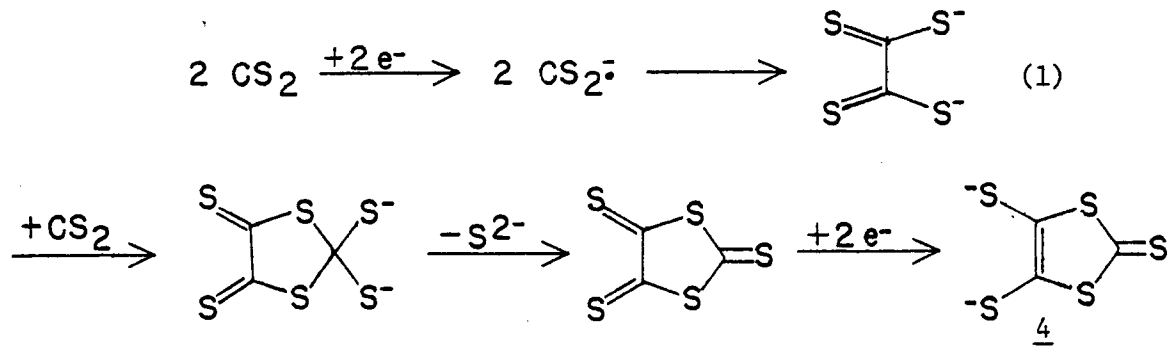


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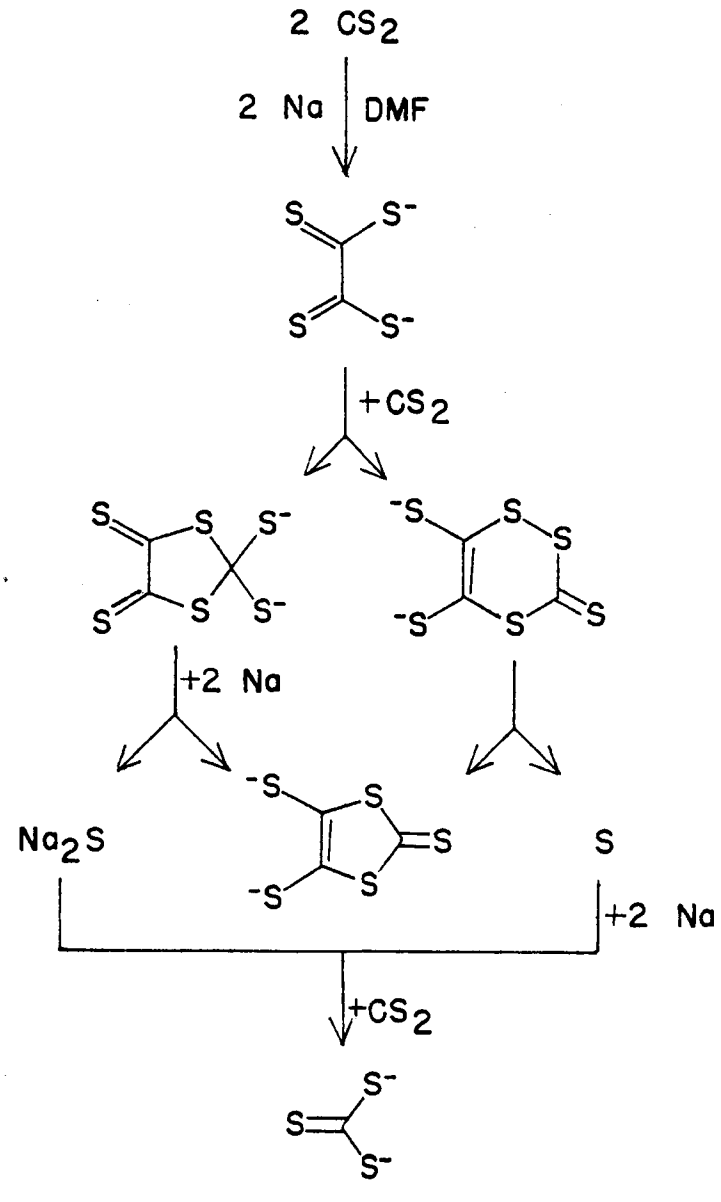
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equation 1, for the formation of the precursors of products 1, 2, and 3.



(1)

Steimecke, Kirmse and Hoyer[16] proposed that another product was formed in the sodium reduction and accounted for the production of the trithiocarbonate via the mechanism in equation 2.

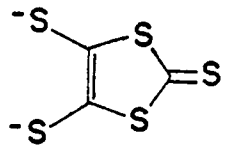


(2)

In 1975, Bontempelli and co-workers[17] proposed an entirely different mechanism, as given in equation 3. They theorized that due to the removal of CS by the nitrogen stream bubbling through the cell, CS_3^{2-} does not react completely and is left as one of the products.

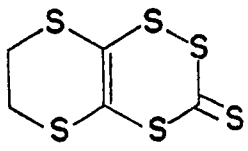
$$2\ CS_2 + 2\ e^- \longrightarrow CS_3^{2-} + CS$$

$$2\ CS + CS_3^{2-} \longrightarrow \quad (3)$$



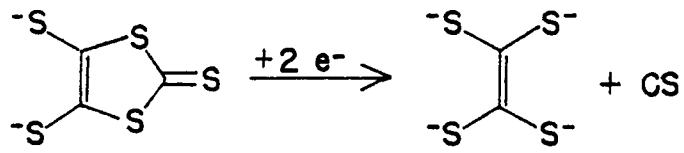
Reuter and Gattow[18] performed the carbon disulfide reduction in five different manners: (a) sodium-amalgam reduction in carbon disulfide, (b) sodium reduction in liquid ammonia, (c) sodium reduction in tetrahydrofuran/napthalene solution, (d) sodium reduction in hexamethylphosphorous triamide, and (f) electrochemical reduction using a mercury cathode in a tetramethylammonium chloride/DMF solution. They found the electrochemical method to give the highest percentage yield of 4.

Harnden[11] reported isolating ethylene-5,6-dimercapto-1,2,4-trithiolen-3-thione, 6, after the addition of 1,2-dibromoethane to a carbon disulfide electrolysis solution. This would seem to add credence to the mechanism of Steimecke et al. Harnden goes on to suggest that the



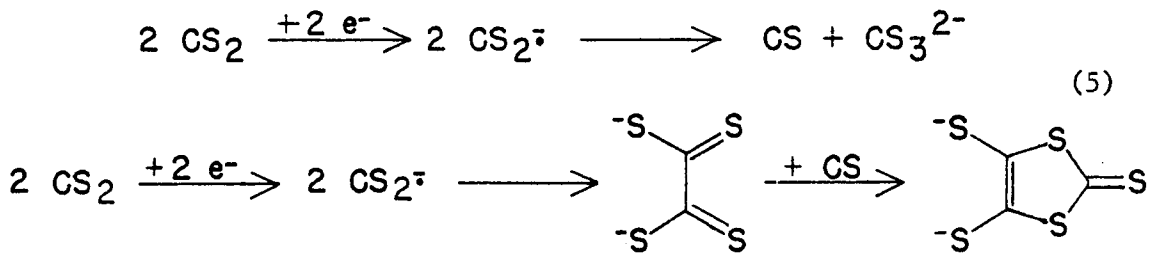
6

reduction may be potential dependent since Bontempelli et al. reduced CS_2 at -2.2 V vs. the saturated calomel electrode (sce), while Steimecke's work was done at -1.5 V vs. sce. Harnden proposed that at -2.2 V the thione was further reduced with the liberation of CS as shown in equation 4.



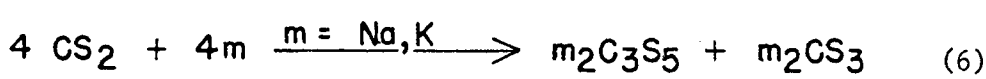
(4)

A few years later, another mechanism was advanced by Jeroschewski.[19] He used the reduction of carbon dioxide as an analogy to the carbon disulfide reduction to develop the mechanism shown in equation 5.



(5)

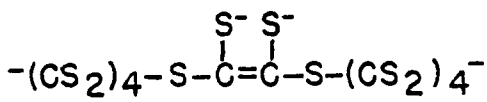
In 1979, Steimecke and co-workers[12] developed preparative methods for the active metal reduction of carbon disulfide. They obtained nearly quantitative yields of $C_3S_5^{2-}$ and CS_3^{2-} according to equation 6.



(6)

The work of Hurley[13] has added more information about the electrochemical carbon disulfide reduction which he also found to give quantitative

yield of $C_3S_5^{2-}$ according to the stoichiometry of equation 6. Hurley found that the reaction is both potential and temperature dependent. If the reduction was carried out at the foot of the wave, -1.7 V vs. sce, then the thione, 4, was not a major product, but instead a partially reduced polymer of carbon disulfide with apparently a structure like 7 was formed. At slightly elevated temperatures or a potential more negative than -1.9 V vs.sce, the oligomer was not present and was further reduced to the thione, 4.

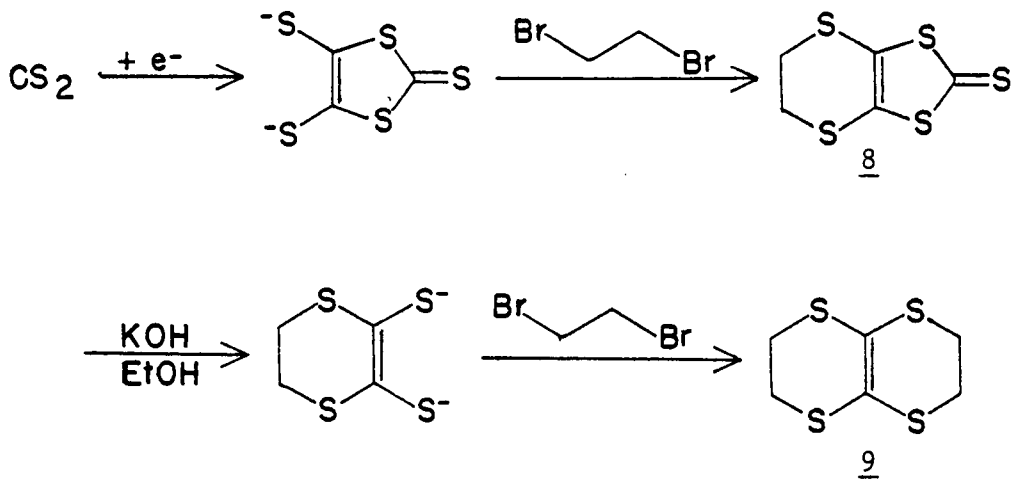


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Another interesting phenomenom that Hurley observed was the change in color of the reduction solution from red to deep green to blue. This occurs at slightly elevated temperature and high current density, in which case the excess carbon disulfide rapidly evaporates from the solution. Addition of even a small amount of carbon disulfide to the green or blue solution returns the color to red. Products after alkylation of the colored solutions are the same, though the green and blue solutions yield slightly less products. One explanation that was considered was the production of solvated electrons, but electron paramagnetic resonance (EPR) studies showed this not to be the case.

Other Applications of HPLC to Organosulfur Chemistry

A final project of this work was to apply the HPLC technique to improve a synthetic procedure that was developed by Harnden previously. Harnden[11] synthesized 2,5,7,10-tetrathiobicylo[4.4.0]dec-1(6)-ene, 9, by the scheme shown in equation 7.



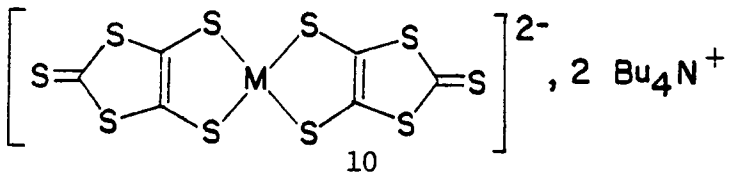
(7)

The synthesis of 8 was first reported in 1976 by Mizuno, Cava and Garito.[10] They added 1,2-dibromoethane to a carbon disulfide reduction solution and isolated 8 in 18% yield. Harnden[11] used the same procedure and obtained a 30% current yield of 8, based on one electron per CS_2, after separation of the products on a silica gel column. Steimecke and coworkers[12] reported the synthesis of 8 in 1979 from the sodium salt of 4, but did not report the percentage yield obtained.

The final step in the preparation of 9 is the alkaline hydrolysis of 8 followed by alkylation with 1,2-dibromoethane. Harnden[11] reported a 43% yield of the product. Electrolysis of 8 to achieve the same end was unsuccessful.

To improve this synthesis, it was desired to eliminate the time consuming column chromatography employed in the isolation of 8 and in so doing, increase the percentage yield. To this end, complexation of of the dianion, 4, with a metal ion seemed desirable.

In 1975, Steimecke, Kirmse and Hoyer[16] reported on the complexes of 4 with several different metal ions. These complexes were isolated as the tetrabutylammonium salt, 10.

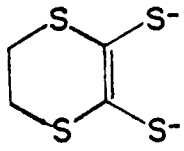


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Addition of both the metal and the tetrabutylammonium salt to the sodium reduction solution resulted in the formation of complexes with Cu^{2+}, Ni^{2+}, Zn^{2+}, Pt^{2+} and Pd^{2+}.

The 1979 paper by Steimecke and co-workers[12] illustrates the use of the metal complexes as intermediates in the synthesis of alkylated thiols. In these reactions the alkyl group attaches to the sulfurs bound to the metal center. Hurley[13] has also shown the usefulness of these metal complexes in organosulfur synthesis reactions.

It was hoped that a metal complex of 4 would improve the yield of 8 and shorten the preparation time. It was also hoped that a metal complex of 11 could likewise be prepared and used to the same advantage. Finally, it was desired to use HPLC analysis during the course of the reaction to monitor the formation of the product and to improve the yield by optimization of the reaction conditions.



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CHAPTER II

EXPERIMENTAL

A. Apparatus

1. Instruments

a. Regulated Power Supplies. Two regulated power sources were used for bulk electrolysis and coulometry: a) Princeton Applied Research Model 173/176 Potentiostat/Galvanostat, and b) Princeton Applied Research Model 173/179 Potentiostat/Coulometer.

b. Potentiostat. A solid state, three-electrode potentiostat, employing LM 747 operational amplifiers, was built following a design by Moses.[20] A schematic diagram of this instrument is shown in Figure 1. An Intersil ICL 7106 digitial voltmeter, built into the instrument, allowed for potential measurements. The instrument was capable of current measurements from 0.1 - 2000 $\mu A\ V^{-1}$. A Princeton Applied Research Model 175 Universal Programmer provided the necessary triangle-wave function. Sweep rate capability ranged from 1 $mV\ sec^{-1}$ to 1000 $V\ sec^{-1}$.

c. Coulometer. A Koslow Scientific Co. Model 541 Coulometer, with output in microequivalents of current, was used in conjunction with power supply (a) above. This coulometer required frequent calibration with a constant current source. A digital coulometer, with output in microcoulombs, Princeton Applied Research Model 179, was incorporated in power supply (b) above.

d. HPLC. A laboratory Data Control High Performance Liquid Chromatograph consisting of the following components was used for all

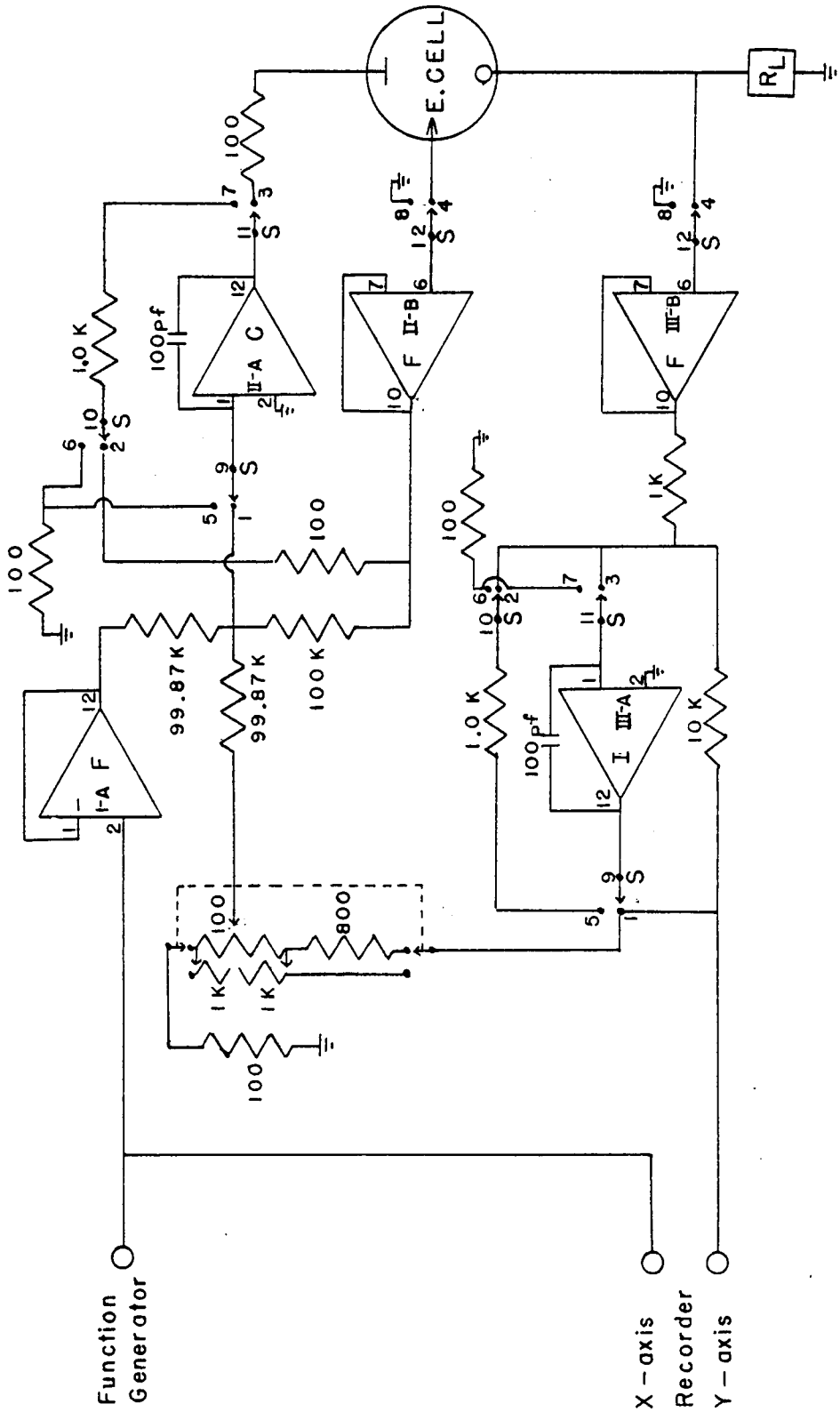


Figure 1. Schematic diagram of potentiostat. Switches (S) shown in operate position.

chromatography analysis: a) Constametric I dual piston pump, b) Constametric II dual piston pump, c) Constametric II control module, d) Gradient Master Model 1601 control module, e) Rheodyne Model 7120 syringe loading, six port, rotary sample injector, f) Whatman precolumn packed with 30-38μ Partisil octadecylsilane (ODS), g) Alltech Associates 25 cm x 4.6 mm I.D. analytical column with 10μ Partisil 10-ODS packing, and h) Spectro-Monitor II Model 1202 variable wavelength UV-visible detector. Figure 2 shows the arrangement of these components in the system. This system is capable of delivering up to 10 mL min^{-1} of solvent at a pressure of up to 5000 psi. The Gradient Master allows for gradient elution programming over time periods ranging from 1 - 1100 min. The detector wavelength can be varied from 190 - 690 nm. Eight absorbance ranges from 0.01 - 1.28 absorbance units full scale and two transmittance scales, 0 - 100% and 90 - 100% allow for control over the sensitivity of the detector.

e. Recorders. Cyclic voltammograms were recorded on a Hewlett-Packard Model 136 AM X-Y-Y' recorder or on an Esterline Angus 575 X-Y recorder. HPLC chromatograms were recorded on a Houston Instrument Omniscrible strip chart recorder.

f. Spectrometers. UV-visible spectra were recorded on a Cary Model 17 spectrometer. Mass spectral data were obtained on a Hewlett-Packard Model 5980A mass spectrometer.

g. Miscellaneous. Melting points were obtained using a Mel-Temp apparatus.

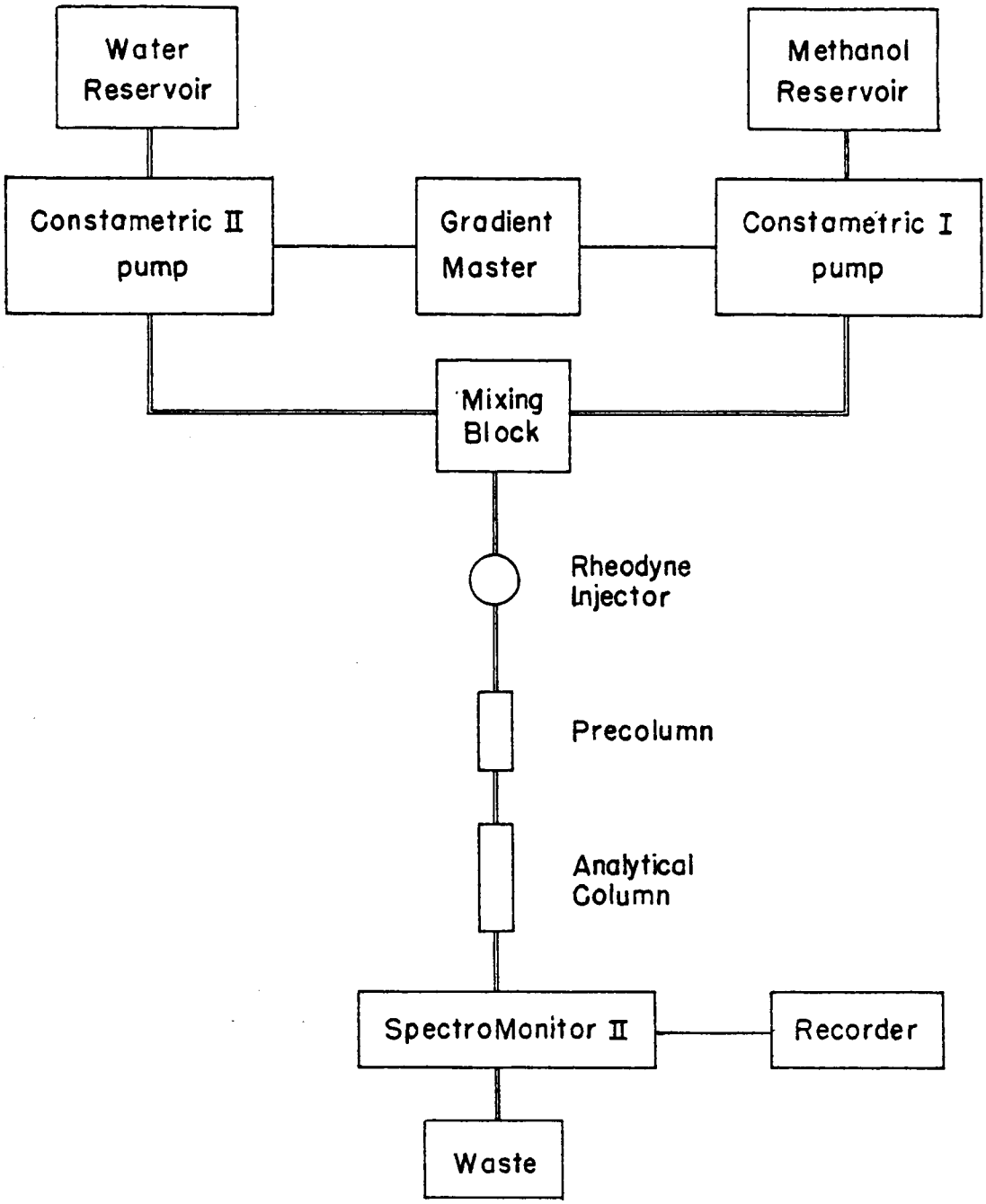


Figure 2. Component arrangement of the Laboratory Data Control HPLC.

2. Electrochemical Cells

a. One-Compartment Cell. For cyclic voltammetry experiments, a one compartment cell with a fine porosity frit in the bottom and a three-way stopcock for directing gas either through the frit or above the solution was used. A Teflon top, with holes for the electrodes, covered the cell.

b. Three-Compartment Cell. For controlled potential coulometry a small three-compartment cell with a coarse frit in the bottom of the main compartment for degassing and a middle compartment separated from the main and counter compartments by fine frits was used. A three-way stopcock directed the gas flow through or over the solution.

Exhaustive electrolyses were performed in a large, H-shaped, three-compartment cell, described previously by Goodman.[21]

3. Electrodes

a. Working Electrodes. For cyclic voltammetry, a platinum inlay electrode of 0.242 cm^2 surface area was employed. Controlled potential coulometry was performed with a rectangular platinum gauze of 17.5 cm^2 surface area fused to a heavy gauge platinum wire. A cylindrical platinum gauze electrode of 40.2 cm^2 surface area fused to a heavy gauge platinum wire was used in exhaustive electrolyses.

b. Counter Electrodes. The counter electrode employed in cyclic voltammetry was a rectangular platinum gauze of 17.5 cm^2 surface area fused to a heavy gauge platinum wire. Spectroscopic grade carbon rod electrodes were used in coulometry and exhaustive electrolyses.

c. Reference Electrode. A Saturated Calomel Electrode (sce) was used in all cases as the reference electrode. The electrode was

constructed from the design by Adams.[22] In coulometry and exhaustive electrolyses, the electrode was placed in a fine-fritted glass tube to isolate it from the working compartment.

B. Chemicals

1. Solvents

a. Acetonitrile (MeCN). Spectroquality Gold Label acetonitrile was purchased from Aldrich Chemical Company and used with no additional preparation.

b. N,N-Dimethylformamide (DMF). DMF was purified by a variation of the procedure of Faulkner and Bard.[23] To 1ℓ of certified ACS DMF (Fisher Scientific Company) was added 10 - 15 g of anhydrous copper(II) sulfate. After sitting for at least one day, the solution was vacuum distilled. The DMF collected was kept in sealed flasks until use.

c. Ethanol (95%). Ethanol, 95%, for alkaline hydrolysis, was prepared by the procedure used by Harnden.[11] To 700 mL of drum grade 95% ethanol was added 150 g of potassium hydroxide. After refluxing overnight, the ethanol was distilled and the middle 500 mL of distillate was collected.

d. Acetone. Certified ACS acetone (Fisher Scientific Company) was used with no further preparation.

e. Methanol. For purification and synthesis work, certified ACS methanol (Fisher Scientific Company) was used. For use as a HPLC solvent, HPLC grade methanol was obtained from Burdick and Jackson Laboratories.

f. Diethyl Ether. Certified ACS (Fisher Scientific Company) diethyl ether was used for purifications and extractions.

g. Water. Water, for use as an HPLC solvent, was prepared in the following manner. Distilled water from the department still was redistilled in a glass distillation apparatus. The redistilled water was then filtered through a 4.5μ Milipore filter (Model XX10 047 00).

2. Reagents

a. Carbon Disulfide. Certified ACS reagent grade carbon disulfide (Fisher Scientific Company) was used in electrolysis with no further purification.

b. Potassium Hydroxide. Certified ACS reagent grade potassium hydroxide (Fisher Scientific Company) was used in alkaline hydrolysis with no further purification.

c. Zinc Chloride. Certified ACS reagent grade zinc chloride (Fisher Scientific Company) was used in preparation of the zinc complexes.

d. Ethylene Trithiocarbonate. ACS certified ethylene trithiocarbonate (Pfaltz and Bauer, Incorporated) was used in HPLC verification of the presence of trithiocarbonate in the reduction of carbon disulfide.

e. Potassium Trithiocarbonate. ACS certified potassium trithiocarbonate (Alfa Inorganics) was used as a source of dimethyl trithiocarbonate by adding methyl iodide to a DMF solution of the potassium salt.

f. Potassium Sulfide. ACS certified potassium sulfide (Alfa Products) was used as a source of dimethyl sulfide in the same manner as above.

g. Methyl Disulfide. ACS certified methyl disulfide (Aldrich Chemical Company Incorporated) was used in identifying products of the carbon disulfide reduction.

h. Ammonium Hydroxide. ACS certified ammonium hydroxide (Fisher Scientific Company) was used in the synthesis of the zinc complex.

i. Alkylating Agents. Certified ACS methyl iodide (Aldrich Chemical Company Incorporated) and 1,2-dibromoethane (Fisher Scientific Company) were used without further purification.

3. Supporting Electrolytes

a. Tetrabutylammonium Iodide (TBAI). Technical grade TBAI (Eastman Kodak Company) was used in bulk and coulometric electrolyses without further purification.

b. Tetraethylammonium Perchlorate (TEAP). For cyclic voltammetry studies, TEAP (Eastman Kodak Company) was recrystallized three times from water and then vacuum dried at 60°C for two days.

c. Tetrabutylammonium Tetrafluoroborate ($TBABF_4$). $TBABF_4$ (Eastman Kocak Company) was used in coulometric and bulk electrolyses with no further purification.

4. Miscellaneous

Ether extracts of reaction products were dried over anhydrous magnesium sulfate (Fisher Scientific Company). Nitrogen and argon used in this work were obtained as prepurified from Selox Incorporated.

C. Techniques

1. Electrochemical Techniques

a. Exhaustive Electrolysis. The electrochemical reduction of carbon disulfide was carried out in a 250 mL, three-compartment cell. All compartments of the cell were filled with a 0.4M TBAI/DMF solution, leaving

room for volume expansion when the solution warmed up. Nitrogen or argon was bubbled through the working compartment, via the fritted bottom, to deaerate the solution. While the dearation was continuing, the working, reference and counter electrodes were put in place and connected to the potentiostat and coulometer. Prereduction was then performed at -1.9 V vs.sce until the current dropped to a low level.

After prereduction, the potential was set to -1.8 V vs. sce and approximately 0.5 mL of CS_2 was added to the working compartment. Periodically, additional CS_2 was added, usually a few drops at a time. If excess CS_2 was added, an overload condition existed in which the current became too great for the potentiostat to maintain the desired potential.

The electrolysis was discontinued after a desired number of coulombs or microequivalents of current had been passed.

b. Linear Sweep Voltammetry. Linear sweep or cyclic voltammetry was performed in the one-compartment cell. A 0.1M TEAP/MeCN solution was used in most studies. The cell was filled to approximately a two-thirds level and the solution was then deareated by bubbling nitrogen or argon through the bottom frit. After 10-15 minutes, the gas flow was directed over the solution and a background voltammogram was recorded over the potential range of interest. A pre-weighed amount of the electro-active species was then added and nitrogen or argon was again bubbled through the solution to aid in dissolution of the compound. After all of the compound appeared to have dissolved, the gas flow was directed over the top of the solution. The solution was allowed to sit approximately one minute before voltammograms were recorded.

c. Controlled Potential Coulometry. For the determination of n-values, controlled potential coulometry was used. A small, three-compartment cell was used in these studies. The electrolyte solution was 0.4M TBAI/DMF or 0.1M $TBABF_4$/DMF. The $TBABF_4$ solution allows for potentials more negative than -2.0 V vs. sce to be employed without the supporting electrolyte being reduced. Argon or nitrogen was bubbled through the cell and a prereduction was carried out at a potential equal to or more negative than the potential of the electrolysis. A background cyclic voltammogram was often made. After a satisfactory background was obtained, a pre-weighed amount of the compound was added to the main compartment. After complete dissolution, the electrolysis was started and allowed to continue until the current dropped to almost zero. The ratio of microequivalents of current to micromoles of compound gave the n-value.

2. HPLC Techniques

a. HPLC Analysis of Electrolysis Solutions. To analyze the contents of an electrolysis solution, it was necessary to convert the ionic species present to molecular species so that the ODS column would retain the products of interest. With the organosulfur species that are formed in the carbon disulfide electrolysis, methyl iodide was found to react rapidly with the thiol groups on the species to form methylated compounds.

To perform an analysis, approximately 0.5 mL of the electrolysis solution was drawn into a 1-mL glass syringe via a six inch stainless steel needle. This needle was removed and a shorter needle was placed

on the syringe. Methyl iodide was drawn into the syringe until it first appeared in the barrel, the needle was withdrawn from the methyl iodide and the remainder of the methyl iodide in the needle was drawn into the barrel. The syringe was gently shaken to mix the contents and then the needle was replaced with a blunt needle which fit the Rheodyne injector. The syringe contents were then injected into the Rheodyne valve port as indicated in the HPLC directions found in the Appendix. The chromatogram was then obtained in the manner given in the Appendix.

b. HPLC Analysis of Alkylation and Purification Solutions. To monitor the products formed in an alkylation step or the amount of a desired product in a purification step of a synthesis scheme, a sample of the solution or of a dissolved solid was directly injected into the HPLC with no additional workup.

c. Chromatographic Peak Analysis. The following parameters were used in analyzing chromatograms:

(1) t_R, the retention time of the component;

(2) t_M, the retention time of a non-retained component, which is 0.5 minutes in all cases presented here;

(3) t_R', the adjusted retention time, where $t_R' = t_R - t_M$

(4) k', the sample partition ratio which is a measure of how long a substance is retained, where $k' = \frac{t_R'}{t_M}$

(5) α, the relative retention of two components where $\alpha = \frac{t_R', 2}{t_R', 1} = \frac{k'2}{k'1}$

(6) $w_{1/2}$, the peak width at half the peak height, and

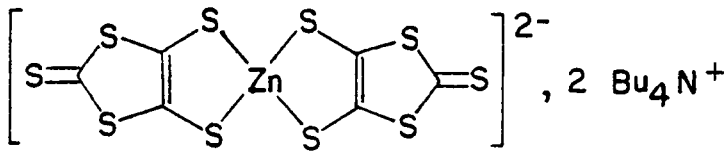
(7) N_{eff}, the effective plate number, which is a measure of the column efficiency, where $N_{eff} = 5.54 \left(\frac{t'R}{w_{1/2}}\right)^2$

D. Synthetic Procedures

1. Synthesis of Tetra-n-butylammonium bis(4,5-dimercapto-1,3-dithiolen-2-thione)-zincate(II), 12.

The Zn^{2+} complex of 4 was synthesized following the procedure employed by Steimecke.[12]

The carbon disulfide reduction solution from the main and middle compartments of the electrolysis cell was poured into a one liter flask containing 150 mL of water. A solution of 5 g of zinc chloride, 200 mL of methanol and 200 mL of ammonia was then added to the flask. The solution was cooled overnight and the red crystals which precipitated out of solution were filtered and recrystalized two times from hot methanol.



12

Compound 12 was obtained in 90% current yield, based on the formation of one mole per eight equivalents of electrons. A melting point of 174.0-174.5°C was obtained. The UV-visible spectrum showed λ_{max} = 515 nm.

The cyclic voltammetry of 12 yielded some interesting results. Figure 3 shows a series of four voltammograms of 12 in which the only experimental difference was the potential at which the sweep was reversed from the positive direction to the negative direction. The reduction peak, initially at -0.77 vs. sce, is shown to be dependent upon the switching potential. At switching potentials more positive than +0.6 V vs. sce no change in the voltammogram is noted, but at switching potentials increasingly more negative, the reduction peak potential shifts to more

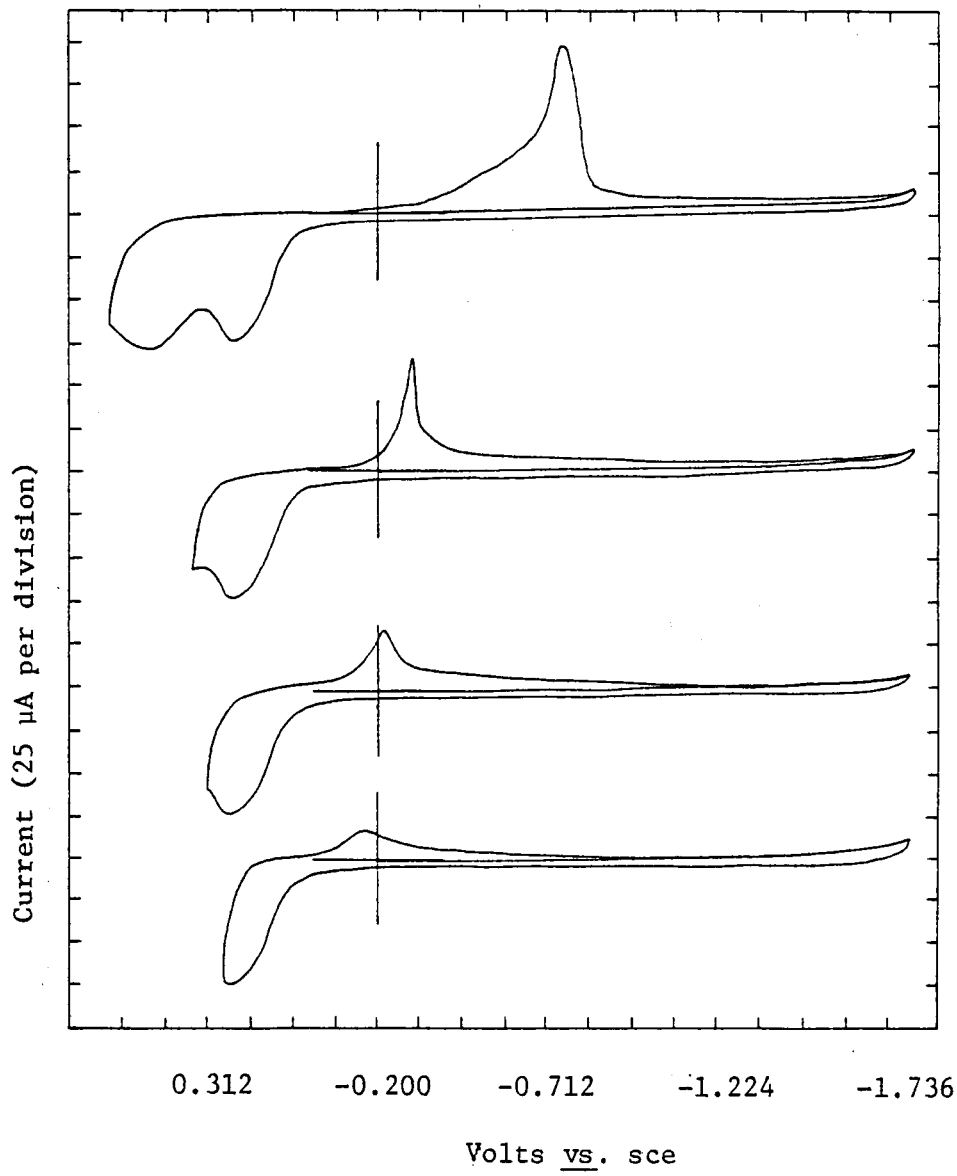


Figure 3. Cyclic voltammograms of 12, 9.8×10^{-4} M.

Conditions: 0.1M TEAP/MeCN; sweep rate 100 mV sec^{-1}; platinum.

positive potentials and the peak area decreases. At switching potentials much more negative than -0.25 V vs. sce the reduction peak is not observed.

2. Synthesis of Ethylene-4,5-dimercapto-1,3-ditholen-2-thione, 8.

Approximately 10 g of 12 was dissolved in 1-ℓ of acetone in a 2-ℓ, three-neck, round-bottom flask. The solution was refluxed under argon atmosphere. Aliquots (2 mL) of 1,2-dibromoethane were added until HPLC analysis showed that no 12 was present in the solution. The solvent was flash evaporated and the solid was extracted with diethyl ether until HPLC chromatograms showed little or no 8 present in the ether aliquots. The ether solution was dried over magnesium sulfate and then flash evaporated. The remaining dark-colored solid was sublimed to give a yellow solid which was collected and recrystalized twice from hot acetonitrile. Eight was obtained as golden flakes melting at 121.5-122.5°C (lit. 121.5-122.5°C)[10] in 73% yield.

The UV-visible spectrum showed a λ_{max} = 412 nm. The mass spectrum obtained at 70 eV consisted of the following major m/e fragments: 224 (parent$^+$, base peak), 196 ($C_3S_5^+$, loss of C_2H_4), 180 ($C_4H_4S_4^+$, loss of CS), 148 ($C_4H_4S_3^+$, loss of CS_2), 120 ($C_2S_3^+$), 88 ($C_2S_2^+$), 76 (CS_2^+).

Cyclic voltammograms, see Figure 4, show a reversible reduction wave at -1.56 V vs. sce, R1/OX1, an oxidation wave at +1.00 V vs. sce, OX3, and a large oxidation wave at +1.9 V vs. sce. The reduction peak at about 0.0 V vs. sce is probably due to the decomposition products of this oxidation. The reduction peak at -0.4 V vs. sce is associated with R1. All of the above data are in agreement with the results of Harnden.[11]

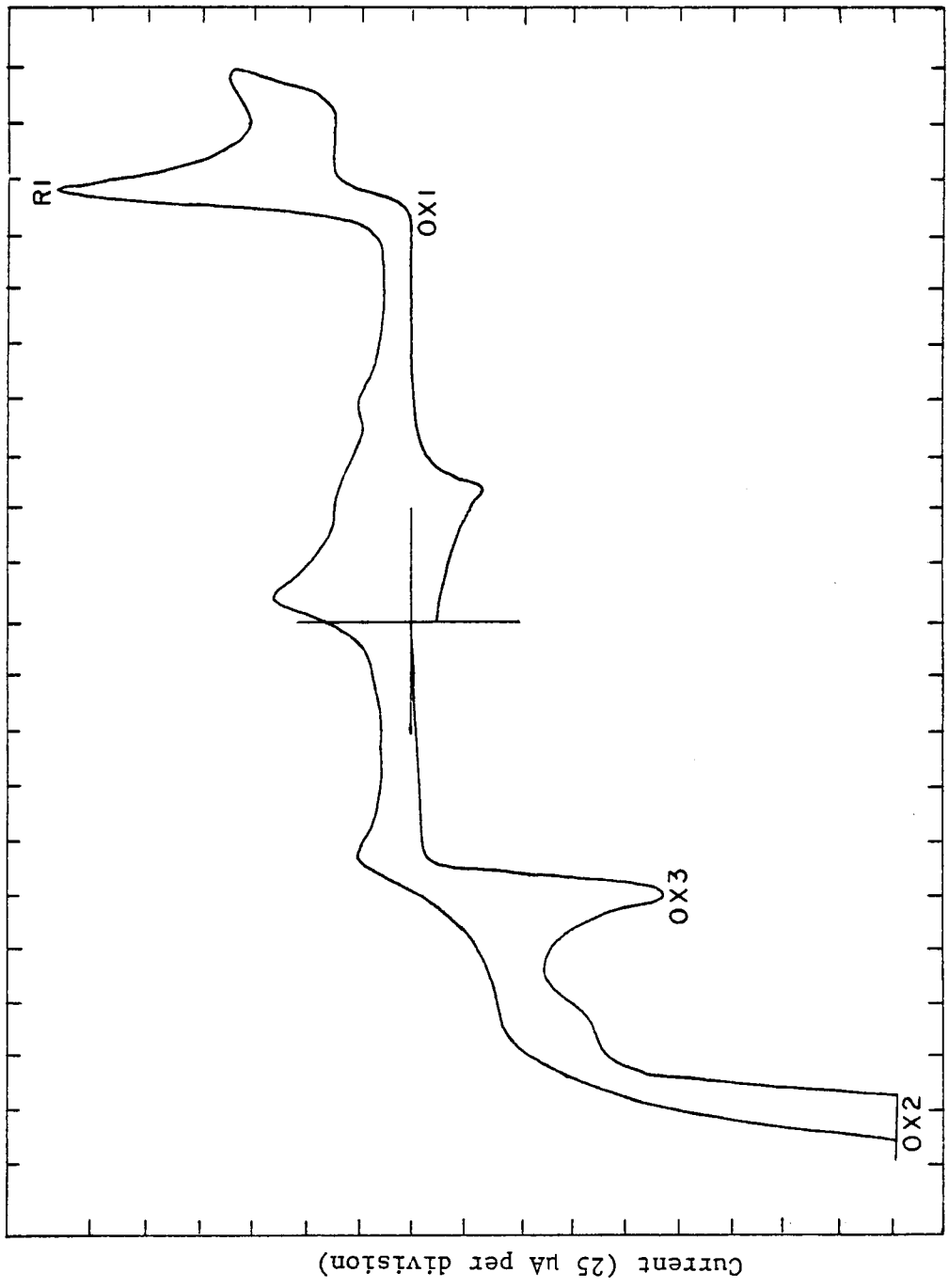


Figure 4. Cyclic voltammogram of 8, 6.9 x 10^{-4}M.

Conditions: 0.1M TEAP/MeCN; sweep rate 100 mV sec^{-1}; platinum.

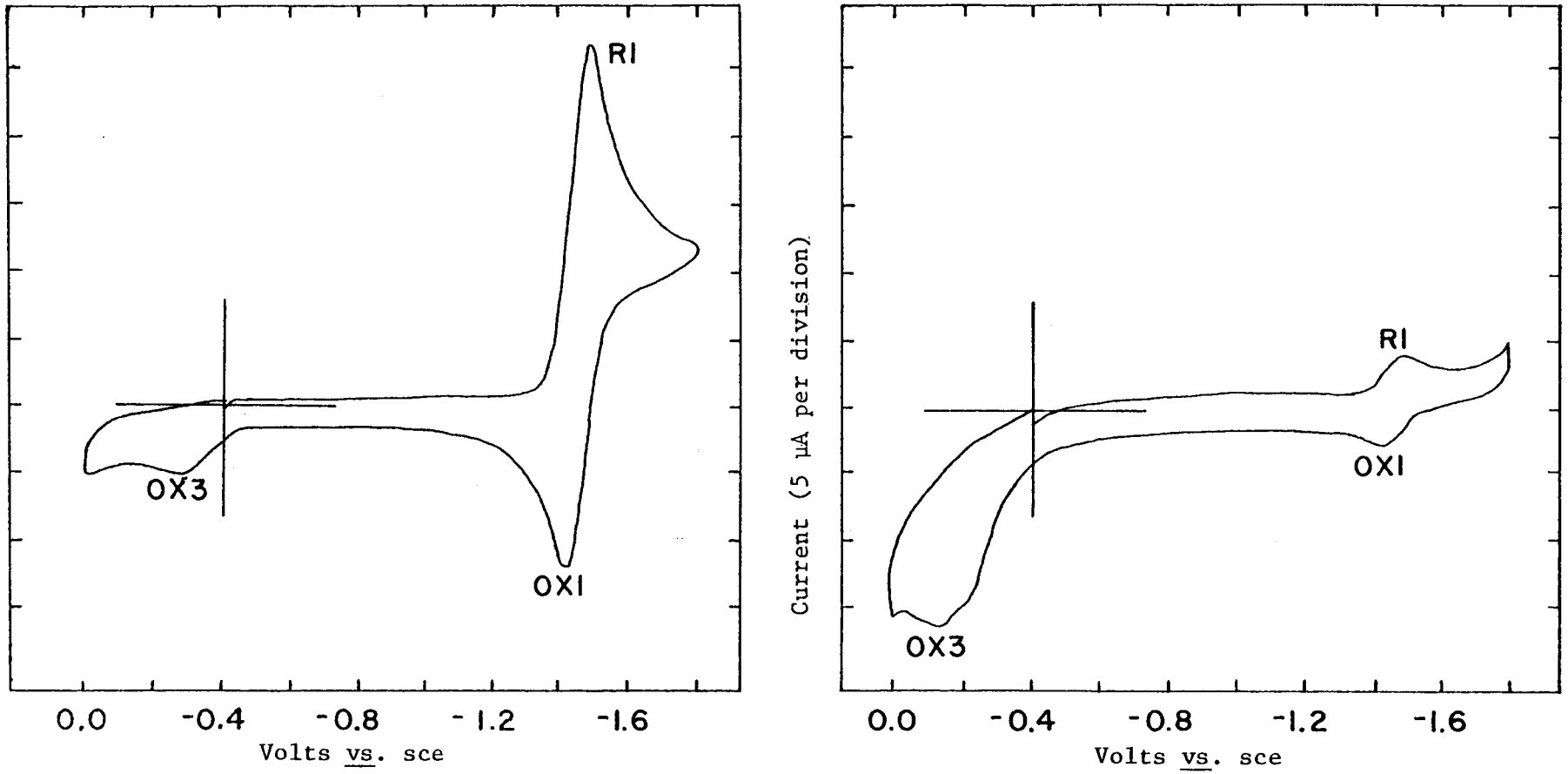
3. Attempted Reduction of Ethylene-4,5-dimercapto-1,3-dithiolen-2-thione, 8.

An electrochemical reduction of 8 was attempted in order to obtain 11. It was desired to obtain the Zn(II) complex of 11 which would then be used in the synthesis of 9.

Reductions at -1.7 V vs. sce at normal electrolysis concentrations, 100 - 300 mg of 8, resulted in an n-value of approximately 1.4, instead of the expected value of 2. However, a reduction at a very low concentration, approximately 1 mM, resulted in an n-value of 1.9, but the concentration was too low to be used for synthetic purposes.

To determine if the reduction was actually concentration dependent, a study was performed in which approximately 20 mg samples of 8 were added periodically to the electrolysis cell after the current had dropped to almost zero from the previous addition. Figure 5 shows cyclic voltammograms taken during the electrolysis. After the final addition, at which point 145 mg of 8 had been added, a reversible reduction wave at -1.06 V vs. sce, R2/OX2, appears that is not observed at lower concentrations. This does seem to indicate that there is some type of concentration dependence, but the exact effect is not known. The species responsible for the R2/OX2 couple which appears at the higher concentrations has not been identified. It is also unknown as to whether or not 11 is the product even at low concentrations.

An electrolysis at a more negative potential, -2.2 V vs. sce was attempted. After almost seven times the expected microequivalents of current had passed, the electrolysis was discontinued. An attempt to form a complex of the products was unsuccessful.

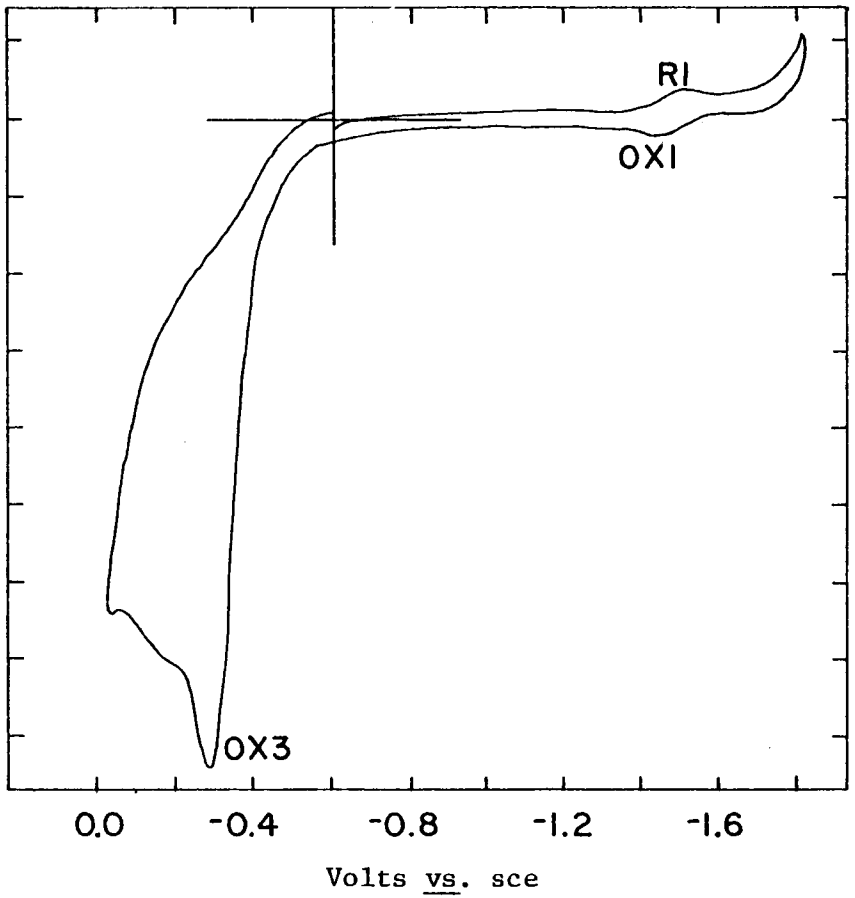


(a) 20 mg of 8, µeq current passed = 0.0

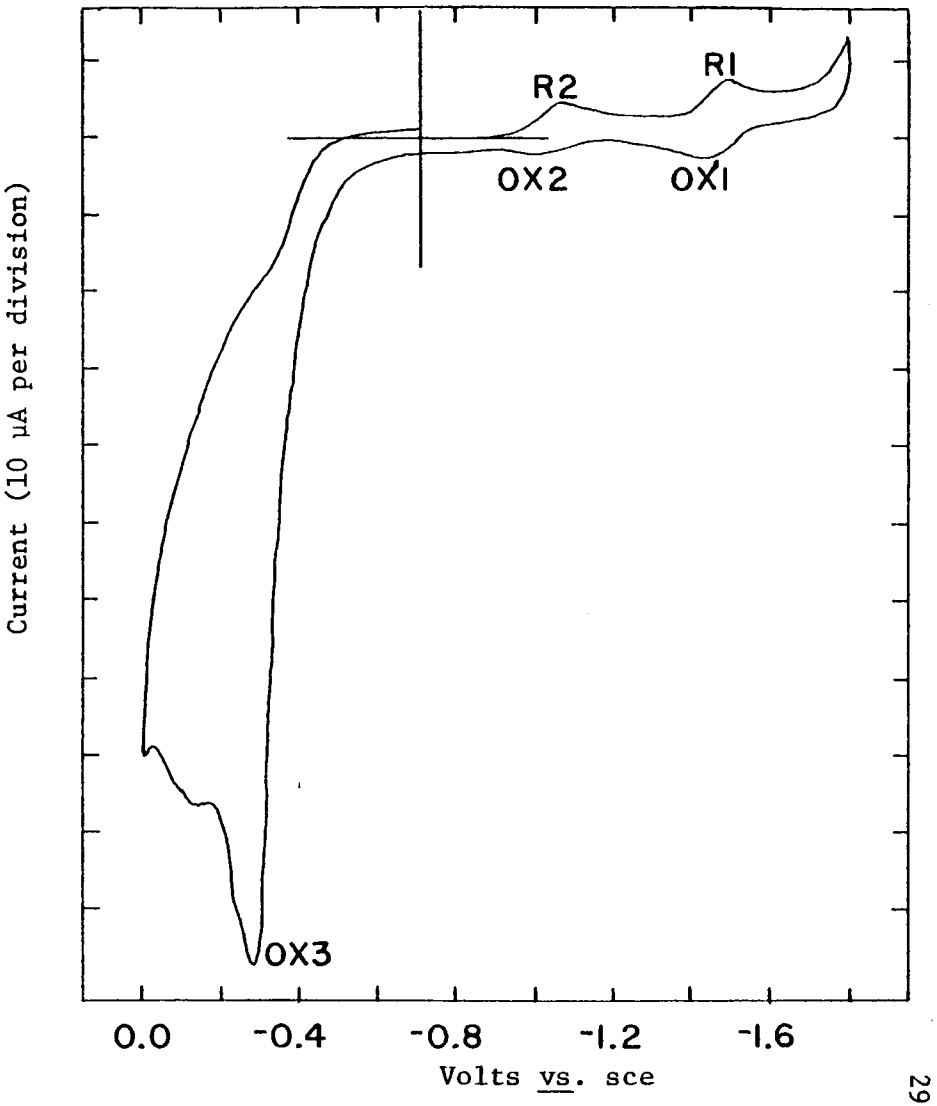
(b) 20 mg of 8, µeq current passed = 114.6

Figure 5. Cyclic voltammograms during reduction of 8.

Conditions: 0.4 M TBAI/DMF; sweep rate 100 mV sec^{-1}; platinum.



(c) 120 mg of 8, μeq current passed = 718.7



(d) 145 mg of 8, μeq current passed = 910.6

Figure 5 (continued)

4. Alkaline Hydrolysis of Ethylene-4,5-dimercapto-1,3-dithiolen-2-thione, 8

Harnden[11] had successfully synthesized 9 by refluxing 8 in alcoholic base and then adding 1,2-dibromoethane to the hydrolysis solution. Repetition of this procedure resulted in the synthesis of approximately 100 mg of 9.

After verifying that 9 could be synthesized by the alkaline hydrolysis procedure, attempts were made to synthesize 12 by this method. In all attempts, a solution of 8.4 g of potassium hydroxide in 100 mL of 95% ethanol was brought to reflux under argon. At this point 200 - 300 mg of 8 was added and the solution was allowed to reflux overnight. The following procedures were then used in attempts to synthesize a Zn^{2+} complex of 11: a) filter the precipitate formed in the hydrolysis and add it to a solution of 100 mL of methanol, 100 mL of ammonia, 2 g of zinc chloride and 5 g of TABI, b) add 2 g of zinc chloride and 5 g of TBAI to the hydrolysis solution, c) add hydrochloric acid to the hydrolysis solution until the pH is approximately 7 and then add 2 g of zinc chloride and 5 g of TBAI, d) add acetic acid until the hydrolysis solution is neutralized and then add 2 g of zinc chloride and 5 g of TBAI, e) add acetic acid until the hydrolysis solution is neutralized and then add a solution of zinc powder dissolved in acetic acid and 5 g of TBAI. In none of these attempts was there a visual indication, such as a change in solution color, that a complex had formed, nor did any precipitate ever form after cooling the solutions. Either the complex did not form under these conditions or, if it did form, it did not precipitate from the solution.

CHAPTER III

RESULTS AND DISCUSSION

1. HPLC Analysis of the Electrochemical Reduction of Carbon Disulfide

Analysis of the DMF solution containing the carbon disulfide reduction products by HPLC has lead to new information concerning this electrosynthetic process. This technique has proven to be invaluable for the qualitative analysis of the electrolysis solution, as well as for semi-quantitative analysis of the alkylation reaction solutions and purification procedures. This success is very encouraging for the expanded use of HPLC in the area of electrosynthesis.

Figure 6 shows a typical chromatogram of 1, which is one of the products obtained after addition of methyl iodide to a carbon disulfide reduction solution. Individual chromatograms, like this, of the known products and reactants present in a carbon disulfide reduction solution indicated that it should be possible to obtain a chromatogram of the reduction solution. The α-values for these components, derived from the chromatograms, indicate that satisfactory resolution of all known products and reactants should be possible. The effective plate number was not as high as might be expected, but since satisfactory resolution seemed possible, this problem was not further investigated. Furthermore, since the retention times of these compounds are all less than five minutes, the total analysis time should be less than ten minutes.

The retention times obtained from the chromatograms of the individual compounds were compared to the chromatograms run on an electrolysis solution from a carbon disulfide reduction process. The chromatographic

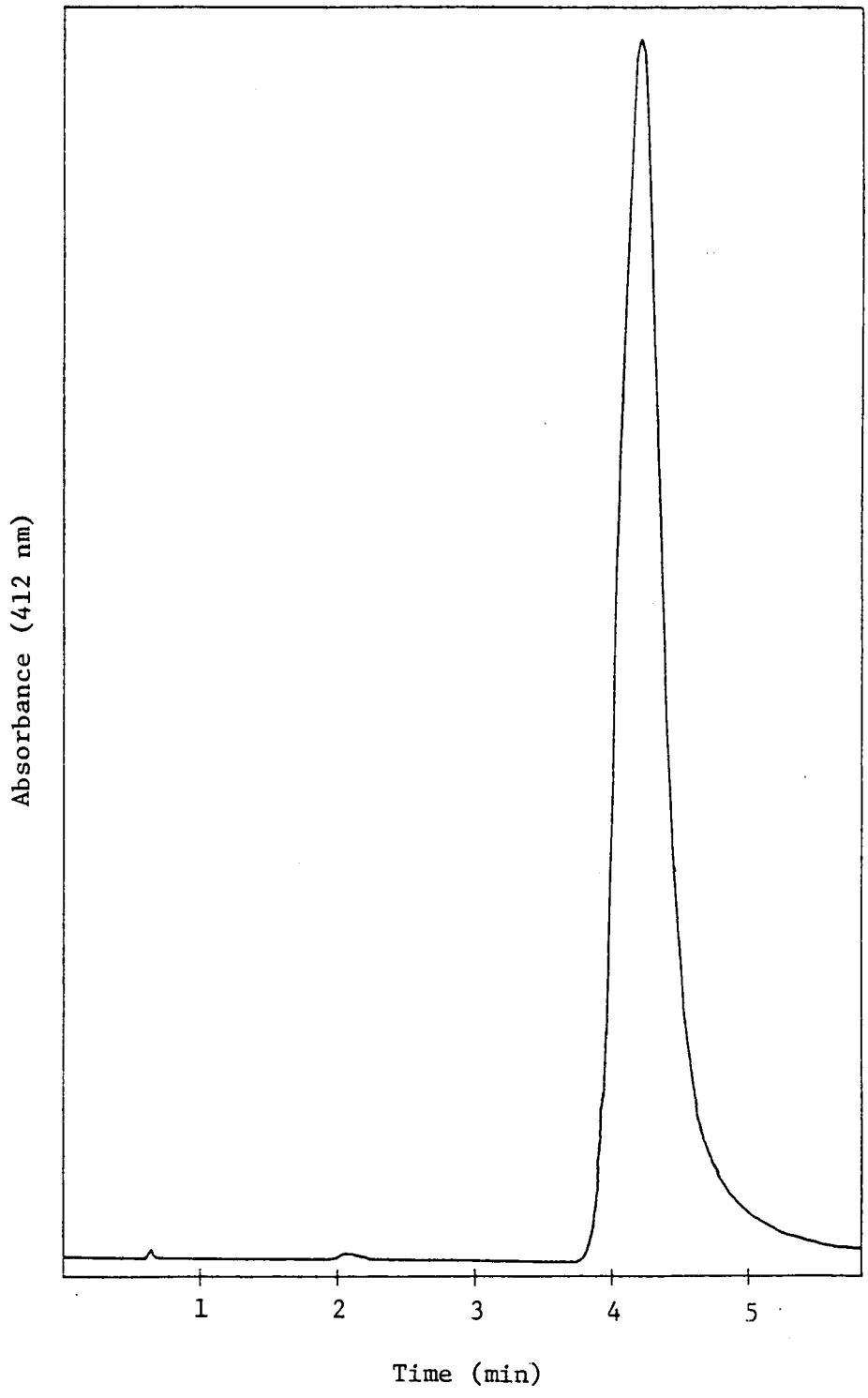
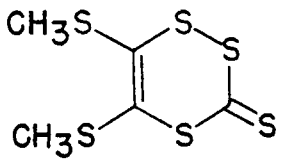


Figure 6. Chromatogram of 1, concentration unknown.

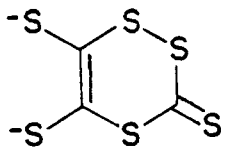
Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 Methanol/Water.

data are given in Tables I and II.

Figure 7 shows a chromatogram of an electrolysis solution at the same conditions employed in obtaining the individual chromatograms. Even then, since small changes in retention times were noted from day to day, reference standards of 1 and 3 were run each day. This chromatogram shows that there are at least six products in this electrochemical reduction of carbon disulfide. Previous work had indicated that there were only two major products, 4 and 5, and one minor product, 14. Table II summarizes the information obtained from this chromatogram. The peaks of 4 and 5, as well as those of methyl iodide, carbon disulfide and DMF have been positively identified by comparison of the retention times with the retention times obtained from the chromatograms of the individual compounds, see Table I. It is speculated that peak 9 is compound 13.



13



14

This is based on the fact that Harnden[11] showed 13 to be a product of the carbon disulfide reduction and the expectation that 13 would have a retention time greater than that of 1. The reason for expecting the retention time of 13 to be longer than the retention time of 1 is based on the close similarity of the structures of 1 and 13 and the presence of an additional sulfur atom in 13. Remaining unidentified in this chromatogram are peaks 5, 6 and 7. Peak 6 is of particular interest since it is apparently a major product which is not mentioned in the literature.

TABLE I

CHROMATOGRAPHIC DATA OF KNOWN CARBON DISULFIDE REDUCTION PRODUCTS AND REACTANTS

Compound	t_R (min)	t_R' (min)	k′	$w_{1/2}$(min)	N_{eff}	α
DMF	0.8	0.3	0.6	---	---	2.0
MeI	1.0	0.6	1.2	0.20	50	1.2
CS_2	1.2	0.7	1.4	0.1o	270	1.4
3	1.6	1.0	2.0	0.12	390	3.6
1	4.2	3.6	7.2	0.35	590	

Conditions: Flow Rate, 5.0 mL min^{-1}; Solvent, 50:50 Methanol/Water

TABLE II

CHROMATOGRAPHIC DATA OF CARBON DISULFIDE REDUCTION SOLUTION

Peak No.	t_R (min)	t_R' (min)	k'	$w_{1/2}$ (min)	N_{eff}	α	Probable Compound
1	0.8	0.3	0.6	---	---		DMF
						1.7	
2	1.0	0.5	1.0	0.05	550		MeI
						1.6	
3	1.3	0.8	1.6	0.10	360		CS_2
						1.4	
4	1.6	1.1	2.2	0.15	300		3
						1.6	
5	2.3	1.8	3.6	0.20	450		
						1.2	
6	2.9	2.1	4.2	0.25	390		
						1.5	
7	3.5	2.7	5.4	---	---		
						1.3	
8	4.1	3.6	7.2	0.35	580		1
						1.2	
9	4.8	4.3	8.6	---	---		13

Conditions: Flow Rate, 5.0 mL min^{-1}; Solvent, 50:50 Methanol/Water

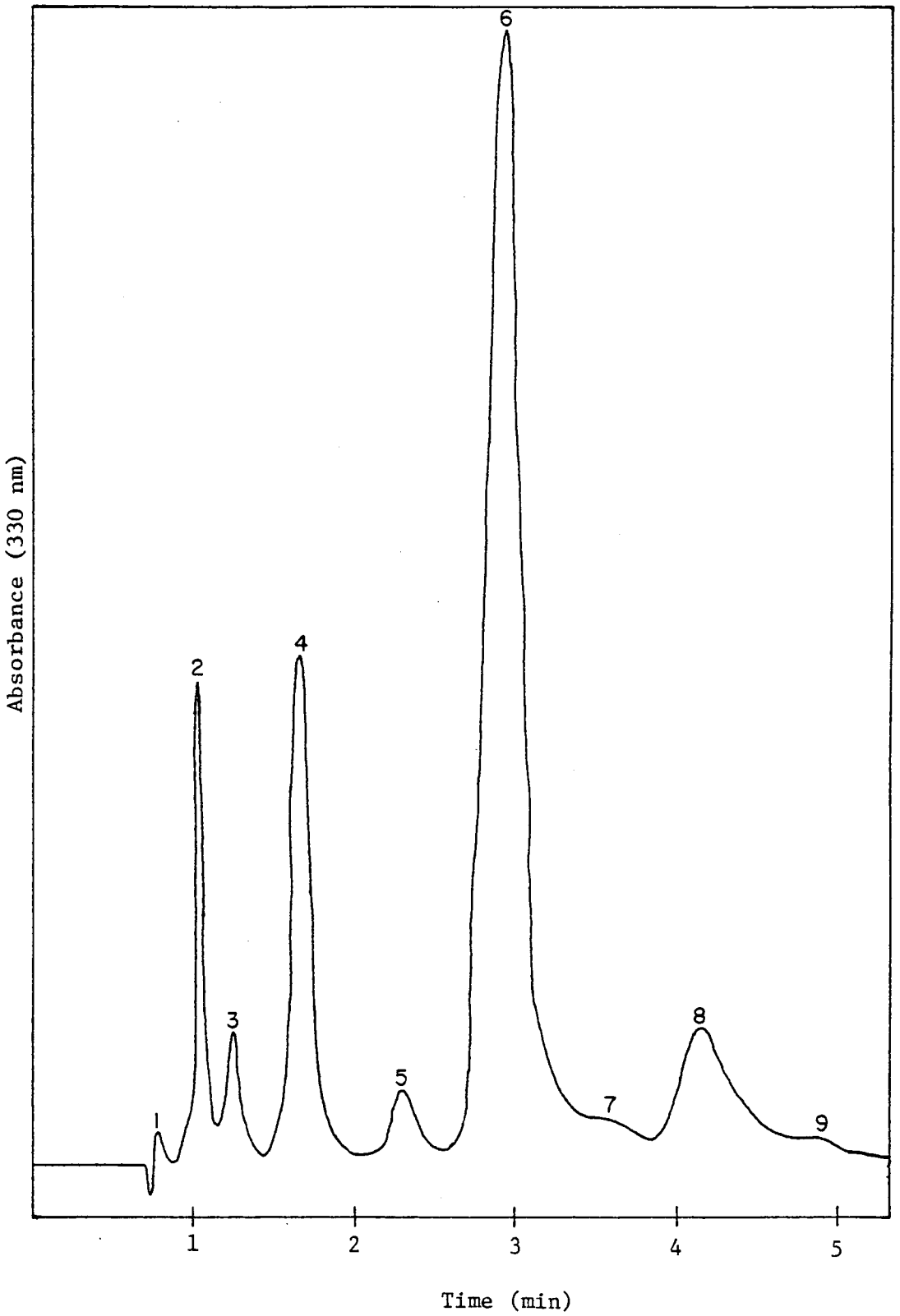


Figure 7. Chromatogram of carbon disulfide reduction solution (red). Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 methanol/water.

In an attempt to identify these peaks, chromatograms were obtained of available compounds that might be expected as products in this type of reaction. Table III lists three compounds and the pertinent data. The retention time of neither methyl disulfide or dimethyl sulfide matched those of the unknown products. Sulfur did not appear at the detector wavelength, 330 nm, employed in the chromatogram shown in Figure 7. A mass spectrum of an evaporated portion of the carbon disulfide electrolysis solution, after the addition of methyl iodide was taken in hopes of obtaining additional information about the products. The mass spectrum showed the following major m/e fragments: 226, 150, 135, 103, 91, 88, and 76. These were attributed to 1 by comparison to a mass spectrum of 1. Other major m/e fragments were 300, 285, 97, 71, 69 and 55. Minor m/e fragments appeared at 388, 368 and 332. No structure could be assigned to any of these m/e fragments.

Further work yielded an unexpected piece of data about peak 6 in Figure 7. Figure 8 shows a chromatogram of the same solution as in Figure 7 after it had set in a closed flask for four days. Peak 6 of Figure 7 was no longer observed and the peak attributed to 3 and unknown peak 5 had increased in area. It was concluded that the product, peak 6, was unstable and had decomposed to give 3 and the unknown product, peak 5, as decomposition products.

Additional information was obtained by variation of the detector wavelength. This feature of the instrument was not exploited to its fullest, but it appears that the product has a maximum absorbance in the vicinity of 330 nm. This is illustrated in Figures 7 and 9. These are chromatograms of the same solution with the detector set at 330 nm

TABLE III

CHROMATOGRAPHIC DATA OF POSSIBLE CARBON DISULFIDE REDUCTION PRODUCTS

Compound	t_R (min)	t_R' (min)	k′	$w_{1/2}$ (min)	N_{eff}
Methyl disulfide	2.1	1.6	3.2	0.15	630
Dimethyl sulfide	1.2	0.7	1.4	0.075	480
Sulfur	Does Not Appear at 330 nm				

Conditions: Flow Rate, 5.0 mL min^{-1}; Solvent, 50:50 Methanol/Water

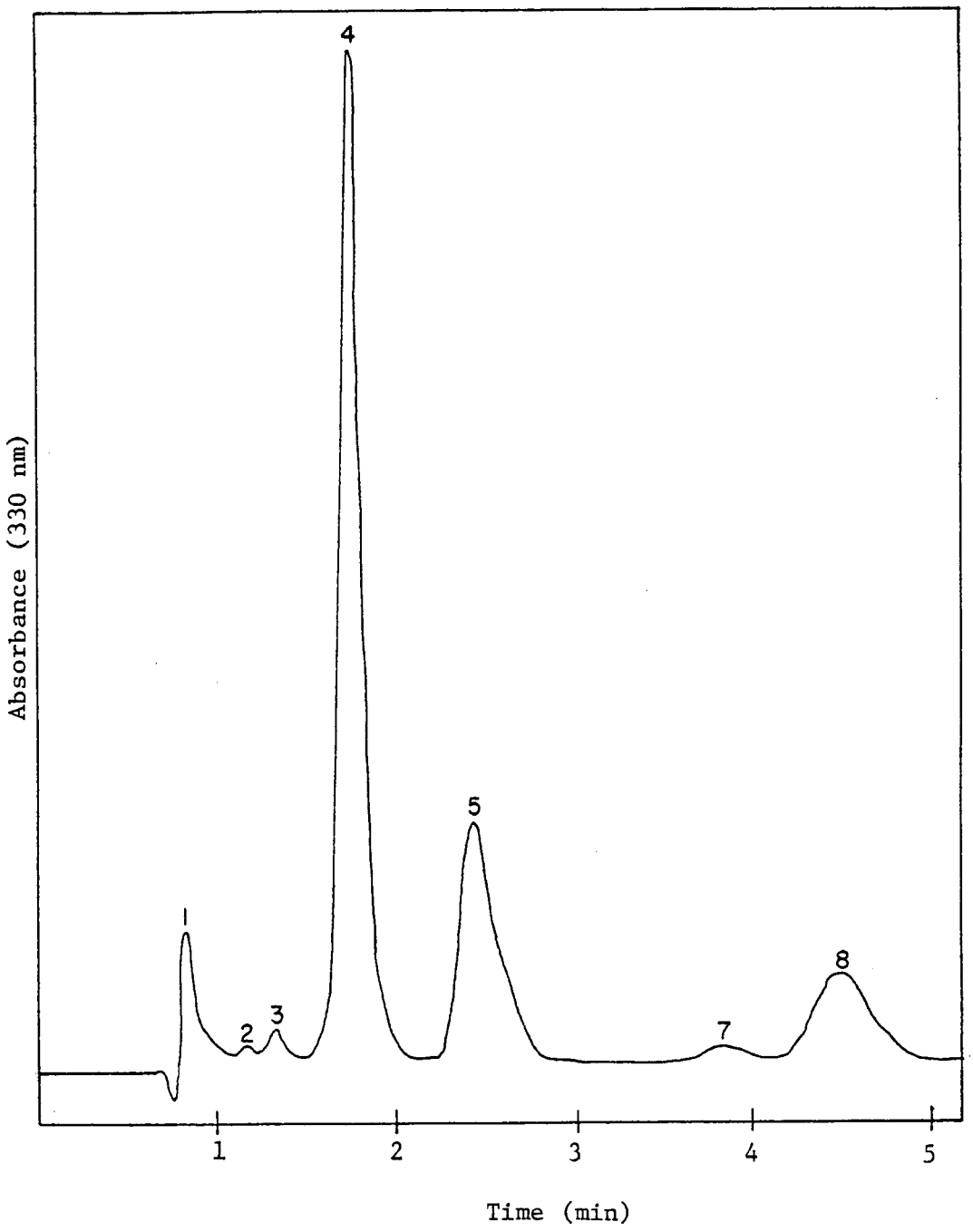


Figure 8. Chromatogram of carbon disulfide reduction solution, 4 days old. Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 methanol/water.

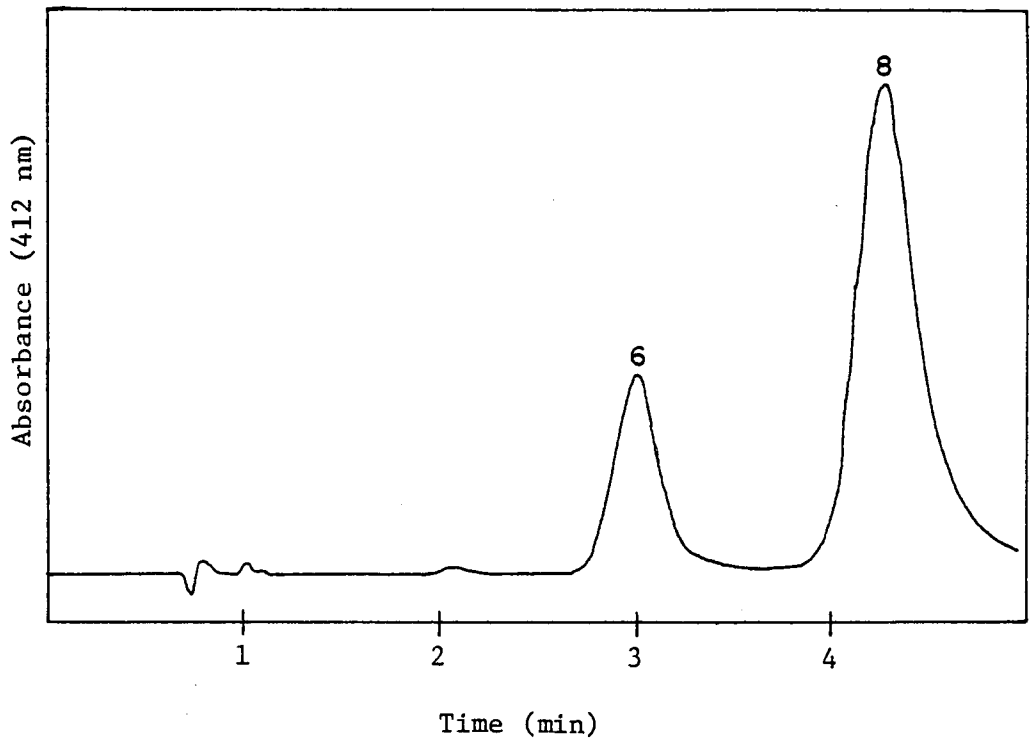
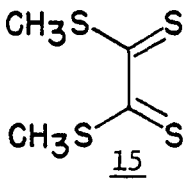


Figure 9. Chromatogram of carbon disulfide reduction solution.

Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 methanol/water.

in Figure 7 and at 412 nm in Figure 9. As can be seen in these chromatograms, most of the components observed when the detector is set at 330 nm have little or no absorbance at 412 nm and do not appear in the chromatogram of Figure 9. The peak corresponding to compound 1, however, is enhanced in this chromatogram since it has an absorbance maximum at 412 nm.

Based on the above information, it is speculated that the product may be a species similar to 15, which has a λ_{max} of 362 nm in benzene[24]



15

and would probably have a retention time between 3 and 1, based on size and structure comparisons. However, no logical decomposition reaction with 3 as a product can be proposed.

A second aspect of the carbon disulfide reduction analysis concerns the change in color of the reduction solution from red to green to blue that was observed by Hurley.[13] This occurs when the electrolysis is continued without additional carbon disulfide being added. HPLC analysis was used in this study to investigate the possibility of the formation of new products or a change in the relative concentrations of the existing products.

Figure 7 shows a chromatogram obtained while the electrolysis solution was still in the red phase. Figure 10 shows a chromatogram obtained on the same solution after it had turned to a greenish-blue color. The same products appear in both chromatograms. The relative concentrations of the products appear to have changed slightly, but the change is so small that no conclusions

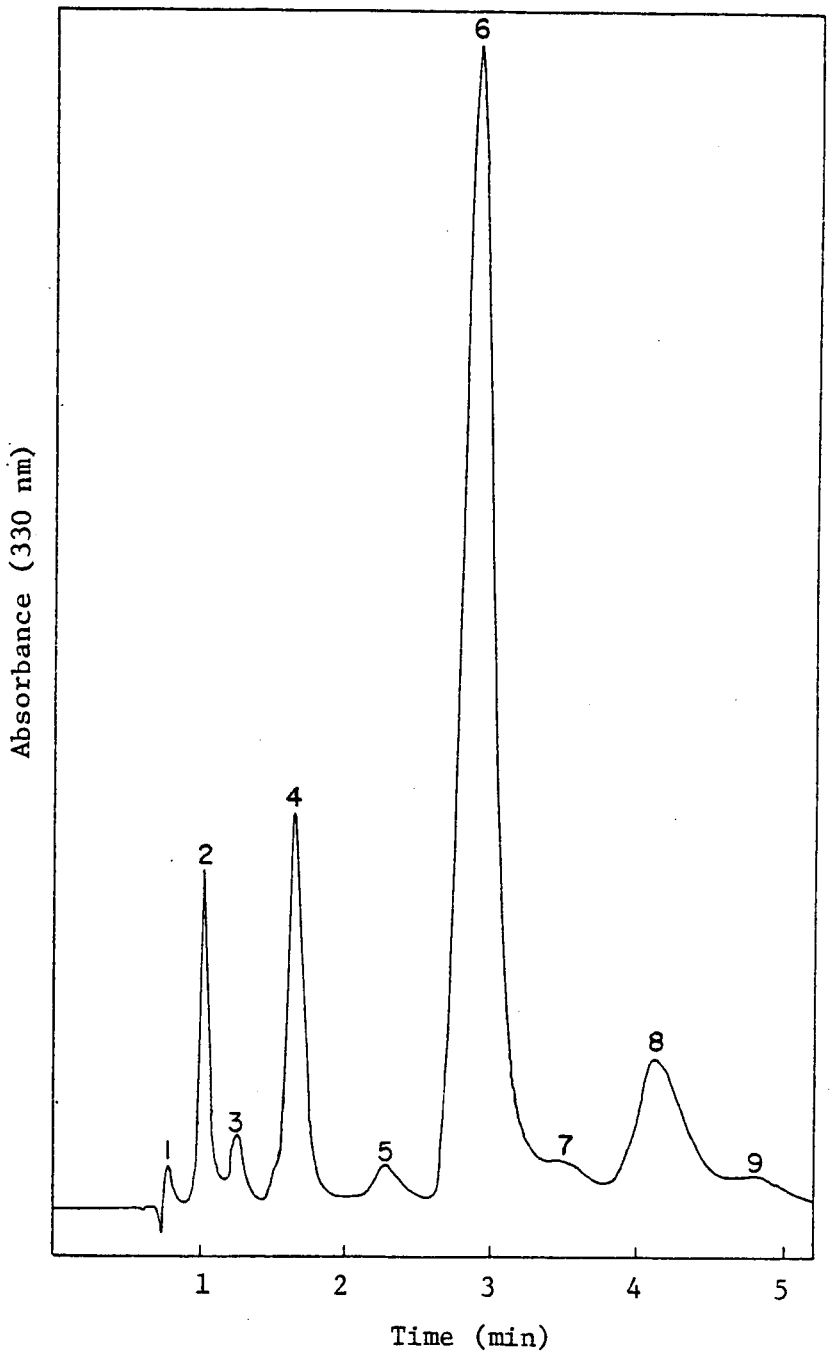


Figure 10. Chromatogram of carbon disulfide reduction solution (green). Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 methanol/water.

can be drawn from the data. In the green solution it appears that the concentrations of 1 and of the unknown product, peak 6, have increased slightly while the concentrations of 3 and the unknown product, peak 5, have decreased slightly. Additional chromatograms of red and green solutions yielded the same results.

A time dependence study was performed in which chromatograms were taken periodically as the electrolysis proceeded. No time dependence of the formation of the different products was found. The products observed in these chromatograms were the same as the products observed in Figures 7 and 10. The only difference in the chromatograms was the change in peak areas as the concentration of the products increased as the electrolysis proceeded.

One explanation for this behavior could be that the electrolysis product which is responsible for the blue-green color change does not give a detectable alkylation product using the HPLC detector. The species may not have any absorbance at either wavelength employed in this experiment and, therefore not be detected.

The more likely explanation is the one espoused by Hurley.[13] He suggested that a species is formed between an existing product and carbon disulfide and that upon alkylation, the bonding is broken and the original product and carbon disulfide are observed. In this hypothesis, the red color would be assigned to a partially reduced CS_2 species which loses CS_2 and forms 1 and 3 upon alkylation with methyl iodide.

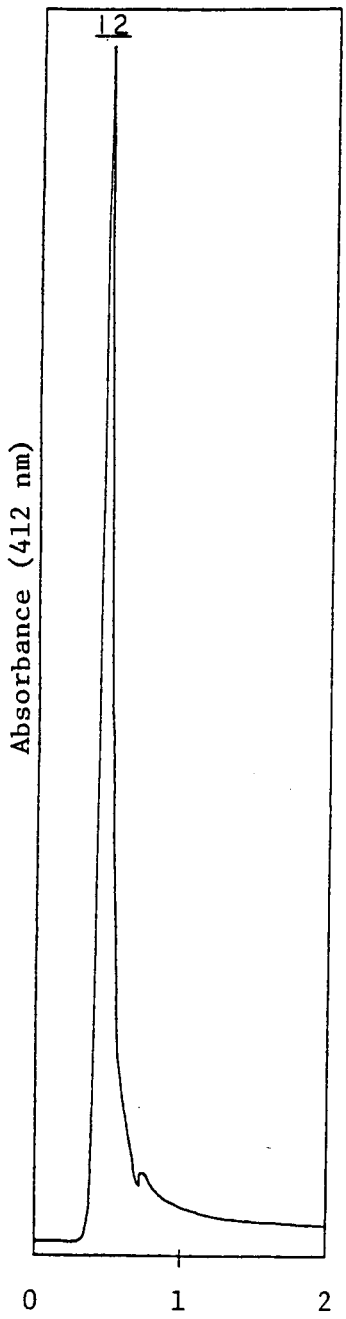
2. Results of the Zinc(II) Complex Reaction

The Zn^{2+} complex of 4 was used in synthesis work with excellent results. Addition of the alkylating agent results in the formation of 8.

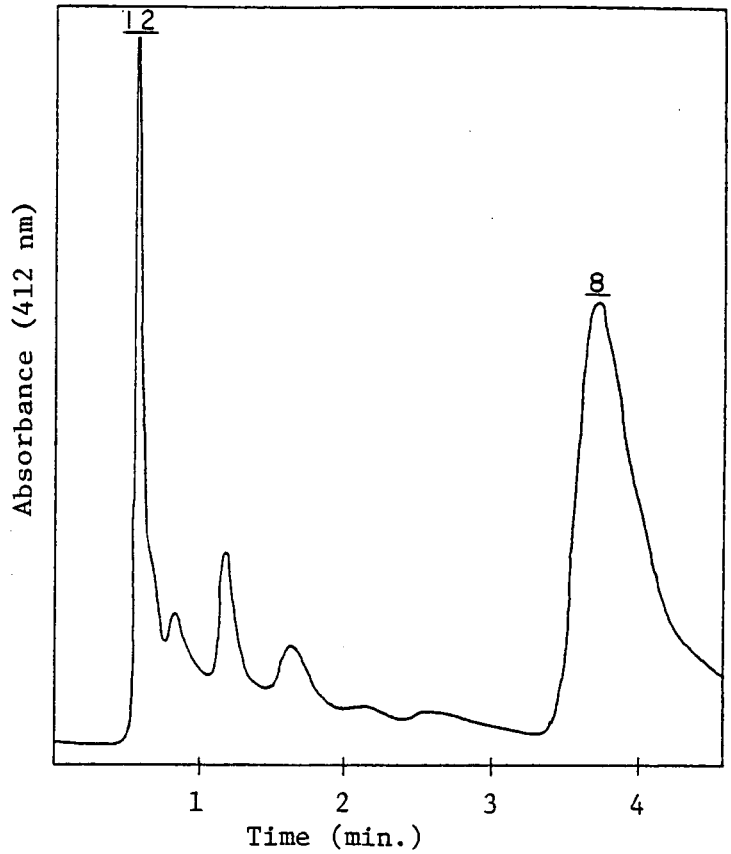
This procedure is much easier than the method used by Harnden and is less time consuming. No column chromatography work-up was needed, which allowed for the rapid work-up of much larger quantities than Harnden was able to obtain. Using this procedure, several grams of 8 could be synthesized at one time as compared to the gram qualities and less by Harnden. The overall percentage yield of this procedure was also better. The percentage yield, based on current passed in the electrolysis, of 8 through the zinc complex procedure was as high as 65% compared to 30% by alkylation of the reduction solution.

HPLC analysis was used in this work to monitor the alkylation of the Zn complex. The chromatograms showed the degree of alkylation which signaled the completion of the alkylation process. Figure 11 shows typical chromatograms from this work. The zinc complex, though not retained, appears on the chromatogram as well as the product, 8. Using this information, it was found that an alkylation could be finished in a few hours by refluxing the solution with a large excess of alkylating agent rather than overnight as had been done in the past. The chromatograms also indicated the presence or absence of impurities in the solution.

HPLC also proved invaluable in monitoring the purification of 8. The step involving an ether extraction was monitored periodically by HPLC and was continued until the ether solution showed little or no presence of 8. At this point it was concluded that all of 8 had been extracted.



(a) before addition of 1,2-dibromoethane



(b) after addition of 1,2-dibromoethane

Figure 11. Chromatograms of 12.

Conditions: Flow rate, 5.0 mL min^{-1}; solvent, 50:50 Methanol/Water

LIST OF REFERENCES

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1. D. T. Day, Proc. Am. Phil Soc., 36, 112 (1897).

2. D. T. Day, Science, 17, 1007 (1903).

3. M. Tswett, Proc. Warsaw Soc. Nat. Sci., Biol. Sect., 14, No. 6 (1903), from N. A. Parris, "Instrumental Liquid Chromatography," Elsevier Scientific Pub. Co., New York, 1976, p. 4.

4. A. J. P. Martin and R. L. M. Synge, Biochem. J., 35, 1358 (1941).

5. F. K. Huber, J. Chromatogr. Sci., 7, 85 (1969).

6. J. J. Kirkland, J. Chromatogr. Sci., 7, 7 (1969).

7. C. G. Horvath, B. A. Preiss, and S. R. Lipsky, Anal. Chem., 39, 1422 (1967).

8. N. A. Parris, "Instrumental Liquid Chromatography," Elsevier Scientific Pub. Co., New York, 1976, p. 4.

9. L. Syper and A. Sucharda-Sobezyk, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 23, 563 (1975).

10. M. Mizuno, M. P. Cava, and A. F. Garito, J. Org. Chem., 41, 1481 (1976).

11. R. M. Harnden, Master Thesis, Univ. of Tenn., Knoxville, Tennessee, 1976.

12. G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, Phosphorus and Sulfur, 7, 49 (1979).

13. M. F. Hurley, Doctoral Dissertation, Univ. of Tenn., Knoxville, Tennessee, 1980.

14. B. Fetkenheuer, H. Fetkenheuer, and H. Lecus, Ber. 60B, 2528 (1927).

15. S. Wawzonek and S. M. Heilman, J. Org. Chem., 39, 511 (1974).

16. G. Steimecke, R. Kirmse, and E. Hoyer, Z. Chem., 15, 28 (1975).

17. G. Bontempelli, F. Magno, G. Mazzochia, and R. Seeber, J. Electroanal. Chem., 63, 231 (1975).

18. U. Reuter and G. Gattow, Z. Anorg. Allgem. Chem., 421, 143 (1976).

19. P. Jeroschewski, Z. Chem., 18, 27 (1978).

20. P. R. Moses, Doctoral Dissertation, Univ. of Tenn., Knoxville, Tennessee, 1974.

21. F. J. Goodman, Master Thesis, Univ. of Tenn., Knoxville, Tennessee, 1975.

22. R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, 1969, p. 288.

23. L. R. Faulkner and A. J. Bard, J. Amer. Chem. Soc., 90, 6284 (1968).

24. T. Kissel, R. Matusch, and K. Hortke, Z. Chem., 16, 318 (1976).

APPENDIX

APPENDIX

OPERATION OF THE LABORATORY DATA CONTROL HIGH PERFORMANCE LIQUID CHROMATOGRAPH

A. Preliminary

The solvent reserviors should be filled as follows:

1. Reservoir A is filled with water which has been distilled twice and filtered through a 4.5 μ Millipore filter; and

2. Reservoir B is filled with HPLC grade methanol.

B. Warmup

These procedures should be performed at least thirty minutes prior to use:

1. Turn the heaters on the solvent reservoirs to LO and turn the stirrers on. If the instrument is used frequently the heaters and stirrers can be left on.

2. Turn the Gradient Master power on.

3. Simultaneously turn the Constametric I and Constatmetric II power on.

4. Set the Run/Standby switch on the Constametric II to Standby.

5. Select the wavelength and the corresponding lamp on the Spectro-Monitor II.

6. Turn the SpectroMonitor II power on and, if the UV2 lamp is to be used, turn the Start/Run switch to start. Press the start button and hold until the energy meter shows a sudden increase in energy. Turn the Start/Run switch to Run.

7. Turn the recorder power on by turning the chart speed dial to the desired chart speed, usually one inch per minute.

C. Operation

1. Set the pump conditions on the Gradient Master.

   a. For Isocratic Operation

      (1) Run/Hold button to Hold

      (2) Start %B to the desired solvent mixture

      (3) Select the flow rate

      (4) Run/Standby button on the Constametric II to Run

   b. For Gradient Operation

      (1) Set Start %B and Final %B

      (2) Select exponent by referring to the diagram on top of the Gradient Master

      (3) Select the gradient time and multiplier

      (4) Set Auto Repeat to On or Off

      (5) Select the flow rate

      (6) Run/Stanby button on the Constametric II to Run

      (7) Run/Hold button to Run

      (8) To start the gradient, push the Reset/Start button.

2. Set the SpectroMonitor II range to S and adjust the recorder pen to the zero position with the recorder zero adjust knob.

3. With solvent flowing, set the spectroMonitor II range to the desired sensitivity and adjust the recorder pen to the zero position using the SpectroMonitor II zero adjust knob.

4. Draw a sample into a syringe. For a 20 µℓ sample loop, a 100 µℓ sample is desirable. If a sharp needle was used in drawing the sample,

replace it with a No. 20 blunt needle.

5. Injection

   a. Turn the injector counter-clockwise to the Load position.

   b. Gently insert the needle into the injector until it contacts the back of the injector port. Slowly inject the sample into the injector port.

   c. Leave the syringe or at least the needle in the injector port.

   d. Turn the recorder toggle switch to On.

   e. When the pen has reached a heavy line, simultaneously turn the injector clockwise to the inject position and momentarily press the mark button on the SpectroMonitor II. The injector must be turned very rapidly in this step.

   f. Flush the injection port with solvent in the Inject position and then in the load position. The system is now ready for a new sample injection.

   g. If another injection is not to be made immediately, turn the recorder chart feed off and stop the solvent flow by turning the Run/Standby switch on the Constametric II to Standby.

D. Shut-down

1. Thoroughly flush the injector in both positions.

2. Allow enough solvent to flow through the system to wash any sample material into the waste container.

3. Set the Run/Standby switch on the Constametric II to Standby.

4. Turn the recorder off.

5. Turn the SpectroMonitor II to S and then turn the power off.

6. Simultaneously turn the Constametric I and Constametric II off.

7. Turn the Gradient Master Off.

8. Turn the solvent heaters and stirrers off.

E. Trouble Shooting

If the recorder pen is very erratic and/or if the pressure varies more than ±10 psi, then air is probably trapped in the system.

1. Turn %B to 100% methanol and then slowly turn the flow rate to the maximum that the instrument will allow. After approximately one minute, reduce the flow and %B to the normal settings.

2. If the problem still exists, loosen and bleed each solvent line connection, beginning at the inlet of each pump.

VITA

Joseph Carl Lodmell was born on June 12, 1955 in the city of Beckley, located in the mountains of southern West Virginia. He was raised in nearby Piney View, where he remained until after graduation from high school.

In the fall of 1973 he entered Concord College in Athens, West Virginia. He spent the next four years earning a Bachelor of Science degree in Chemistry, which was awarded to him in June of 1977.

He came to the University of Tennessee in September of 1977 to begin work on a Ph.D. in Chemistry. Plans changed during the summer of 1979, at which time he changed to a Master of Science program. Following a concentrated research effort during the last of 1979 and the beginning of 1980, he was awarded the Master of Science degree in the spring of 1980.

On August 24, 1979, Mr. Lodmell enlisted in the United States Navy as a nuclear propulsion officer candidate. In June of 1980, he will go to Newport, Rhode Island where he will spend four months in Naval Officer Candidate School.