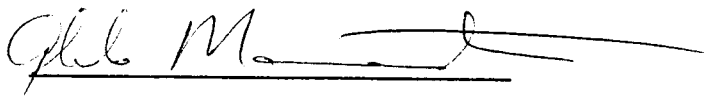


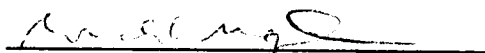
To the Graduate Council:

I am submitting herewith a dissertation written by William C. Anderson entitled "The Electrochemical Characterization of CS_2 Reduction Products and Intermediates, and Related Sulfur Containing Compounds." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


James Q. Chambers, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:


Vice Provost
and Dean of The Graduate School

THE ELECTROCHEMICAL CHARACTERIZATION
OF CS₂ REDUCTION PRODUCTS AND INTERMEDIATES,
AND RELATED SULFUR CONTAINING COMPOUNDS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

William C. Anderson

June 1988

ACKNOWLEDGEMENTS

This work is dedicated, with love and appreciation, to my wife, Shannon. Without her sacrifice and support, this dissertation would not have been written.

I would also like to thank, with love, my parents, "Red" and Frances Anderson for the support and encouragement they have given me throughout my educational career.

Special thanks are extended to my friend and advisor, Dr. James Q. Chambers, who has given freely of his knowledge, experience and patience throughout the course of my work. For all of his help and guidance, I am grateful.

I would also like to thank my friends in the glassblowing shop, L. H. Norman and Art Pratt. Your contributions as glassblowers and philosophers are greatly appreciated.

Finally, appreciation is extended to the University of Tennessee and the National Science Foundation for financial support during my work at UT.

ABSTRACT

The electrochemical reduction of carbon disulfide in DMF was studied using HPLC and mass spectral techniques. Trithiocarbonate was shown not to be formed initially in the electrode processes. Instead, the dimer of carbon disulfide, tetrathiooxalate, forms initially as an intermediate, but slowly decomposes to form trithiocarbonate, and other species. The principal product of interest from this reduction, 4,5-dimercapto-1,3-dithiole-2-thione, was not formed directly from the intermediate decomposition. Mass spectra of carbon disulfide reduction solutions display a complex pattern of fragment ions representative of the variety of products derived from this reduction. Formation of some high molecular weight carbon-sulfur compounds is indicated by the pattern.

The electrochemical behavior of 4,5-bis(methylthio)-1,3-dithiole-2-one was also studied. Oxidation of this compound gave the radical cation which disproportionated to the dication and the starting compound. Further reaction with residual water led to sulfoxide formation.

The principal product from the photolysis of the 1,3-dithiole-2-one was dimethyltetrathiooxalate. Electrochemical reduction of this product to the dianion gave tetramethylthioethylene after methylation. The crude photolysis product was shown by mass spectroscopy to contain minor amounts of high molecular weight species similar to those observed earlier in the carbon disulfide reduction solutions. Several unsuccessful experiments in which the isolation of these species was

attempted using standard chromatography methods and electrocrystallization are also described.

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CHAPTER I

INTRODUCTION

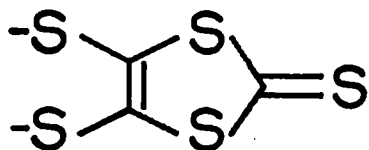
The research described in this dissertation concerns the electrochemical characterization of novel sulfur-containing molecules. The understanding of reaction mechanisms can often lead to broader utilization of a molecule for synthetic purposes. Investigations into the electrochemical behavior of carbon disulfide, and related sulfur-containing adducts were undertaken in hopes of extending the synthetic utility of these systems. An introductory literature survey covering the reduction of carbon disulfide and the pertinent organic electrochemistry of sulfur-containing molecules related to the 1,3-dithiole system will put this work in perspective.

A. The Reduction of Carbon Disulfide

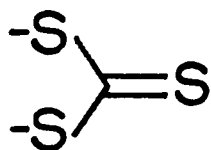
Electroorganic chemistry has frequently been a useful tool for obtaining compounds which would otherwise be difficult to synthesize by ordinary chemical means. In some cases electrochemical methods allow the chemist to survey redox properties of a substrate on a small scale that requires little time. Subsequently, chemical reductants or oxidants may prove to be more convenient for the synthesis of larger amounts of product. The reduction of carbon disulfide is an example of such a system. In this system, from a relatively simple triatomic molecule, several more complex molecules have been obtained, some of which subsequently have been synthesized chemically. Investigators have

pursued this work vigorously over the past fourteen years, attempting to elucidate the reduction mechanism. Different intermediates have been proposed along the way, and as new evidence has become available, the recognized mechanism has taken on different versions to account for the new findings. The presently accepted scheme has a number of contributors. A survey of this scheme's evolution is presented.

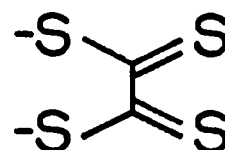
Carbon disulfide was initially reduced by alkali metals,¹⁻⁴ although the products were not identified correctly until later work using electrochemical means.⁵⁻¹⁰ The principal products are 4,5-dimercapto-1,3-dithiole-2-thione, 1, trithiocarbonate, 2, and



1

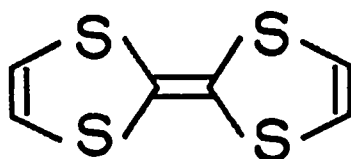


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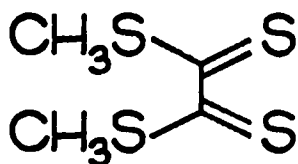
product distribution that depends markedly on conditions. Compound 1 has been used as a precursor for the synthesis of some chemically important molecules^{5,11} including tetrathiofulvalene (TTF, 4) derivatives.¹²⁻¹⁴



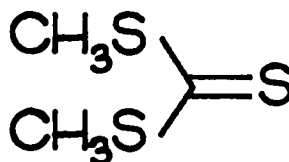
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1. Products

The only report of CS₂ reduction prior to 1974 which proves pertinent to this work came from Fetkenheuer et al. in 1927.¹ Liquid CS₂ was reduced using a sodium amalgam. A dark red solution ensued, which upon alkylation with CH₃I and addition of chloroform, afforded a brown precipitate reported to be dimethyltetrathiooxalate (5). Dimethyltrithiocarbonate, (6), and some higher molecular weight sulfur analogues were isolated as well when diethyl ether was used to extract the reaction mixture.

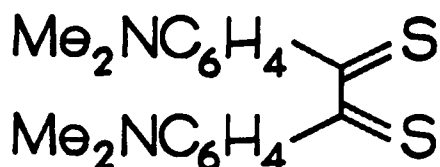


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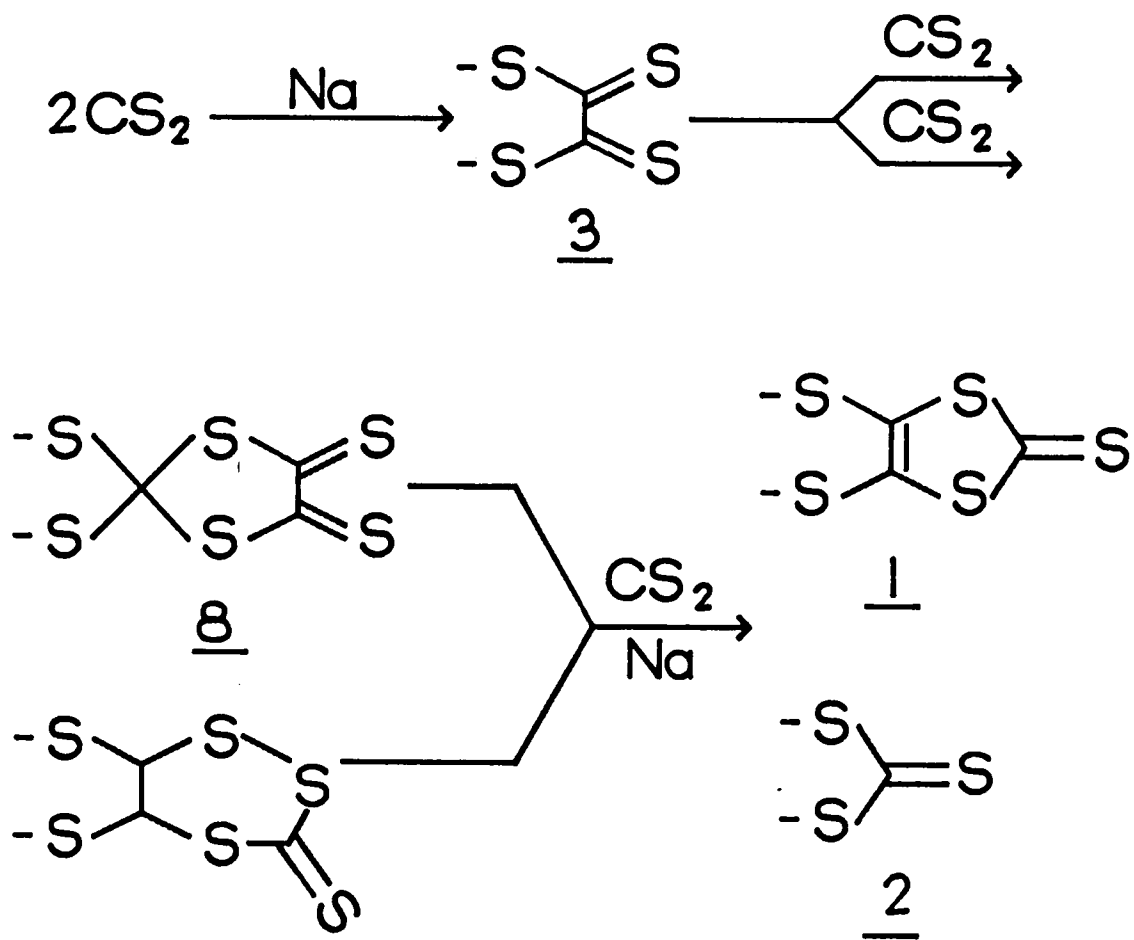
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It turns out that the identification of dimethyltetrathiooxalate was incorrectly assigned as shown by Wawzonek and Heilmann⁵ some fifty years later. It should be pointed out that dimethyltetrathiooxalate (5) was not only incorrectly identified in 1927, but was not successfully isolated until 1976.¹¹ It was only the second α-dithione to be reported in the chemical literature:^{11,15} the first was 4-4'-bis(dimethylamino)dithiobenzil, 7 synthesized by Kusters and de Mayo in 1974.¹⁵ The α-dithione system has been shown to be very reactive and at times elusive depending on the particular adduct being sought.^{11,15,16} It seems probable that Fetkenheuer isolated 2, and not 3, based on the reported melting point.



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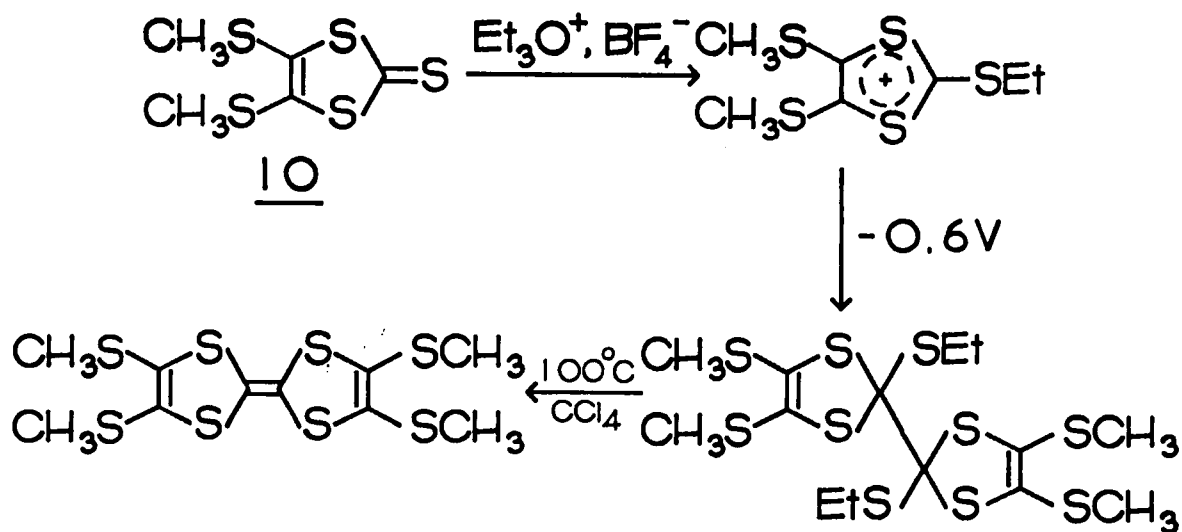
It was not until 1975 that another paper appeared addressing the alkali metal reduction of CS_2 . Steimecke et al. reduced a solution of CS_2 in N,N'-dimethylformamide (DMF) with sodium and potassium metals,^{3,4} while Reuter and Gattow were doing the same in tetrahydrofuran (THF) and liquid ammonia.² Both of these research groups reported the formation of the cyclic dianion 1, and trithiocarbonate 2. In each case, dianion 1 was found to be the major product based on isolation of the alkylated products after addition of CH_3Cl or CH_3I . The alkylated derivative of tetrathiooxalate (5) was not reported. Steimecke and coworkers³ proposed a mechanism for the formation of dianion 1 via an intermediate tetrathiooxalate dianion. Compound 1 and trithiocarbonate were accounted for by the reaction of CS_2 with tetrathiooxalate to form a cyclic dianion intermediate (Scheme 1). This intermediate was proposed to react further with CS_2 in the presence of sodium to give 1 and 2. The intermediates were not isolated, thus precluding their positive identification. Meanwhile, the reduction of CS_2 was simultaneously being investigated electrochemically by a couple of research groups. Polarographic experiments carried out by Wawzonek and Heilmann⁵ in DMF showed two one-electron reductions while Bontempelli et al.⁷ observed only one



SCHEME 1

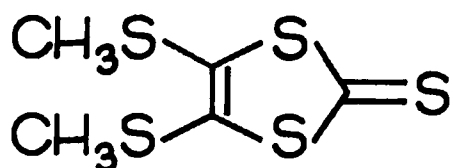
irreversible reduction wave at a platinum working electrode in acetonitrile. In the cyclic voltammograms of Bontempelli et al. the wave which appeared at about -2.0 volts vs. a saturated calomel reference electrode (SCE) was followed by several poorly defined oxidation waves in the region of about -0.2 volts. It was determined by coulometry that the reduction wave involved a one-electron process ($n = 1$).

The major product from the CS_2 reduction process was shown to be an effective precursor for the synthesis of TTF derivatives. Moses and Chambers alkylated 1,3-dithiole-2-thiones to form 2-thioethoxy-1,3-dithiolium ions.¹⁷ Electrochemical reduction of this product formed the 2,2'-dimer, an orthothiooxalate, which was converted into the tetrathiafulvalene by pyrolysis. Their method was shown to be a more general preparation of tetrathioethylenes from trithiocarbonates than earlier methods involving desulfurization by trivalent phosphorus compounds.^{18,19}

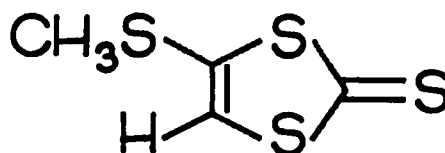


The main products of the reductions carried out electrochemically were identical to those obtained by alkali metal reduction. In agreement with Steimecke et al. and Bontempelli et al., methylated dianion 1

was the product which Wawzonek and Heilmann isolated in greatest yield. They reported 4,5-bis(methylthio)-1,3-dithiole-2-thione (10) in yields up to 41.5% when CS_2 was reduced at a mercury pool cathode during large-scale electrolytic reductions followed by methylation with CH_3I . Also isolated and identified were dimethyltrithiocarbonate (6) and dimethyl sulfide. Additionally, Wawzonek and Heilmann confirmed that the reported tetrathiooxalate by Fetkenheuer was in error. Based on the melting point, the product's spectral and polarographic characteristics, and its reaction with morpholine Wawzonek and Heilmann assigned Fetkenheuer's product as the bis(thiomethyl) product, compound 10. A minor product of the Na amalgam reduction was identified as 11, 4-thiomethyl-1,3-dithiole-2-thione.

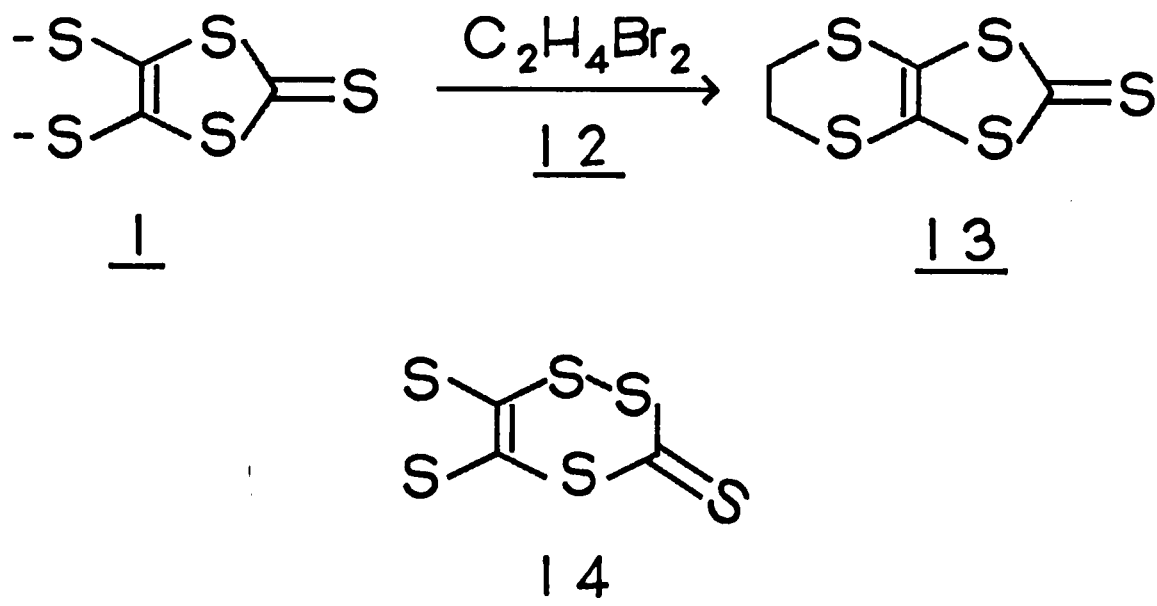


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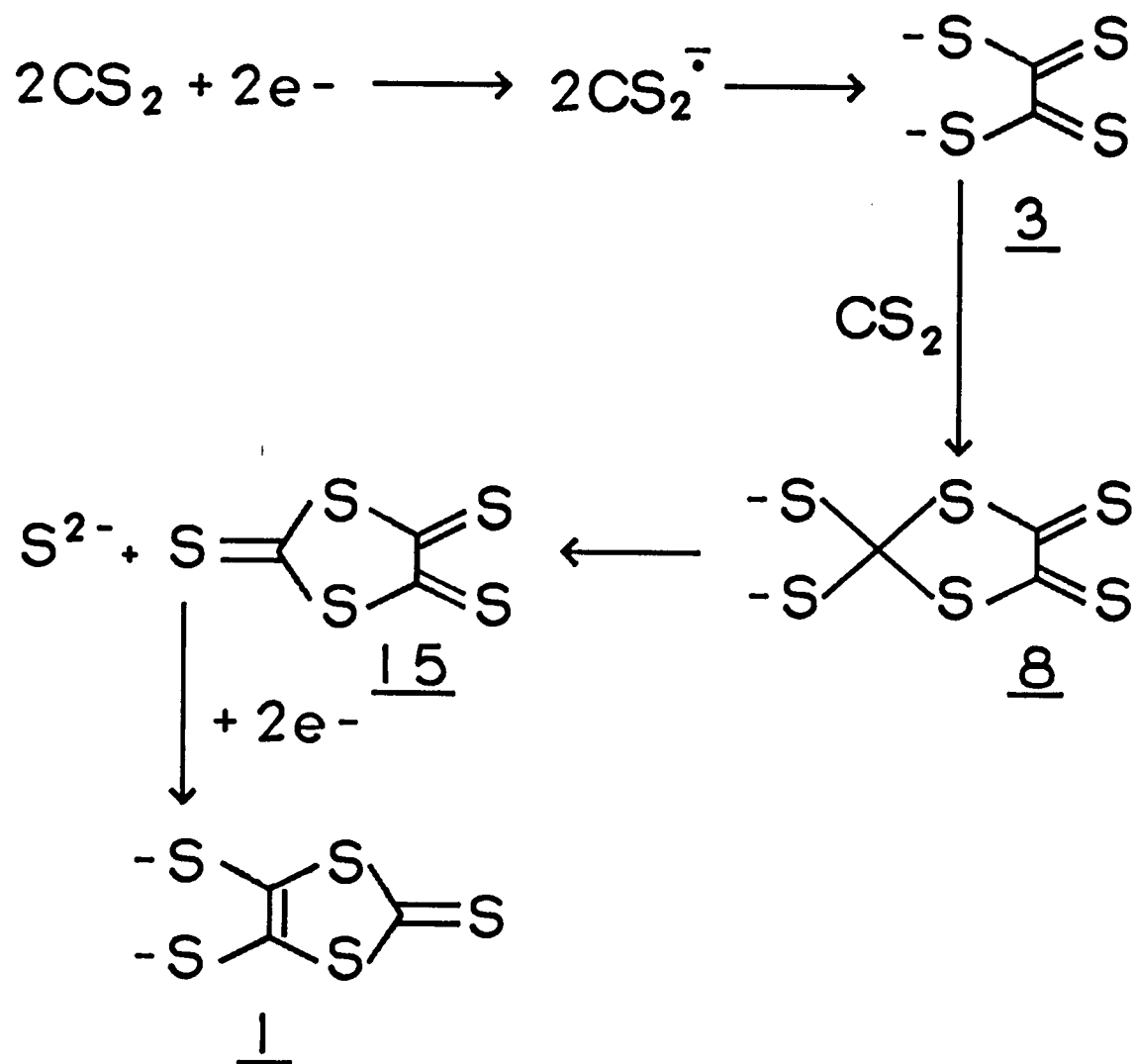
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In an extension of this work, the dianion reduction product in DMF was capped by Harnden⁸ with 1,2-dibromoethane to form a six membered ring adduct, (13), via a similar alkylation process. In addition, Harnden isolated product 14 from the electrolysis solution. The dianion of this product (9) was suggested earlier by Steimecke and coworkers³ in their mechanism as an intermediate to 1 and 2. These findings suggest that the chemical and electrochemical reductions of CS_2 proceed via similar mechanisms.

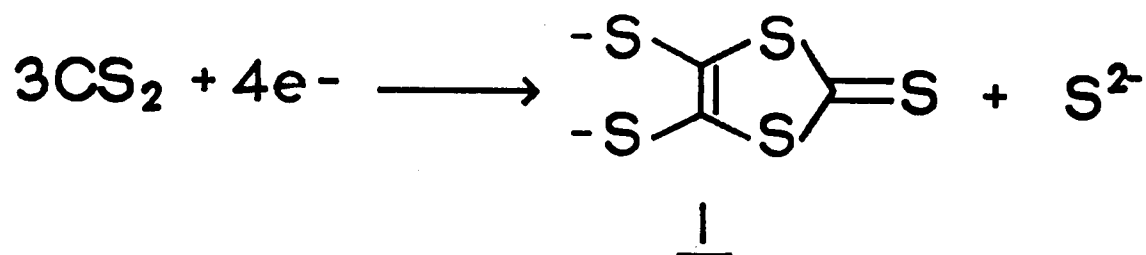


2. Mechanisms for the Reduction of CS_2

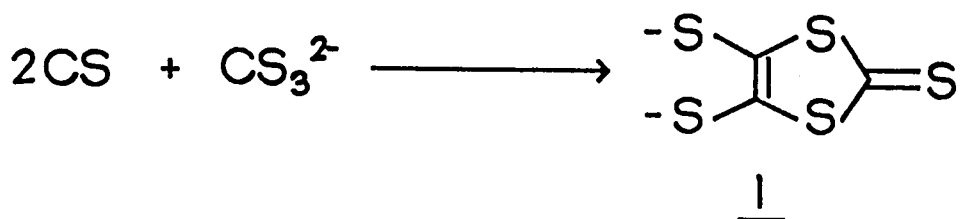
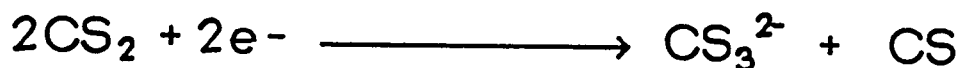
Several variations of the mechanism leading to the major products of CS_2 reductions have been proposed by the groups working on this project. Wawzonek and Heilmann reported the first scheme in which compound 1 is accounted for at an electrode reaction.⁵ The initial step is the heterogeneous formation of the $CS_2^{\cdot -}$ radical anion followed by dimerization to the tetrathiooxalate dianion. This species undergoes further reaction with carbon disulfide to form 1,3-dithiole-2,4,5-trithione (15) and S^{2-} , followed by a second electrochemical reduction to dianion 1. Scheme 2 represents an ECCCE mechanism in that an electron transfer precedes three successive chemical steps, followed by a final electrochemical step. The overall reaction consumes four moles of electrons for three moles of CS_2 . The n -value therefore becomes 1.33 Faradays per mole ($F \text{ mole}^{-1}$) for the mechanism. Coulometric data were not reported by Wawzonek and Heilmann, in their original paper, but the



SCHEME 2

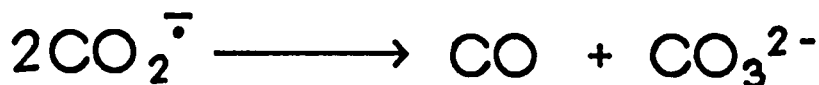
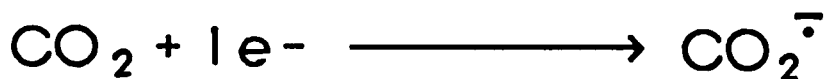


process was later shown to consume one Faraday per mole by Bontempelli et al.⁷ In the same paper Bontempelli and coworkers claimed that the reaction pathway followed direct formation of trithiocarbonate, in addition to the extremely reactive CS entity. Dianion 1 is formed, then, by further reaction of these initial products (Scheme 3).



SCHEME 3

It seems that Bontempelli was compelled to realize the similarities which should exist between the two Lewis acids CO_2 and CS_2 .

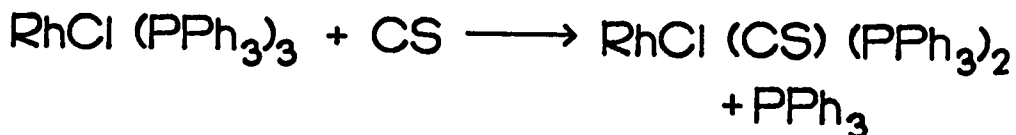


SCHEME 4

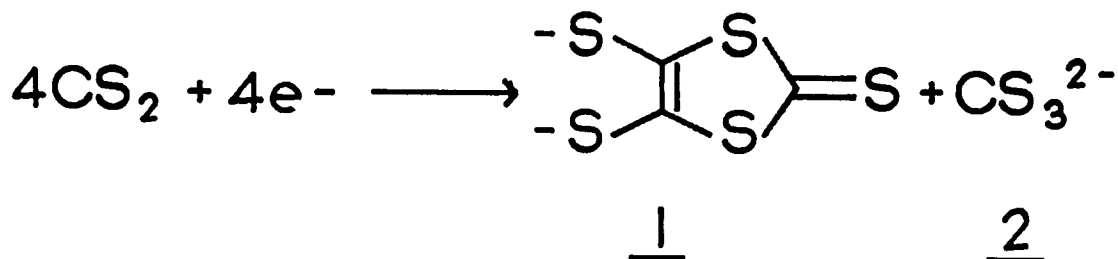
Electrochemical investigations had shown that CO_2 undergoes a one-electron cathodic reduction in aprotic media to form carbon monoxide and carbonate dianion.^{20,21} Logically, CS_2 should follow a similar reduction pathway, which has prompted efforts to confirm formation of CS_3^{2-} and CS in the CS_2 electrolyses.

The formation of CS_3^{2-} in the electrochemical process was proven by isolation of BaCS_3 .⁷ This was accomplished by dilution of the electrolyzed solution with alkaline water which forced the precipitation of the supporting electrolyte (tetrabutylammonium perchlorate, TBAP), followed by addition of Ba(OH)_2 to precipitate BaCS_3 . The IR spectrum of the product was in agreement with the literature spectrum of BaCS_3 .

Proving the existence of CS in the reduction solution posed a greater challenge. At that time, CS had only been prepared in the gas phase by the decomposition of CS_2 using methods such as electric discharge,²²⁻²⁴ high flux photolysis,²⁵ and high frequency discharge.²⁵⁻²⁷ Therefore, the reactive CS had to be verified by indirect complexation with tris(triphenylphosphine)chlororhodium.



When nitrogen was bubbled through a freshly electrolyzed solution of CS_2 and into a benzene solution of RhCl(PPh)_3 , a precipitate whose IR spectrum was identical with that of an authentic sample of RhCl(CS)(PPh)_3 was obtained upon the addition of ether. Additionally, coulometric analysis showed the n -value to be one, suggesting the overall equation for the reduction to be:



The CS_3^{2-} dianion is accounted for in the Bontempelli scheme, but this evidence alone would not invalidate the Wawzonek and Heilmann scheme. Their scheme gave S^{2-} as an end product which could further react with excess substrate to form CS_3^{2-} directly.

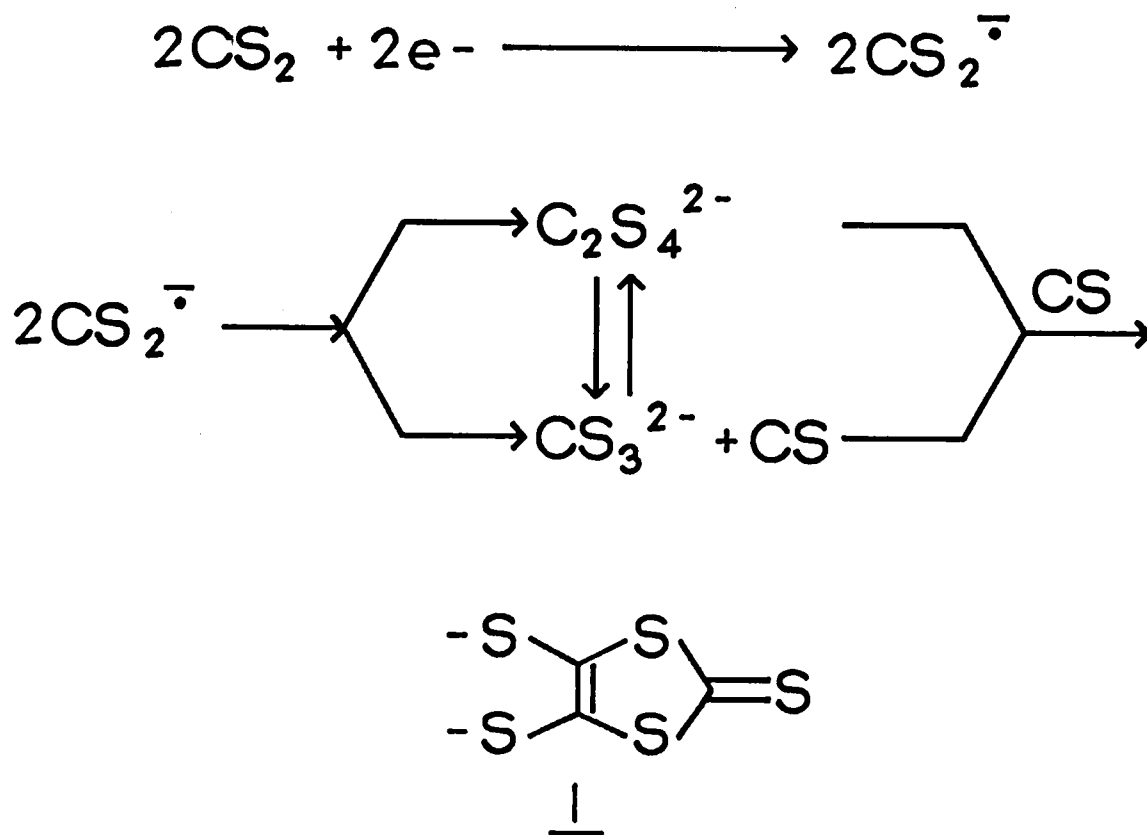


In addition, if the above equation is added to the scheme of Wawzonek and Heilmann to allow for the consumption of another mole of CS_2 , the n value necessary for exhaustive coulometry is reduced from 1.33 Faradays per mole to 1 Faraday per mole in agreement with Bontempelli. There remains, however, one aspect of the two schemes which is very different, and that is the intermediates involved in the formation of dianion 1.

There is a close resemblance in Bontempelli's mechanism to that presented for CO_2 reductions. However, there is one aspect of his scheme which, on further investigation, suggests that the scheme is challengeable: the proposed CS intermediate. Before 1975, CS had never been reported in solution, and until 1984,²⁸⁻³⁰ only two have suggested its existence in solution.^{31,32} Researchers later challenged Bontempelli's evidence for the existence of CS in the reduction

solution, which will be discussed in Chapter III, Results and Discussion.

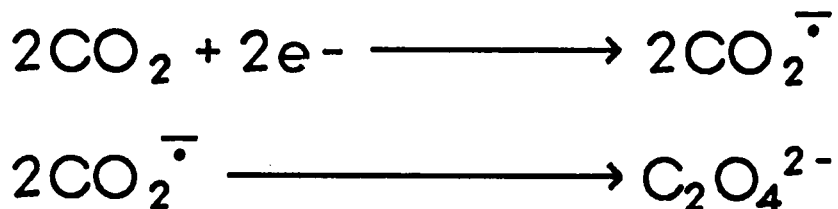
A third CS_2 reduction scheme, which appeared subsequent to Bontempelli's work, is due to Jeroschewski.⁶ He suggested that a dimerization reaction probably occurs between two radical anions of CS_2 which competes with Bontempelli's initial disproportionation reaction.



SCHEME 5

A tetrathiooxalate intermediate would further demonstrate the parallel between CS_2 and CO_2 reduction pathways. Weakly nucleophilic aprotic

solvents such as acetonitrile and propylene carbonate have been shown to favor oxalate formation,³³ so this reaction pathway is to some degree

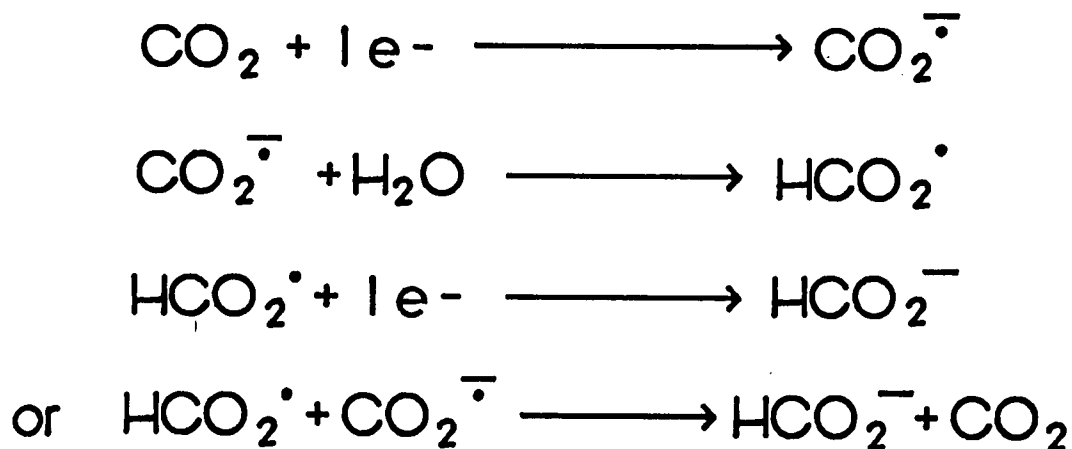


SCHEME 6

more tractable than the one Bontempelli presented. Jeroschewski, however, provided no experimental evidence for the predominance of either intermediate's or for the suggested equilibrium between them.

There remains one aspect of the CO_2 reduction which hasn't found a counterpart in the discussions presented for CS_2 : proton involvement as a third competing pathway to products. In solvents of low proton availability CO_2 is reduced to give oxalate or carbon monoxide and carbonate. But depending on the water content of the solvent, varying amounts of formic acid can be observed.^{20,34-36} Wawzonek and Heilmann alluded to similar behavior with CS_2 when they isolated 4-methylthio-1,3-dithiole-2-thione, (11) (page 7). This compound requires the involvement of some hydrogen-containing donor to provide a workable scheme for its formation. Other undetermined operational factors which will influence the product distribution are current density, concentration of substrate, and diffusion layer thickness. The results of microelectrolytic

techniques are often rendered uncertain when extrapolation is made to the conditions prevailing in macroscale electrolysis.

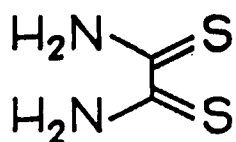


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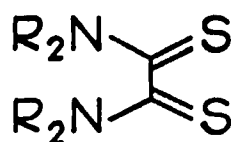
B. Alpha Dithiones and Related Chemistry

The chemistry of α -dithiones is related to the properties of the intermediates in the CS_2 reduction process. Specifically, tetrathio-oxalate has the α -dithione functionality.

While rubeanic acid (16) and substituted dithiooxamides (17) have been known for some time,^{37,38} the first attempt to prepare either an α -dithione or its valence tautomer, a 1,2-dithiete, was reported by Guha and Chakladar in 1925.³⁹

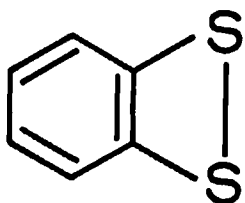
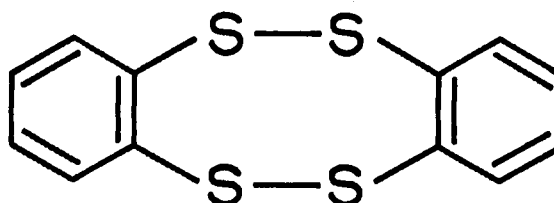


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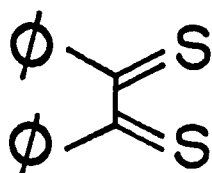


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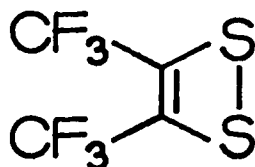
These authors described the preparation of benzo-1,2-dithiete (18) by the oxidation of dithiocatechol with I_2 in ethanol.

1819

A later paper in 1961 showed that the simplest substance that had been isolated in the earlier work was the dimer (19), and that the overall product of the reaction was primarily a polymeric mixture.⁴⁰ Mitra reported the isolation of dithiobenzil (20),⁴¹ but was subsequently shown to be in error,^{42,43} and dithiobenzil was never isolated.

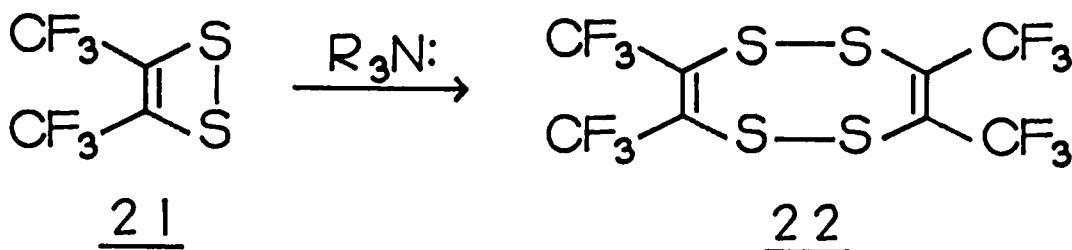
20

The first successful preparation of a 1,2-dithiete was carried out by Krespan and coworkers who prepared bis-(perfluoroalkyl)-1,2-dithietes, (21), by the reaction of sulfur with fluoroacetylenes.^{44,45} No evidence was found, however, for the existence of the acyclic valence tautomeric α -dithione structure for these compounds.

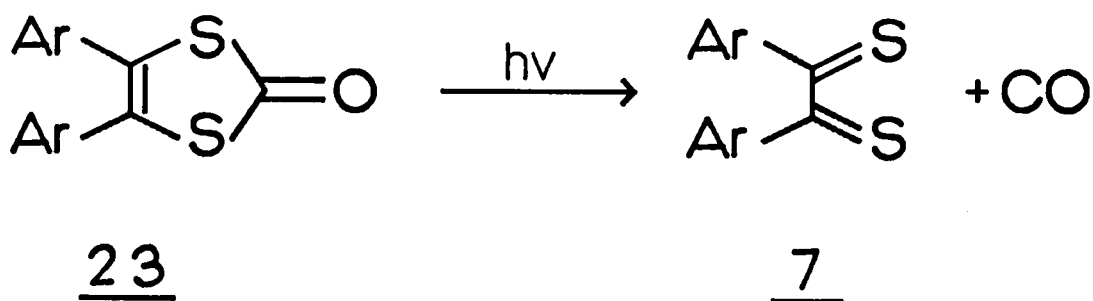


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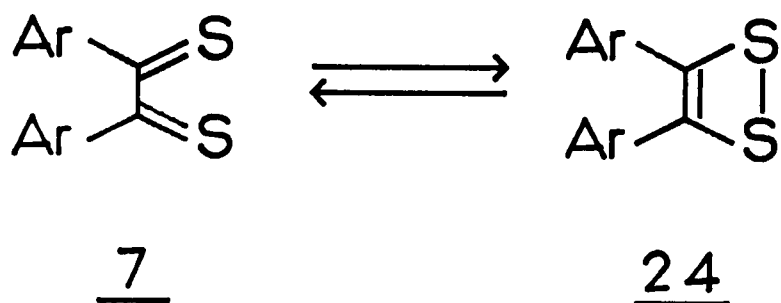
The reactivity at the strained and labile disulfide bond of (21) was demonstrated by its exothermic conversion into the dimer (22), in the presence of a catalyst such as triethylamine.⁴⁶



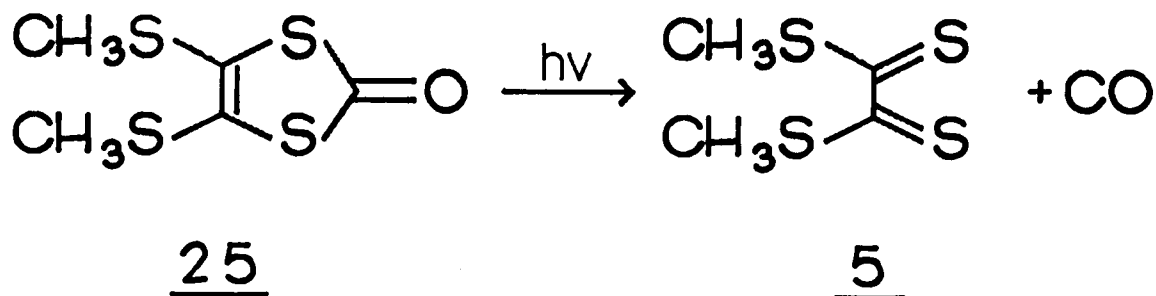
It was not until 1974 that the first report appeared describing the isolation and characterization of an α -dithione as such.¹⁵ Metal complexes containing α -sulfur atoms had been prepared indirectly and were well known,⁴² but Kusters and de Mayo reported the first synthesis of a compound stable in the α -dithione form. They obtained 4-4'-bis(dimethylamino)dithiobenzil (7) in moderate yield by photolysis of bis(p-dimethylaminophenyl)vinylene dithiocarbonate (23) in benzene.



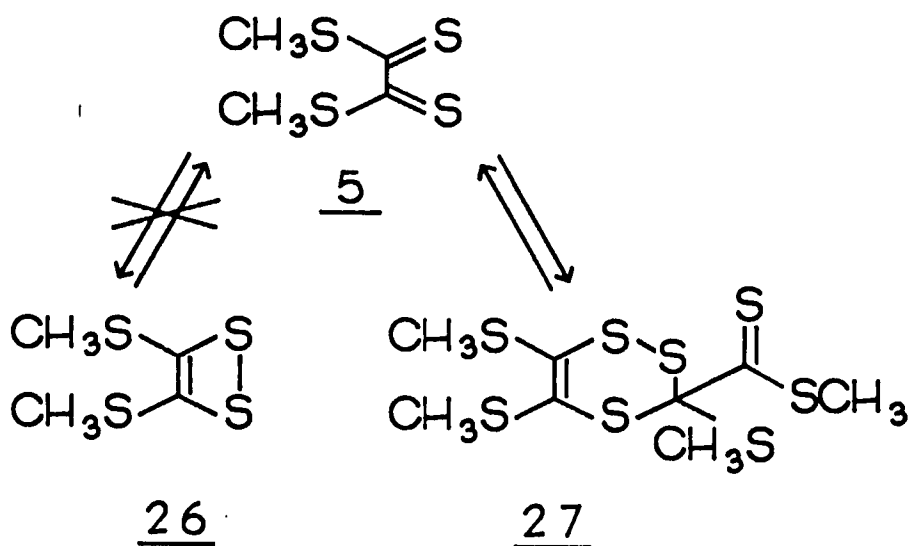
Careful attempts to obtain dithiobenzil (20) failed, as they had for previous investigators. Compound 7 proved to be in equilibrium with the corresponding valence tautomer 1,2-dithiete (24). The equilibrium constant was dependent on solvent, light and temperature.



Following a similar scheme, the dimethyl ester of tetrathiooxalate was synthesized and isolated by Kissel et al.¹¹

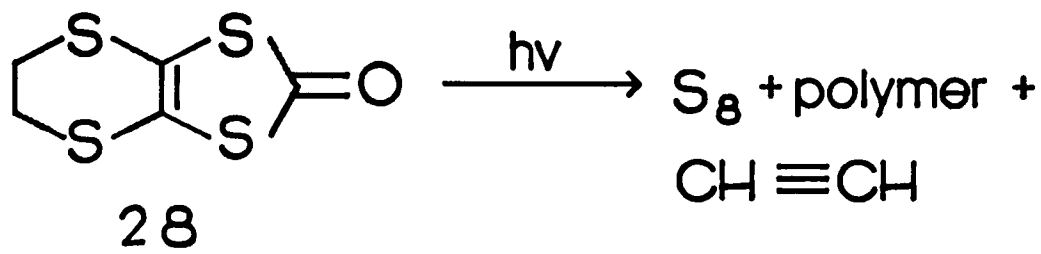


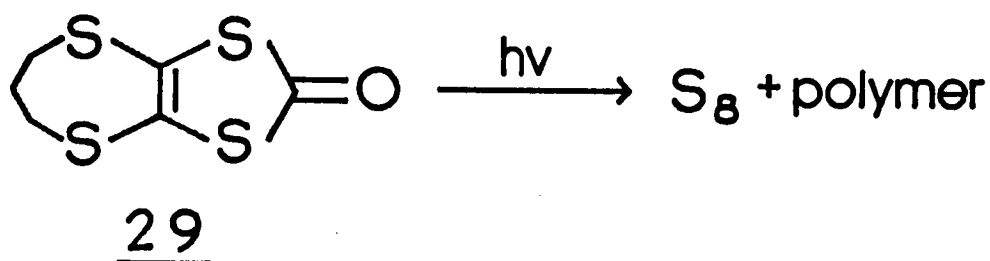
This compound is the first reported tetrathiooxalate to be isolated and therefore means were provided to investigate the suspected intermediacy of thiooxalates in the CS₂ reductions. Kissel showed that unlike the 1,2-dithietes reported by Krespan,^{44,45} dimerization of 5 gives the 4+2 addition product (27) while no 1,2-dithiete (26) forms.



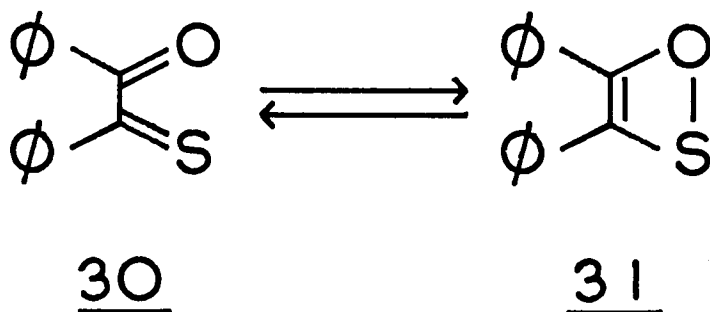
SCHEME 8

Hartke et al.¹⁶ also attempted to synthesize cyclic tetrathiooxalates, but the products proved very unstable, decomposing to elemental sulfur and polymeric mixtures.

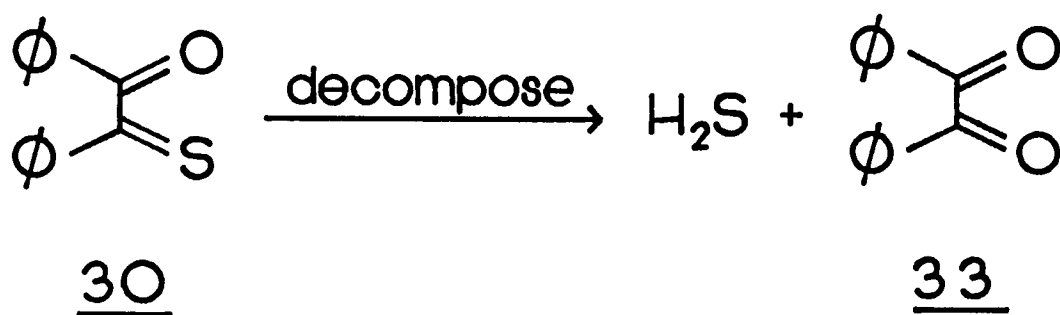
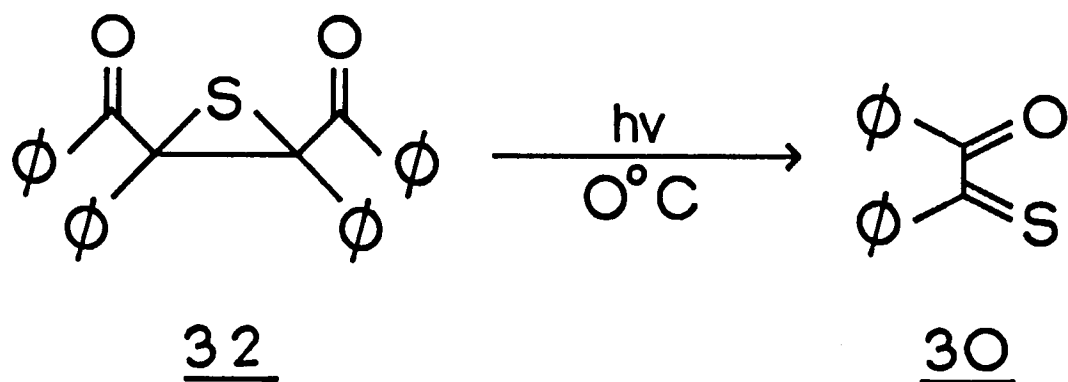




While those efforts were being made to characterize α -dithiones, the interaction of several molecules with very short S-O interatomic distances was also being investigated. Dittmer and Kuhlmann studied monothiobenzil (30), to see if a strong interaction took place between the sulfur and oxygen.⁴⁷ The oxathiete structure (31) was expected to be in equilibrium with 30.

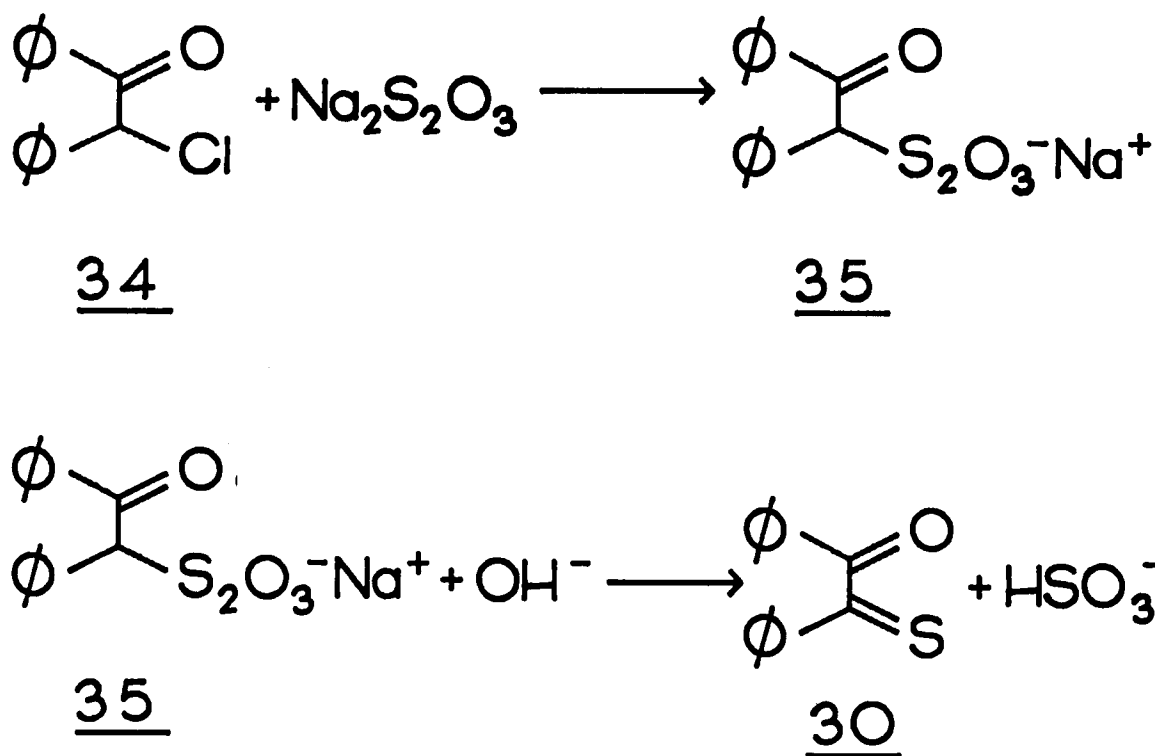


Monothiobenzil was obtained as a blue oil from a cooled irradiated solution of dibenzylstilbene episulfoxide (32) in benzene.⁴⁸ Structure confirmation was achieved by infrared and mass spectroscopy, and it was inferred that the oxathiete structure (31) was isolated. The oil proved to be unstable, decomposing in a few days to H_2S and benzil (Scheme 9). Saville and Steer⁴⁹ pursued this project further and reported an alternate synthetic route for monothiobenzil. Sodium desyl thiosulfate (35) was obtained by reaction of desyl chloride (34) with sodium thiosulfate.



SCHEME 9

The thiosulfate group was then converted into a thione group with dilute NaOH. The product was extracted with methylene chloride as it formed. This clever synthesis resulted in a nearly quantitative yield of monothiobenzil, while suppressing any competitive reactions occurring in the aqueous phase. Possible side reactions include bisulfite addition across the carbonyl or thiocarbonyl groups, alkaline hydrolysis of the product to benzil, and reactions involving any liberated sulfide ion,

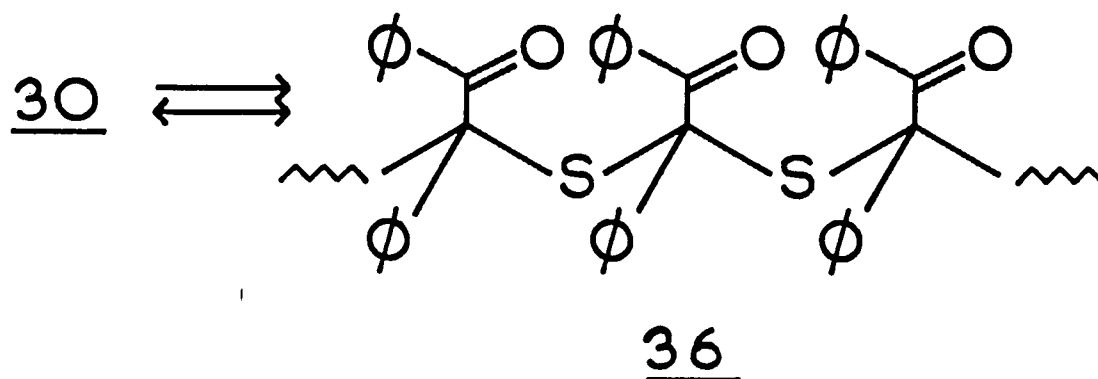


SCHEME 10

all of which could occur in the absence of partitioning solvent. Instead the product moves to the organic phase before further reaction occurs.

Saville and Steer⁴⁹ reported that compound (30) polymerized reversibly when taken in and out of solutions with CH_2Cl_2 . When the CH_2Cl_2 is removed, the product's deep blue color continually intensifies until it changes to emerald green just before the solvent is completely gone. A glassy polymer is rapidly deposited. Monomeric monothiobenzil shows an absorption band at 608 nm ($=\text{S}$, $n \rightarrow \pi^*$ transition) which disappears in the polymeric form, but monothiobenzil, unlike other thiones, does not

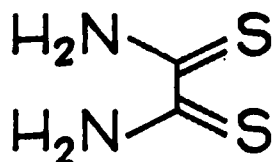
appear to be particularly unstable towards oxygen. The depolymerization represents an easy formation of thiocarbonyl groups of low π bond energy in the monomer from a formally strong σ -bond in the polymer.



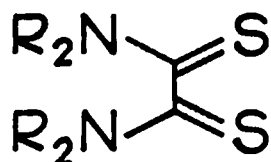
SCHEME 11

It is the influence of the neighboring benzoyl group which can render monothiobenzil an enophile or a dienophile. A combination of electron withdrawing and resonance stabilizations apparently contributes to the ability of the molecule to exist as a thione or as a sulfide.

A third class of compounds containing α -dithiones are the dithio-oxamides of which rubeanic acid (16) is the simplest.



16



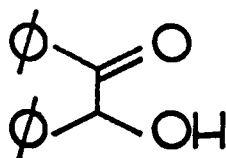
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By substituting various entities for the hydrogens at the nitrogen atoms, compounds are formed which have exhibited a wide range of applications. Some of these include metal deactivation in the petroleum and

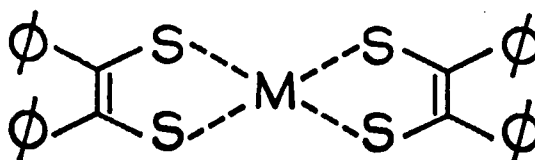
organic products industry, vulcanization accelerators, and inhibitors for certain bacterial growth.³⁷ Like thiooxamides,⁵⁰ dithiooxamides characteristically form stable, highly colored metal complexes⁵¹ which have also been used as color sources in duplicating processes.^{37,38} The strong electron withdrawing power of the nitrogen-containing functions apparently stabilizes the adjacent thiones much the same way that oxygen stabilizes oxalates.

The ability of transition metal cations to stabilize adjacent sulfur atoms in metal complexes is seen in the large variety of stable metal complexes formed with dithiooxamides. Furthermore, eleven different metals were used to synthesize metal complexes having a dithiobenzil ligand,⁴² twelve years prior to the report of an α -dithione.

The ligand was prepared by reaction of P_2S_5 on acyloins (37) in xylene.

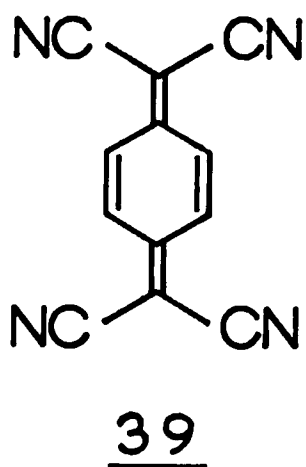
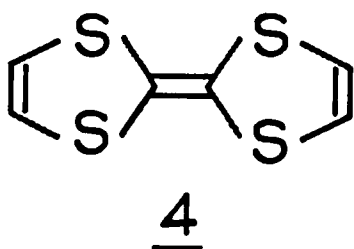


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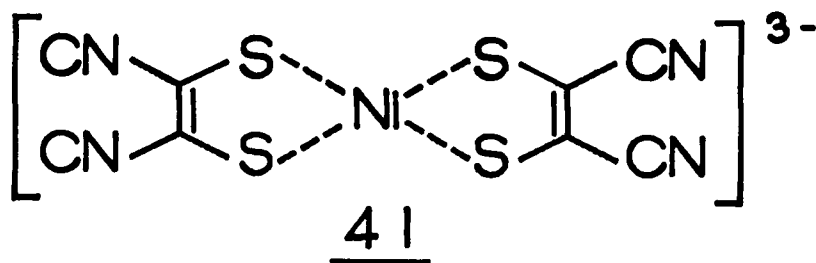
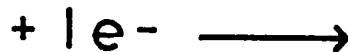
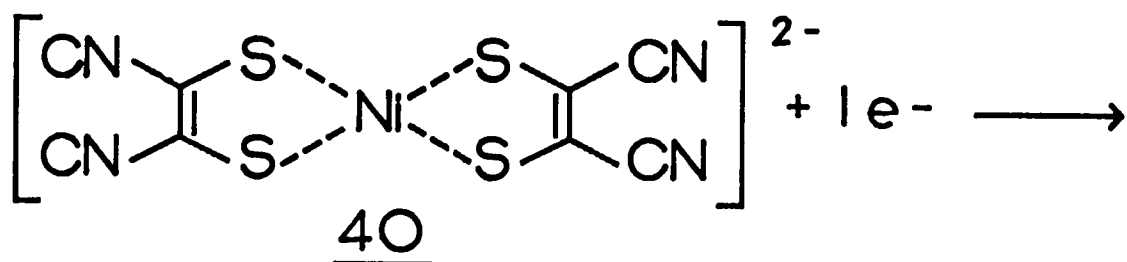


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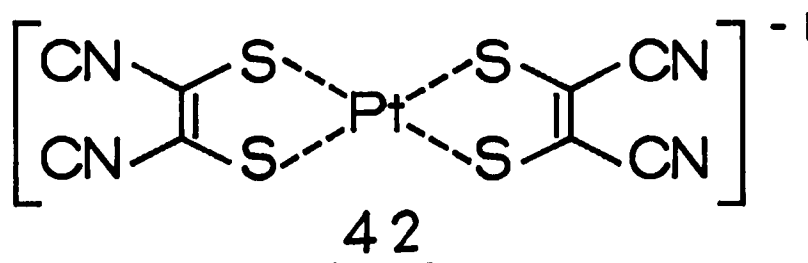
A great deal of interest was shown in dithiolene complexes of this type (38),⁴ particularly when the report of the charge transfer properties of TTF (4) and TCNQ (39) appeared.⁵² The bis-dithiolene metal complexes are typically square-planar and show varying degrees of electrochemical activity. The maleonitrile adduct (40), for example,



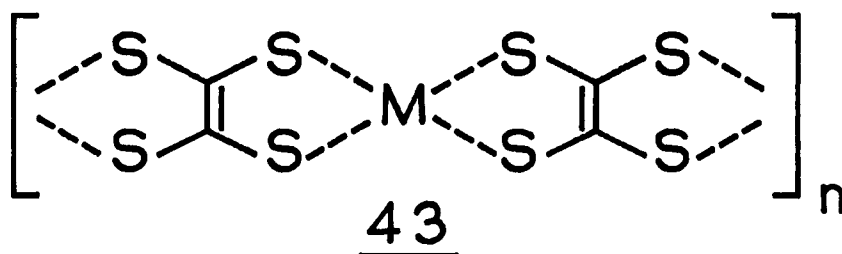
was shown to exhibit three reversible electron transfers. One reduction formed a trianion in which nickel was shown to exist in the unusual +1 oxidation state.⁵³⁻⁵⁵



The platinum adduct of the above compound in the -1 oxidation state exhibited high conductivity in the solid state. Lithium salts of 42 gave conductivities in the range of $30\text{-}200 \text{ ohm}^{-1} \text{ cm}^{-1}$.^{55,56}



Also, the preparation by a multistep organic synthesis, of highly conductive poly(metal-ethylenetetra-thiolate) polymers (43) containing transition metals has been reported.^{57,58}



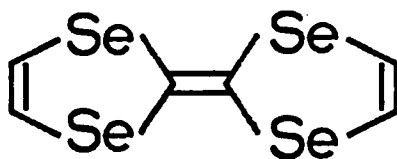
Considerably lower conductivities relative to the polymerized form were observed when the unpolymerized form of the bis(dithiolene) transition metal complexes was employed as an "acceptor" molecule with TTF (4).^{56,59} These reactions typically afforded salts with the ratio of TTF to dithiolene ligand being 2:1. Mixed valence behavior was apparently not prevalent in these compounds.

Intense research efforts pursuant of unusual chemical and electrical properties of these types of compounds was intensified by the discovery of highly conducting TTF/TCNQ mixed valence salts.⁵² Of central importance to the electrical properties reported, are two required conditions which must be fulfilled for an organic complex to be a conductor. First, the donor and acceptor molecules must crystallize into separate stacks such that they remain segregated.⁶⁰ Also, the degree of

charge transfer, (ρ), from donor to acceptor must be fractional ($\rho < 1$), i.e., the resulting complex must "be mixed valence".⁶¹ The maximum electrical conductivity previously reported for an organic compound was 170-440 $\text{ohm}^{-1} \text{cm}^{-1}$ at 200 K.⁶² The TTF/TCNQ complex displays room temperature conductivity in the range 200-650 $\text{ohm}^{-1} \text{cm}^{-1}$ which steadily increases as the complex is cooled. An unusual characteristic of this metallic-like charge transfer salt is that a metal to semiconductor transition is initiated by cooling the complex below 58 K. Above 58 K, the conductivities for the cooled complex range from 3,000-15,000 $\text{ohm}^{-1} \text{cm}^{-1}$.^{52,63} For comparison, copper has a room temperature conductivity of $6 \times 10^5 \text{ ohm}^{-1} \text{cm}^{-1}$.

A large number of these derivatives have been studied, varying the substituents primarily on the donor, and to some extent the acceptor molecules.⁶⁴⁻⁶⁶ Some derivatives have been shown to exhibit reversible electrochromism.^{67,68}

The substitution of selenium for sulfur^{64,69,70} in the TTF framework (44) leads to favorable changes relative to the metallic-like properties of TTF/TCNQ salts,⁷¹⁻⁷⁴ and TTF/ X^- salts.⁷⁵

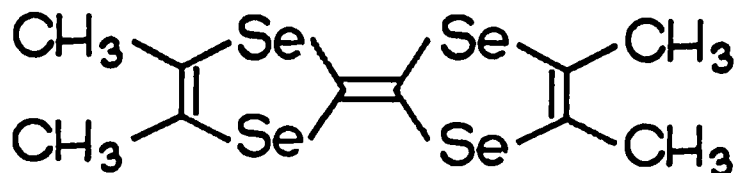


44

The TCNQ salts of TTF, DSeDTF, and TSeF were all shown to be isostructural.⁷¹ The implication is that the selenium analogues perturb the

electronic properties while maintaining the same steric requirements of the original TTF/TCNQ crystal structure. Not only did the TSeF/TCNQ salt show generally higher conductivities than TTF/TCNQ, but the metallic state persisted to much lower temperatures.^{76,78}

Additionally, the tetramethylselenafulvalene (45) was shown to form charge transfer salts with the anions PF_6^- and AsF_6^- which are superconductors under enhanced pressure.⁷⁹ Compound 45 also formed a ClO_4^- adduct which was superconducting at ambient pressure.^{80,81}



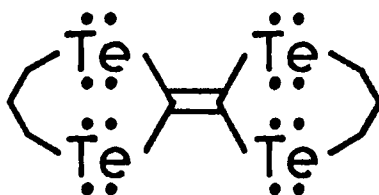
45

Not only did the substitution of selenium for sulfur lead to the first organic superconductor, but it shed considerable insight into the roles of donor and acceptor stacks near phase transition phenomena.⁷⁶ TSeF/TCNQ and its solid solutions with TTF/TCNQ were studied under varying pressure and temperature.⁷⁷

Conductivity measurements on the "organic metals" were made on crystals of the complexes. Crystals were initially grown in solution, but later work reported that uniform, well-defined crystals could be electrochemically grown in acetonitrile.⁸² Wheland and Gillson deposited highly reflective TTF/TCNQ needles on an anode by passing typically $1\mu\text{A}$ through a saturated solution of TTF/TCNQ, and 0.06 M in TTF. These authors reported, however, that this electrochemical crystal

growing procedure may be of great generality, and that extending it to other systems would require trial and error in order to determine the proper conditions and additives.

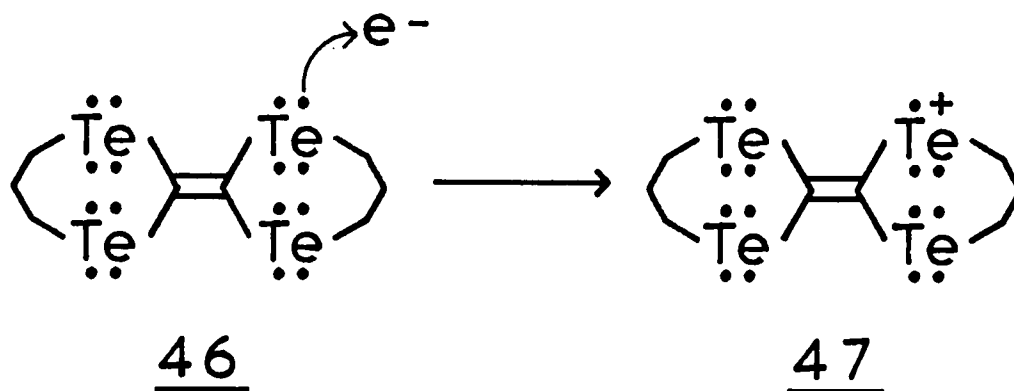
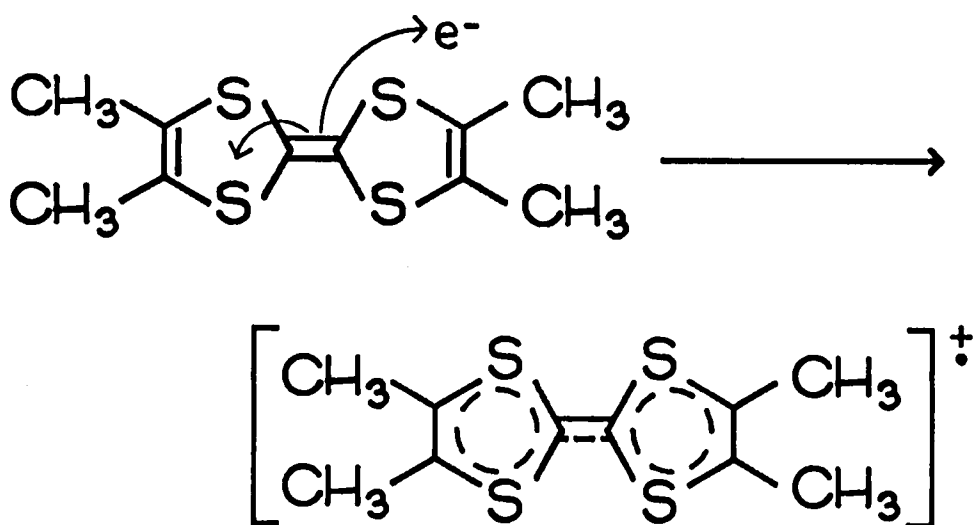
It naturally followed that tellurium was included in the TTF framework to further test electronic perturbations within the complex. Early in these research efforts, it was surmised by several investigators that a molecule of tetratellurafulvene would be very unstable. Tellurium was considered to be too large to be incorporated into a five membered heterocycle with two tellurium atoms in a 1,3-relationship.⁸³ Additionally, it is unlikely that tellurium will form strong double bonds with carbon, suggesting that delocalization of electrons within the fulvalene framework would be limited.⁸⁴ The first tetratellurium fulvalene adduct to be reported was the hexamethylene derivative (46) synthesized by Wudl and Aharon-Shalom.⁸³



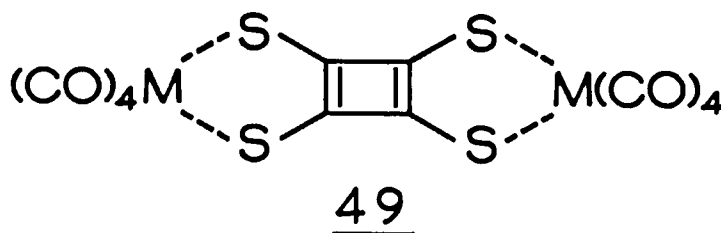
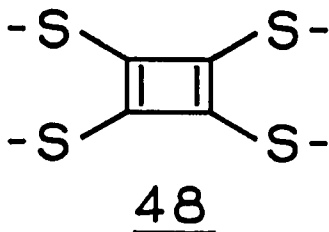
46

Cyclic voltammograms of this compound in benzonitrile exhibited reversible waves for two redox steps, but after one cycle the electrode was passivated by a coating of insoluble salt.⁸³ A comparison of the ΔE values for the series of fulvalene adducts showed a decrease in the order: TMTTF > TMTSeF > HMTTeF where TMTTF is the sulfur derivative of 45, TMTSeF is 45, and HMTTeF is compound 46. The fact that electron

transfer is slowest for TMTTF, and fastest for HMTTeF, led these authors to conclude that ionization of the sulfur fulvalene occurs primarily from the π -bonded network. On the other hand, ionization of the tellurium fulvalene originates from the tellurium lone pairs. Stabilization of 47⁺ was attributed to the lower electronegativity of Te versus Se or S, and to transannular lone pair interaction across the five-membered ring. Pi orbital delocalization was considered to be of little importance in the stabilizing of 47⁺ because of the disparate size of tellurium and carbon.



Finally, the thiosquarato tetraanion (48) was treated with metal complexes to make bimetallic metal-dithiolene complexes such as compound 49.⁸⁵ In bimetallic systems similar to these the metal atoms undergo



metal-based electron transfer reactions and consequently exist in separate oxidation states.⁸⁶⁻⁸⁸ Marked differences have been reported for metal dithiosquarates relative to the 1,2-dithiolene complexes, in that reversible redox behavior was not observed in the former case.⁸⁹ The major differences in behavior were attributed to the large S-S distance in the tetrathiosquarate which favors the formation of tetrahedral complexes rather than the usual square planar geometry assumed by 1,2-dithiolene complexes. The conclusion was drawn by Coucouvanis et al.⁸⁹ that an unsaturated ligand π system is not necessarily a sufficient condition for strong metal-ligand π bonding to occur in sulfur chelates. The energies of the ligand π orbitals must be adequately matched relative to those of the metal orbitals of appropriate symmetry for overlap and π bonding to occur.

C. The Proposed Research

A study of the anionic intermediates and products in the CS₂ reduction process was conducted in an effort to understand the reduction mechanism. It was anticipated that methylation of the anionic species directly in the electrolysis solutions would result in appropriate surrogate products, which would be compatible with reverse phase HPLC. Information was sought regarding the identity of the various products and intermediates as well as the time dependency of their formation, or disappearance. As detailed above, the previously reported schemes for CS₂ reduction disagree on the mechanism of reaction. Accordingly, one aspect of this research was to support or refute the previously reported schemes. The synthesis and analysis of dimethyltetrathiooxalate used in the study of CS₂ reduction solutions required the intermediate synthesis of compound 25 (p. 18). As an alternative to photolytic decarbonylation of 25, electrolytic decarbonylation was considered as a possible entry into the tetrathiooxalate structure. The photolytic and electrochemical properties of 25 were characterized using standard voltammetric and coulometric techniques. Additional information was obtained through mass spectral and HPLC data.

Finally, the electrochemical behaviors of 4-phenyl-2-benzylidene-1,3-dithiole (compound 73, p. 97), and a nitro-adduct of this compound were investigated to see if the electrochemical oxidation mechanism was the same as the chemical oxidation pathway reported by Mayer and Kröber.¹²⁸

CHAPTER II

EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Chemicals

The supporting electrolytes used in this work were typically tetraalkylammonium salts $RN_4^+X^-$. Eastman or Fluka tetraethylammonium perchlorate (TEAP) was purified by recrystallization from doubly distilled water. White needlelike crystals were obtained, and after a third recrystallization, the batch was vacuum dried at 60°C for 48 hours or until no oxidation currents could be seen on background cyclic voltammograms. TEAP and all other supporting electrolytes were stored in a desiccator until use. Tetrabutylammonium iodide (TBAI) supplied by Eastman was recrystallized twice from ethyl acetate and vacuum-dried for 48 hours.⁹⁰ $TBABF_4$ and TBAI obtained from Aldrich were used without further purification.

The organic bases dimethylpyridine and pyridine were selected as reagents to promote proton (H^+) transfer in nonaqueous mechanism studies. The 2,6-lutidine was purified by reduced pressure distillation at ~32-34°C after the solvent had been stirred over BaO overnight.⁹¹ All other chemical reagents were used as received.

B. Solvents

Two solvents were used routinely for the electrochemical experiments: acetonitrile and N,N-dimethylformamide (DMF). Acetonitrile was

obtained from Aldrich (gold label spectrograde) and required no further purification. Molecular sieves (~ 10 g, $3\text{\AA}$), were added to the bottle at the time of opening to scavenge residual water.

Fisher brand N,N-dimethylformamide (DMF) was purified according to Hurley.⁹² One to two liters of DMF was stirred over ~ 20 g of anhydrous CuSO_4 for 24 hours. The stirring was halted and the CuSO_4 was allowed to settle until the DMF could be cleanly decanted. The solvent was then vacuum distilled into a flamed round-bottomed flask, excluding the front end and the tail end cuts. "Finished" solvent was purged with argon and stored over $3\text{\AA}$ molecular sieves in an amber bottle. The shelf life of finished DMF varied from 2-3 weeks to 2-3 months. Fresh batches were prepared any time the background voltammograms demonstrated that the DMF had deteriorated. Typically, a shift in the cathodic limit to more positive potentials (from $\sim -2.10\text{v}$ to -1.70v) indicated that fresh DMF was necessary.

Methylene chloride (Fisher) intended for use as an electroanalytical solvent, was passed through a column of oven-dried neutral alumina to remove traces of water. Otherwise CH_2Cl_2 was used without further purification.

Drum-grade ethanol was purified by first refluxing with KOH overnight followed by distillation. Further clean-up was achieved by adding magnesium turnings and again refluxing overnight.⁹¹ Ethanol of high purity was then obtained from center cuts of a distillation from the solution of magnesium ethoxide.

Certified grade methanol (Fisher) served as a routine chemical solvent. Liquid chromatography grade methanol, however, was used as an HPLC eluent (Burdick and Jackson). Most HPLC experiments were run under isocratic conditions, typically a 50/50 mixture of methanol and water. The water was purified by doubly-distilling a batch (2-3 gallons) of laboratory distilled water and passing it through a .45 μm Millipore filter (XX10-047-00). Both the methanol and the filtered water were stored in 2L round bottom flask modified to serve as reservoirs for the HPLC module. Thermal degassing was provided for by using two Corning PC-351 Hot Plate-Stirrers.

Reagent grade anhydrous ether (Et_2O -Fisher certified) was further dried over anhydrous MgSO_4 or anhydrous K_2CO_3 before use as a partitioning solvent. No drying was necessary, however, when water was the cosolvent.

Certified grade chloroform (CHCl_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), benzene (C_6H_6), carbon disulfide (CS_2), and acetone ($\text{C}_3\text{H}_6\text{O}$) were used without further treatment.

C. Electrochemical Instrumentation and Techniques

1. Voltammetry

The electrode configuration employed in all experiments was the conventional three-electrode design. The working electrode most often was an inlaid platinum button (Beckman) having an area of 0.22 cm^2 . Platinum buttons were polished prior to use by buffing the button on

felt with a slurry of 0.3 μm alumina micropolish (Buehler) and the appropriate solvent.

The counter electrode was routinely a large platinum grid with a platinum wire attached for electrical contact. Grid size was chosen to provide sufficient surface area so that the electrode would not become polarized during voltammetric cycles.

Three types of reference electrodes were used. A home-made saturated calomel electrode (SCE) and a silver wire immersed in 0.01 M AgNO_3 /0.1 M TEAP/ CH_3CN (for use in CH_3CN) were most often used. It was found that very stable potential settings were achieved with a Ag/AgCl quasi-reference electrode. A silver wire was anodized in a saturated solution of KCl until a thin, grey-mossy coating was apparent. In this precipitated coating, the Ag/AgCl couple is locked in close proximity at the Ag wire and "appears" poised as required by the Nernst equation.

Depending upon the experiment, cell design could be of the two- or the three-compartment type. Separation of the working compartment from the other compartments was achieved with fine porosity glass frits. Cells were designed to hold ~100 ml of working cell contents over a larger frit adapted to pass argon or nitrogen purge gases. The separate compartments often were not used when a coulometric determination did not accompany a voltammetric study. Voltammograms were recorded by using one of two potentiostat combinations: a PAR model 173/176 potentiostat coupled with a PAR Model 175 Universal Programmer, or a Bio-analytical Systems model CV-27 potentiostat. Most often cyclic voltammograms were recorded with a Nicolet Explorer I digital oscilloscope. A

hard copy was subsequently produced by transfer of the stored data to a recorder (Hewlett-Packard X-Y,Y' model 135AM or a Houston Instrument model 100 recorder).

Some of the electroactive molecules examined in this work exhibited behavior which could be further understood by slowing the kinetics of reaction after an electron transfer had taken place.^{93,94} To do this, the temperature of the electrochemical cell and its contents were lowered by using an ice bath. Sub-zero temperatures were achieved by adding calcium chloride to melt the ice in the bath. Insulation of the bath in a large-mouth Dewar flask was necessary to maintain the lowest temperatures. Temperatures as low as -35°C were obtainable, but required frequent feeding of the bath. The solvent electrolyte combination used at the lowest temperatures was a 0.1 M TBAP/ CH_2Cl_2 system and a 0.01 M AgNO_3/Ag reference electrode. It was noted that TEAP would precipitate out of acetonitrile at the lower temperatures ($<-20^{\circ}\text{C}$). Several of the voltammograms for this work were recorded in the presence of neutral alumina. Alumina was shown by Svanholm and coworkers to scavenge nucleophiles which react with radical cations and dications in solution.

2. Coulometry

Coulometric determinations were carried out in either a two- or three-compartment cell as described. A PAR model 173 potentiostat equipped with a PAR model 179 digital coulometer was employed to count coulombs passed. The working electrode typically consisted of platinum mesh, and the counter electrode was either identical to the working

electrode or a graphite rod. Argon was continuously passed through the solutions being electrolyzed to flush out O_2 , and to provide convective stirring.

3. Bulk Electrolysis

Carbon disulfide was the only material electrolyzed in bulk as a synthetic starting material. A coulometric cell was set up as described. All compartments of the cell were filled with 0.4 M tetrabutylammonium iodide (TBAI) in DMF. Typically, pre-electrolysis was carried out prior to the initial addition of CS_2 to the working compartment. As the electrolysis proceeded, additional aliquots (ca. 2-3 ml) were added until the desired number of coulombs were passed. Temperature of the cell ranged from ambient to $60^\circ C$ a couple of hours after the electrolysis had begun.

4. Attempted Electrolytic Preparation of Crystalline Ionic High Molecular Weight Organic Species

Attempted separations of higher molecular weight analogs containing sulfur were unsuccessful. This electrocrystallization procedure was adopted according to Wheland and Gillson⁸² and Chiang et al.⁹⁷ A platinum wire was submerged in a quiescent saturated solution of the substrate and a perchlorate electrolyte. A potential, which corresponded to a region of electroactivity previously discerned by voltammetry, was applied for several days in hopes that crystal growth would occur. In all cases the solvent electrolyte system was $CH_3CN/TEAP$.

D. Spectroelectrochemistry Using an ESR Spectrometer

Electron spin resonance (ESR) investigations of electrolytically produced radicals can be used as an aid to the interpretation of voltammetric data since qualitative identification of radical species is frequently possible. Also, electrolytic preparation of radicals for study by ESR offers two distinct advantages over chemical oxidations or reductions. The main advantage is the continuously adjustable range of oxidation and reduction potentials available. Secondly, the tetraalkylammonium salts used as supporting electrolytes typically interact with cation radicals and especially the anion radicals to a much lesser extent than most chemical agents.⁹⁵ For this work, two cell designs were employed. The one most often used was a standard quartz ESR cell adopted for insertion of a thin platinum working electrode into the cavity portion of the cell. Electrical contacts for counter and reference electrodes as well as fritted compartment separators were provided. A second set-up was a flow-through design for the study of rather stable radicals. Electrolysis of substrate was carried out in the usual electrochemical cell, and moved through the ESR quartz cell with a precision, nonpulsing pump (Fluid Metering, Inc. Model RPSY). All connecting tubing was Teflon (1/8") equipped with Swagelok Stainless Steel Quick-Connectors for easy hook-up. At times, it was convenient to test a substrate for paramagnetic behavior prior to setting up elaborate cells. To do this, a small amount of aluminum chloride was added to an in-situ ESR cell containing the substrate.⁹⁶ In this way a radical

could be quickly generated by chemical oxidation, and the center of the spectrum located. In-situ and flow cell electron spin resonance spectra were obtained using a Varian E-line spectrometer equipped with a E-101 microwave bridge.

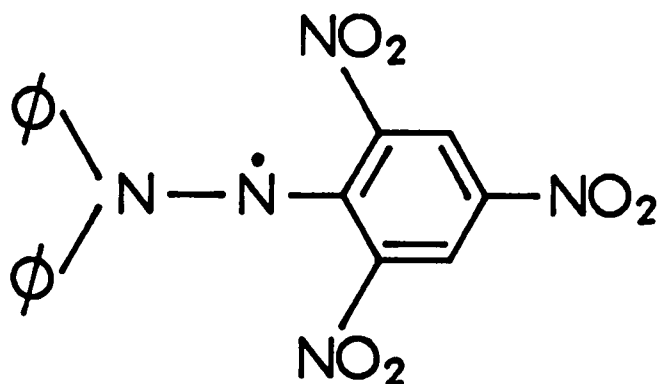
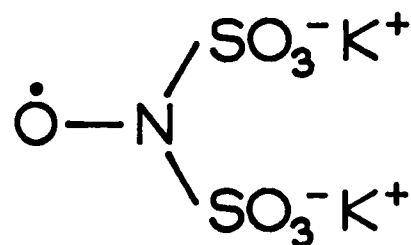
E. Photolysis Equipment and Techniques

Photoreactive substrates were dissolved in CH_2Cl_2 and placed in either a quartz or pyrex photolysis cell. Irradiation was carried out with an Ace-Hanovia 450 Watt medium pressure mercury arc lamp. Continuous purging of the solution with a N_2 stream removed O_2 and CO as it was formed. The N_2 was scrubbed through solvent washing towers to remove traces of moisture and residual O_2 in the stream⁹⁸ prior to purging through the photolysis solution.

A few solid state photolyses were carried out by placing crystals of a substrate in a capillary tube and fastening the capillary directly to the lamp jacket. In this way, direct probe injection of all products could be made into the mass spectrometer.

F. Spectroscopy

Electron spin resonance (ESR) spectra were recorded using a Varian E-line spectrometer model E-109S, equipped with an E-101 microwave bridge. All ESR spectra were recorded at room temperature. All spectra were recorded versus DPPH (50) ($g = 2.0037$) or Fremy's Salt (51) ($g = 2.0057$) as standards. DPPH is 2,2-diphenyl-1-picrylhydrazyl

5051

(50).⁹⁹ Mass spectra were obtained with a Hewlett-Packard model 5934A electron impact instrument. Samples were direct-injected and most often fragmented at 70 eV. For comparison, some spectra were rerun at 25 eV. A Cary 17 or Cary 219 model spectrometer was used to record UV-visible spectra, typically in a 2 mm quartz cell. Nuclear magnetic resonance spectra were recorded on a Varian model T-60A spectrometer. A tetramethylsilane (TMS) internal standard was included in all samples. Chloroform-d or methylene chloride-d were routinely used as NMR solvents. Infrared spectroscopy was carried out using a Perkin-Elmer model 727 spectrometer or a model 1330 spectrophotometer. For solid samples a KBr pellet was prepared using a Blackhawk pellet press, while neat liquid samples were run with a Barnes Engineering Company liquid cell. The windows were the usual NaCl plates. All spectra were standardized using polystyrene film.

Uncorrected melting points of solids were obtained on a Mel-Temp melting point apparatus.

G. Liquid Chromatograph Equipment and Techniques

The HPLC system used in the work consisted of two (Constametric I and II) dual piston pumps with a Gradient Master model 1601 control module (Laboratory Data Control Co.). The sample injector was a six port rotary Rheodyne model 7120 which used a 20 μ l sample loop onto a pre-column packed with 30-38 μ m Partisil octadecylsilane (ODS; Whatman). The analytical column was 25 cm x 4.6 mm i.d. packed with 10 μ m Partisil 10-ODS (Alltech and Associates) and the detection system was a Spectro-Monitor II model 1202 variable-wavelength UV-visible detector (Laboratory Data Control Co.). A component arrangement of the HPLC set-up⁹ is shown in Figure 1. Elution of samples was typically done with methanol/water in the range of 50/50 to 75/25 volume %.

HPLC was used to determine the contents of complex electrolysis solutions of the reduction of CS_2 . For a determination, a fraction of a milliliter of electrolysis solution was drawn into the barrel of a glass syringe through a six inch stainless steel needle. Then the needle was replaced, and an excess of methyl iodide was drawn into the syringe and the contents mixed. After 30-60 seconds the content of the syringe was injected onto the column.

H. Synthetic Work

1. 4,5-Bis(methylthio)-1,3-dithiole-2-thione, (10)

Carbon disulfide was electrochemically reduced in 0.4 M TBAI/DMF at ~ -1.8 to -2.0 V vs. an SCE for 12 to 18 hours.⁹² The CS_2 was added

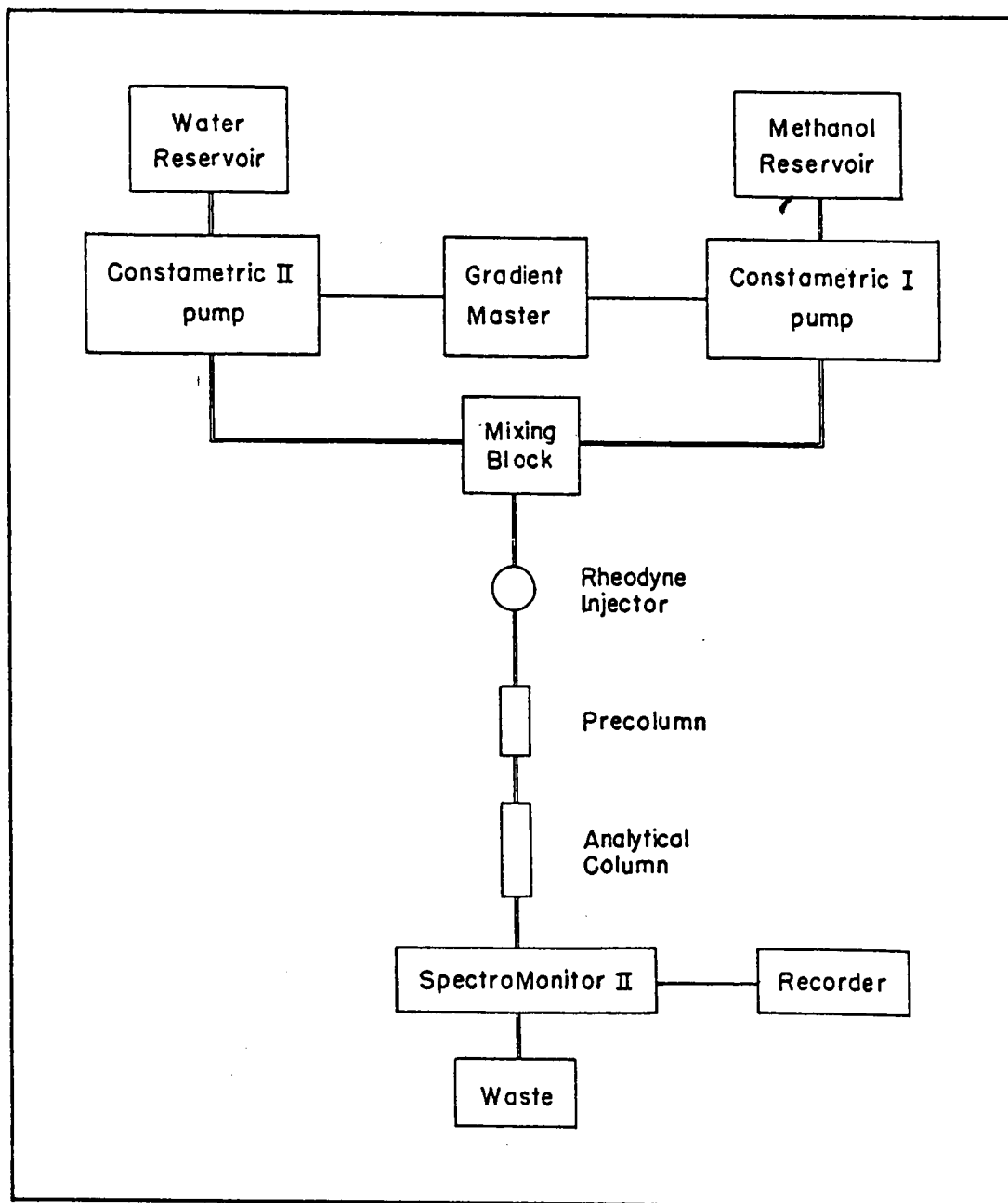
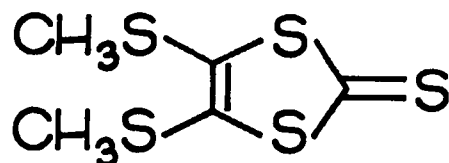


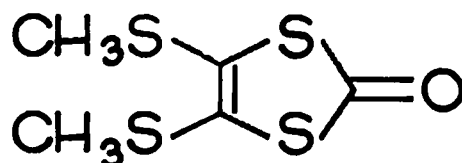
Figure 1. Component arrangement of the Laboratory Data Control HPLC.



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a couple of milliliters at a time and the electrolysis allowed to continue until ~50 milliequivalence of current had passed. The electrolysis solution was then transferred to a round bottom flask where CH_3I was added in slight excess and stirred for about 1 hour. The dark reddish-brown mixture was then poured into a separatory funnel containing 250 ml of distilled water. By the addition of 250 ml of methylene chloride, an organic layer forms which contains the desired product. The organic layer was washed five times with water followed by drying over MgSO_4 , and evaporating in a rotoevaporator to near dryness. The residue was then eluted with benzene from a neutral alumina column, and recrystallized from CH_3CN . Light brown needles were obtained in ~50% current yield which melted at 100-101°C.

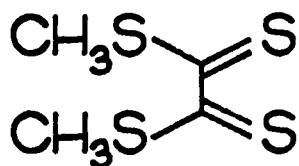
2. 4,5-Bis(methylthio)-1,3-dithiole-2-one, (25)



25

Thione (10), (4.5 g), prepared as above, was dissolved in 50 mL of chloroform. To this solution, 19.2 g of mercury (II) acetate dissolved in acetic acid was added dropwise to giving a three-fold excess of the mercury compound.^{100,101} After gentle warming and stirring for 48 hours, the reaction contents were filtered and poured into a separatory funnel containing 1 L of water, and extracted several times with chloroform. This organic phase was then evaporated to near dryness and chromatographed on a column of Kieselguhr 60 with carbon tetrachloride. The remaining substance was evaporated down and recrystallized from warm hexane, giving bright yellow needles in ~75-80% yield. MP = 63-64°C; UV-VIS, λ max = 285 nm; Mass spec, 210 (100%), 182 (85%), 135 (10.3%), 118 (34.1%), 103 (15.1%), 91 (63.3%); NMR, δ = 2.45.

3. Tetrathiooxalate dimethylester, (5)

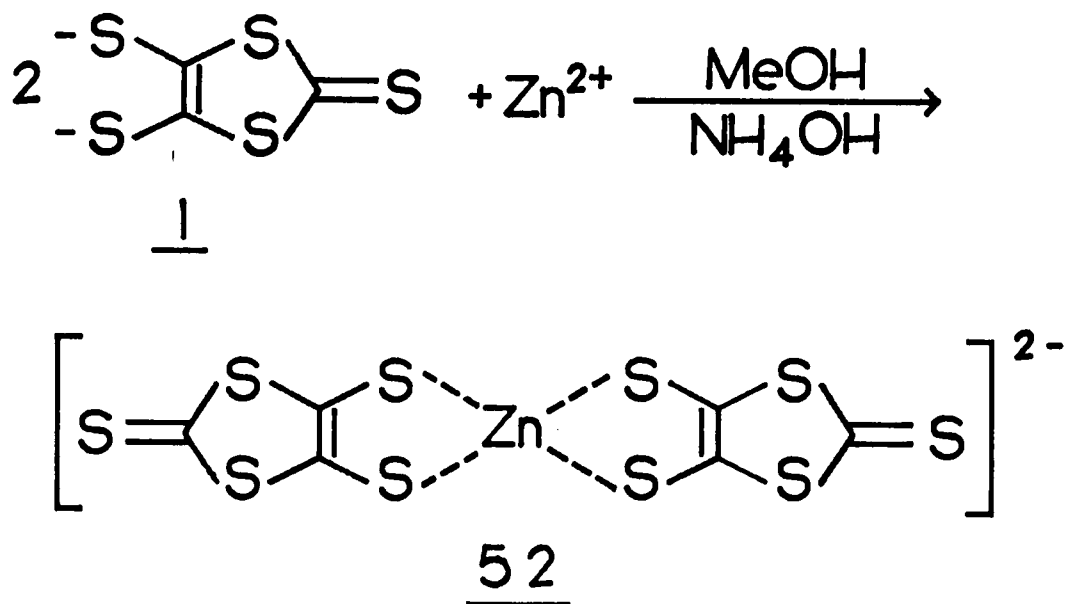


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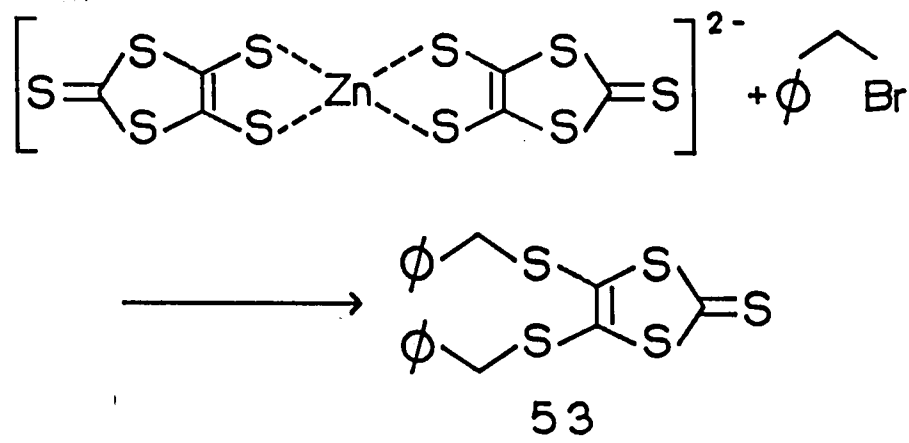
Approximately 2.5 g of 4,5-bis(methylthio)-1,3-dithiol-2-one (25) was dissolved in 100 mL of methylene chloride and irradiated in the photolysis cell previously described for 2 hours. The solution was then evaporated and the residue chromatographed on a column of Kieselguhr 60 with carbon tetrachloride. A foul smelling oil was obtained which matched the literature spectral characteristics of the desired

compound:¹¹ IR, 1045 cm⁻¹(s), 1415 (m), 1400 (m), 1312, 950, 778; Mass Spec, m/e=182 (38.5%), 118 (24.0), 103 (20%), 91 (100%), 88 (32.9%); NMR, δ = 2.65; UV-Vis, δ max = 362 nm.

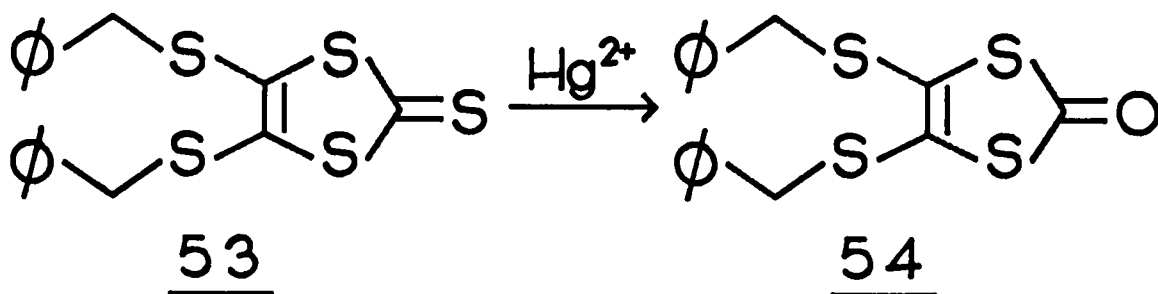
4. Tetra-n-butylammonium bis(4,5-dimercapto-1,3-dithiolen-2-thione)zincate (II), (52)



After an electrolysis was completed, the carbon disulfide reduction solution was poured into a round-bottomed flask containing 5 g of zinc chloride in 200 mL of MeOH and 200 mL of NH_4OH .⁹ The mixture, which immediately turned warm to the touch, was allowed to cool while being stirred overnight. The red crystals which precipitated out of solution were filtered, washed with cold water and recrystallized from hot methanol. UV-VIS, λ_{max} = 515 nm; MP = 174-175°C.

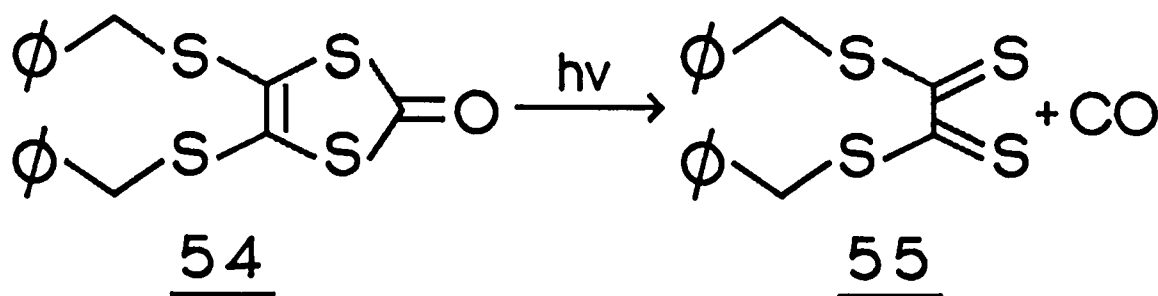
5. 4,5-Bis(benzylthio)-1,3-dithiole-2-thione, (53)

The zinc complex (4.0 g) complex was dissolved in 100 mL of acetone. Benzyl bromide was added dropwise (~ 2 mL) to the solution while stirring. After 3-4 hours, the reaction mixture turned from red to yellow, and the acetone was removed by evaporation. The residue was then dissolved into chloroform, washed three times with water, and evaporated to dryness. Recrystallization from hexane gave yellow needles in $\sim 50\%$ yield: MP = $110-111^{\circ}\text{C}$, UV-Vis $\lambda_{\text{max}} = 280$ nm; Mass Spec, $m/e = 378$ (65%), 334 (42%), 270 (42%), 287 (31%), 196 (38%), 91 (100%). This reaction did not go using benzyl chloride as the methylating agent.

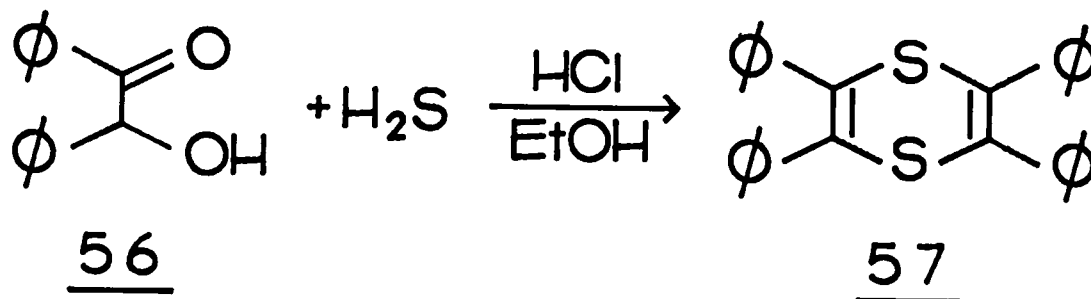
6. 4,5-Bis(benzylthio)-1,3-dithiole-2-one, (54)

The thione (5.0 g) was dissolved in 50 mL of CHCl_3 followed by the addition of 12 g $\text{Hg}(\text{OAc})_2$ dissolved in a minimum amount of acetic acid. After 48 hours, the reaction mixture was filtered and poured into a separatory funnel and washed three times with water. The chloroform was then removed by evaporation and the residue recrystallized from hexane. MP = 70-71°C; Mass Spec, m/e = 362 (43%), 334 (62%), 270 (28%), 271 (62%), 180 (30%), 91 (100%); UV-Vis, λ_{max} = 274 nm.

7. Attempted Synthesis of Tetrathiooxalate Dibenzylester, (55)



Approximately 4.0 g of compound 54 was dissolved in 100 mL of CH_2Cl_2 and placed in the photolysis cell. After irradiation for ~2 hours the CH_2Cl_2 was removed and the brown residue eluted from a column of Kieselguhr (60 mesh) with carbon tetrachloride. As with the dimethyl adduct, no crystalline material could be obtained. Fractions from the column, which were analysed by mass spectroscopy, failed to show a parent ion at m/e = 334, or fragments consistent with structure (55).

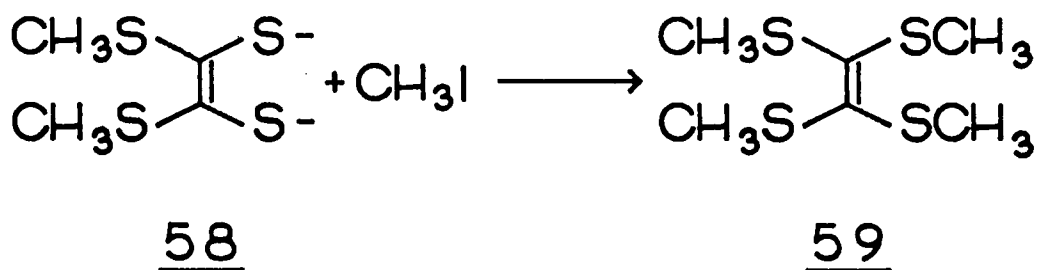
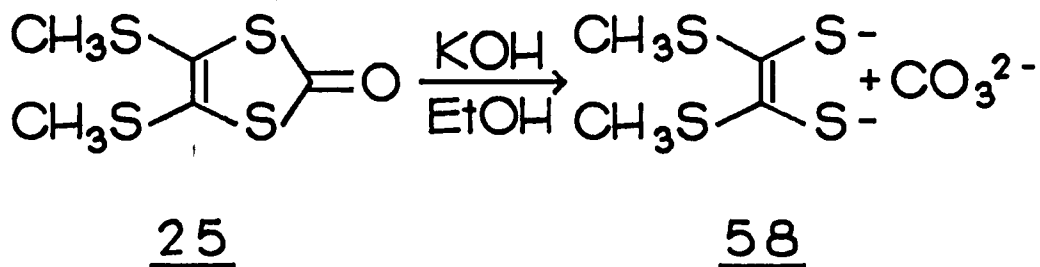
8. Tetraphenyldithiocyclohexadiene, (57)

Approximately 200 mL of ethanol was cooled with ice in a three-neck round bottom flask and bubbled with HCl gas.⁴² As the solution cooled from the heat of dissolution and approached 0°C , the bubbling of HCl was halted and 15 g of benzoin (56) was added. After the benzoin dissolved, H_2S was bubbled through the mixture for 2 hours using a gas dispersion tube. The reaction mixture was allowed to stand for 24 hours at which time the insoluble product was filtered off. The product was then recrystallized twice from a 50/50 mixture of CH_2Cl_2 and CHCl_3 , the yield was ~80%; MP = 180°C ; NMR: $\delta = 7.18$ singlet; Mass Spec, $m/e = 420$ (100%), 388 (18.4%), 178 (10.8%), 210 (2.2%).

9. Tetrakis(methylthio)ethylene, (59)

In an attempt to prove that the reduction of compound (25) followed by methylation leads to tetrakis(methylthio)ethylene, a control standard was prepared as follows. To 25 mL of 1 N KOH in ethanol, was added 500 milligrams of compound 25. The solution was stirred for 1 hour; during this time a white precipitate (presumably K_2CO_3) could be seen in the solution. After one hour, 75 mL of pentane was added to promote further precipitation. The solution was filtered to remove the precipitate and

excess CH_3I was added. After ca. 12 hours, the EtOH and pentane were evaporated under reduced pressure and the product dissolved in CHCl_3 . Recrystallization from methanol gave yellow crystals: MP, 60-61°C; NMR, $\delta = 2.38$; Mass Spec, $m/e = 212$ (79%), 103 (66%), 150 (48%), 118 (100%), 91 (75%); ESR, $g = 2.0111$.



10. Tetrakis(methylthio)ethylene from the Electrochemical Reduction of (25)

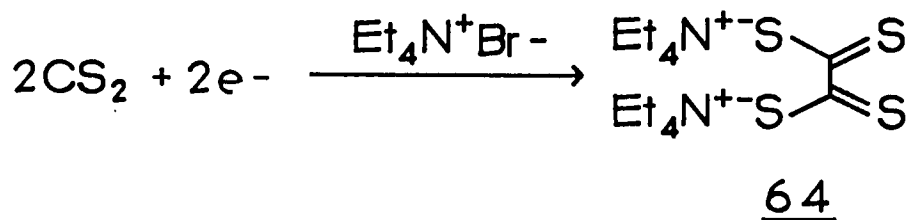
To prepare 59 electrochemically, approximately 0.2 g of 25 was reduced at -2.4 V vs. Ag/Ag^+ in CH_3CN and 0.1 M TEAP. After an equivalent amount of current has passed (~ 4 hrs), CH_3I was added, and the mixture stirred. The cell contents were then evaporated to dryness, and the product was dissolved in chloroform to separate it from supporting electrolyte. After passing the product down a 12' column of neutral alumina, the chloroform was evaporated, and the small amount of product oil was partially dissolved either in a deuterated solvent for NMR

determination, or in methanol for the mass spectral analysis. While the percentages for peak intensities varied from those observed for the known compound described above, the correct m/e values were clearly present, $M/e = 212$ (32%), 165 (24%), 150 (18%), 118 (49%), 91 (22%). The $E_{1/2}$, NMR and ESR data also agreed with known values.¹⁰²

11. Tetrakis(methylthio)ethylene from the Electrochemical Reduction of Dimethyl-tetrathiooxalate, (5)

A spatula was preweighed before dipping its end into the compound (5) and reweighing. Typically, about 0.1 g was transferred to a coulometric cell containing $\text{CH}_3\text{CN}/\text{TEAP}$. Compound 5 had a very limited solubility in CH_3CN , preventing easy dissolution. The sample was electrolyzed at -1.8 V vs. Ag/Ag^+ followed by methylation with CH_3I added directly to the cell. The cell contents were then evaporated to dryness, and the products dissolved in ether. The ether extract was washed three times with distilled water and dried over K_2CO_3 . Evaporation of the ether gave a light brown oil: Mass spec, $m/e = 212$ (41%), 150 (21%), 118 (60%), 91 (31%). The $E_{1/2}$, HPLC and ESR analysis of this product matched the results obtained for compound 59.

12. Preparation of the Tetrathiooxalate Salt (64)



SCHEME 14

Approximately 50 mL of CH_3CN that was 0.2 M in TEABr was added to an electrochemical cell. In this solution, a platinum button electrode was used to electrolyze CS_2 at -1.8 V vs. SCE until the surface of the button was covered with solid crystals.^{103,104} The electrolysis was then stopped, and the electrode removed. The crystals were lightly washed with clean CH_3CN before further treatment. A cyclic voltammogram of these crystals transferred to clean CH_3CN is shown in Figure 2. Larger quantities could be prepared by using a platinum grid electrode. Electrolysis times were very long, typically requiring 18-20 hours to pass 9-11 milliequivalents of charge.

13. Product Characterization from the Oxidation of 4,5-bis(methylthio)-1,3-dithiole-2-one, (25):

Approximately 0.2 g of compound 25 was oxidized at 1.1 V vs. Ag/Ag^+ . Isolation of the product was achieved by evaporation of the solvent (acetonitrile), and dissolution of the product into ether. The supporting electrolyte is only sparingly soluble in the latter solvent. The ether extract was washed thoroughly with saturated sodium bicarbonate, followed by a distilled water wash, and finally dried over K_2CO_3 . Evaporation of the ether on standing afforded a yellow oil: UV-vis, $\lambda_{\text{max}} = 273 \text{ nm}$; IR, 1020 cm^{-1} (S); mass. spec., $m/e = 178$ (22%), 210 (100%), 226 (29%), 179 (19%), 198 (37%).

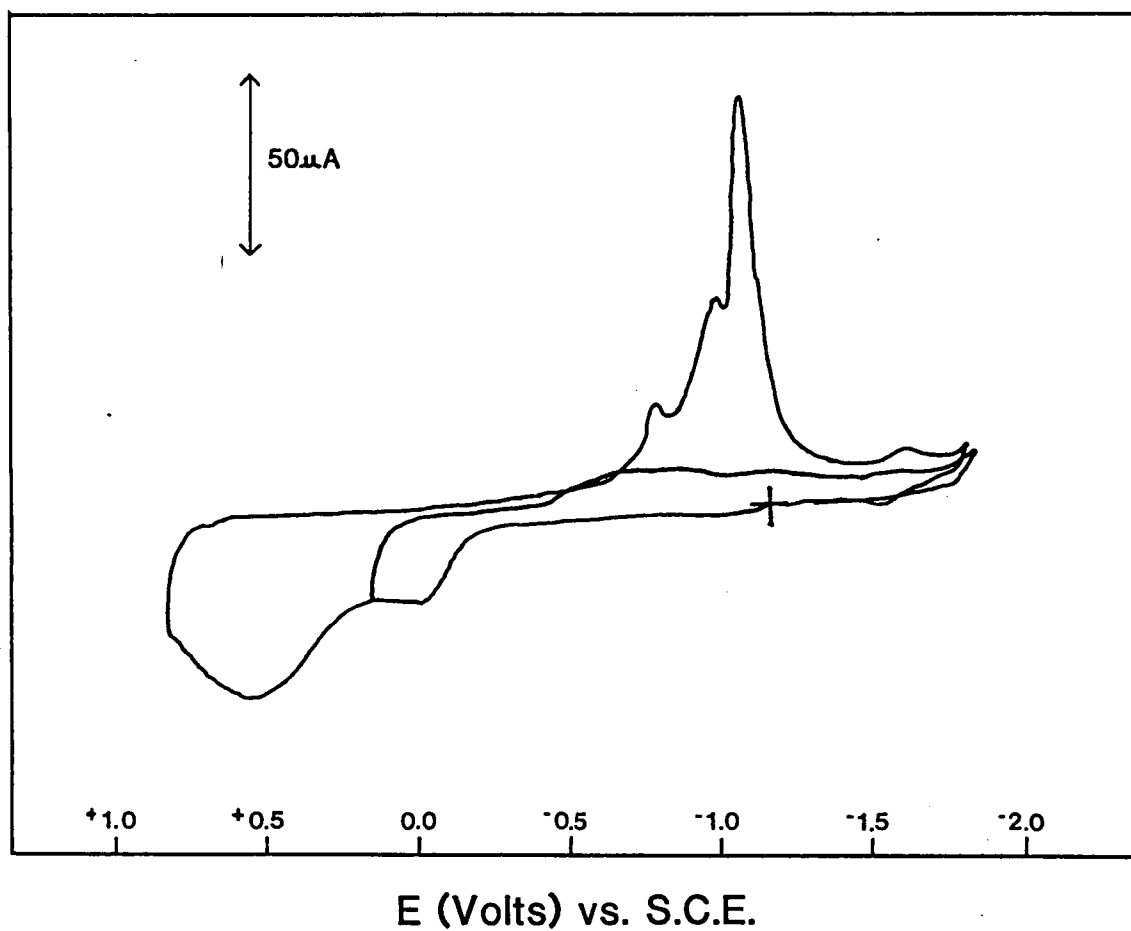


Figure 2. Cyclic voltammogram of $(\text{TEA})_2 \text{C}_2\text{S}_4^{2-}$ salt in 0.1 M TEAP/ CH_3CN . Platinum electrode, sweep rate 200 mV sec^{-1} , initial potential -1.2 V , initial sweep positive.

CHAPTER III

RESULTS AND DISCUSSION

A. More on the Electrochemical Reduction of CS₂

As discussed in Chapter I, the mechanism of reaction for product formation in CS₂ reduction solutions has been published under three variations since Wawzonek and Heilmann's paper in 1974. High performance liquid chromatography was applied to this problem in conjunction with electrochemical and mass spectral techniques in hopes of clarifying some of the mechanistic details of this reduction.

A typical cyclic voltammogram of CS₂ in DMF/0.1 M TEABF₄ is shown in Figure 3. The details of the voltammetry are unexceptional and reveal only a broad irreversible reduction wave at $E_p^C = -2.2$ V vs. a saturated calomel electrode (SCE). On the reverse scan, poorly defined product oxidation waves are evident around 0.0 V followed by other anodic currents at more positive potentials. Multiple cycles through the product waves indicate that oxidation of reduction products films and passivates the electrode surface. Hence, the lack of information retrievable by cyclic voltammetry makes it a poor choice for following the electrolysis products.

High performance liquid chromatography, on the other hand, discloses the complex nature of these electrolysis solutions not revealed by cyclic voltammetry. Figure 4 shows a typical chromatogram of a CS₂ reduction solution sampled during electrolysis, and recorded at the

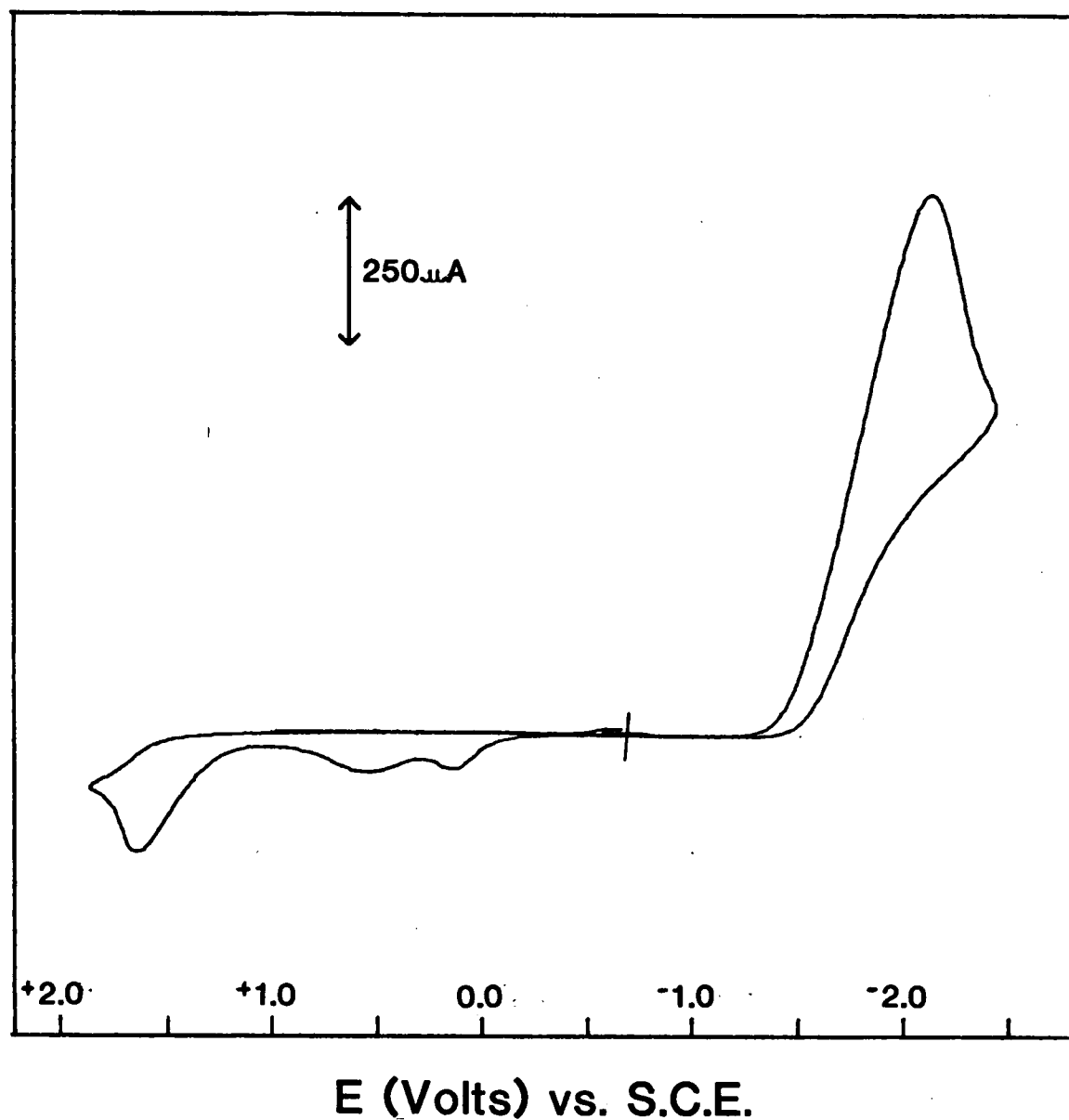


Figure 3. Cyclic voltammogram of CS_2 in 0.1 M $\text{TEABF}_4/\text{DMF}$. Platinum electrode, sweep rate 100 mV sec^{-1} , neutral alumina added.

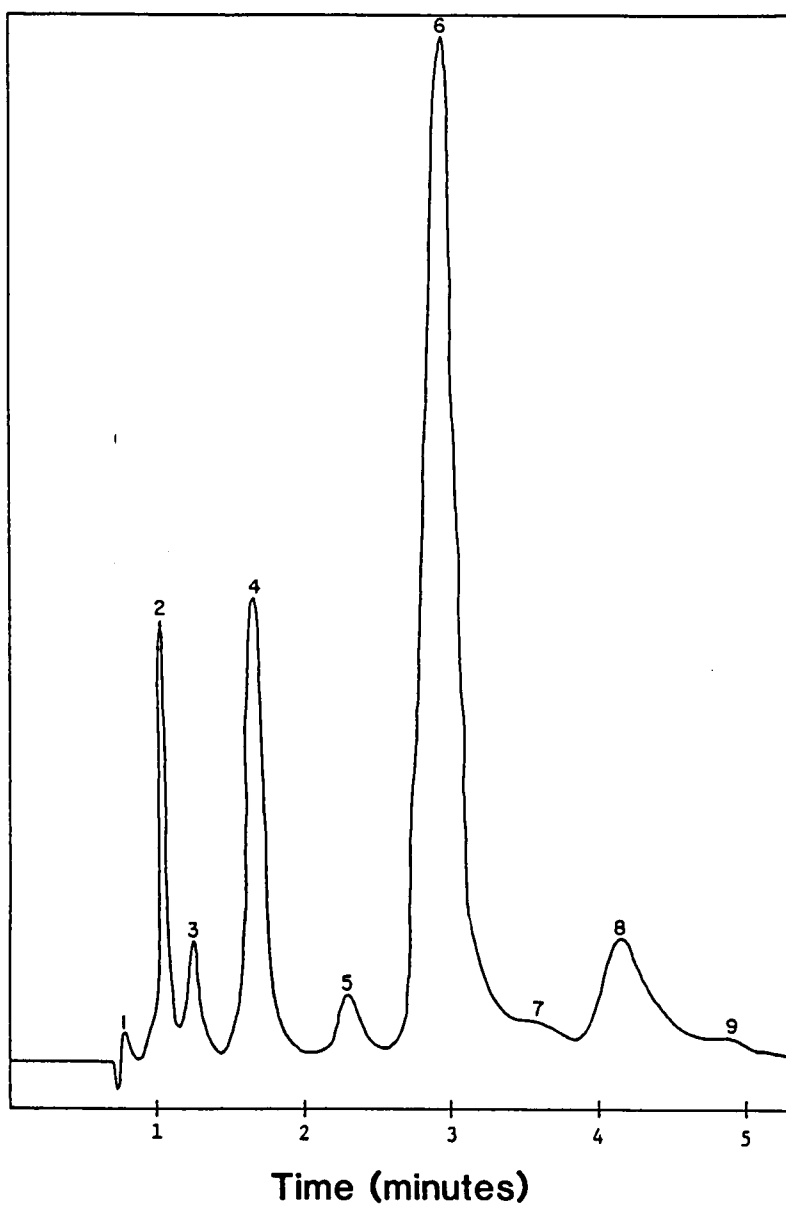
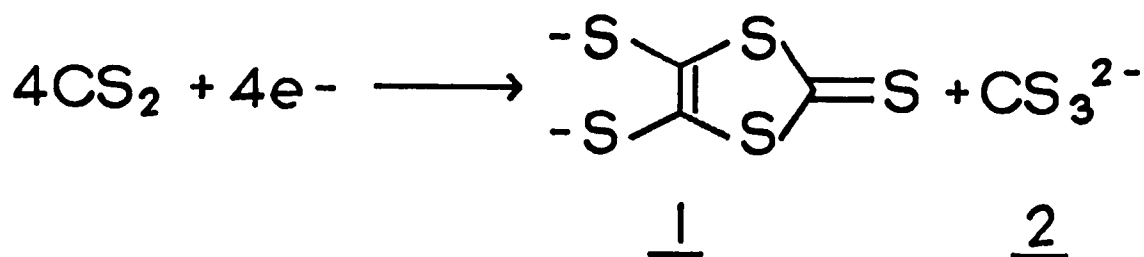


Figure 4.1 Chromatogram of CS_2 reduction solution at 330 nm. Flow rate 5 ml min^{-1} , 50:50 methanol/water, 1.0 absorbance full scale.

absorption maximum of compound 6 (330 nm). Methylation of anions in the solution was carried out according to the procedures described in the experimental section (page 42). A chromatogram of the same electrolysis solution is shown in Figure 5 recorded at the absorption maximum of compound 10 (p. 7) (412 nm). The immediate observation is that the electrolysis solution is more complicated than indicated by Equation 1. Nine absorbing species are designated, but peaks #1, #2, and #3 can readily be assigned to solvent and starting products: DMF, MeI and CS₂, respectively. Identification of these peaks and some of the product peaks was possible by comparison of their individual retention times with chromatograms of a standard reference material of the same compound in DMF. The remaining six peaks are all presumably due to products of electrode processes, and two of the peaks should correspond to the products previously isolated from these reduction solutions. While a variety of products and intermediates have been reported, the following stoichiometry can be realized under suitable conditions:



EQUATION 1

Dianion 1 is the species of synthetic interest in this reduction, and can be isolated in almost quantitative yield by either alkali metal

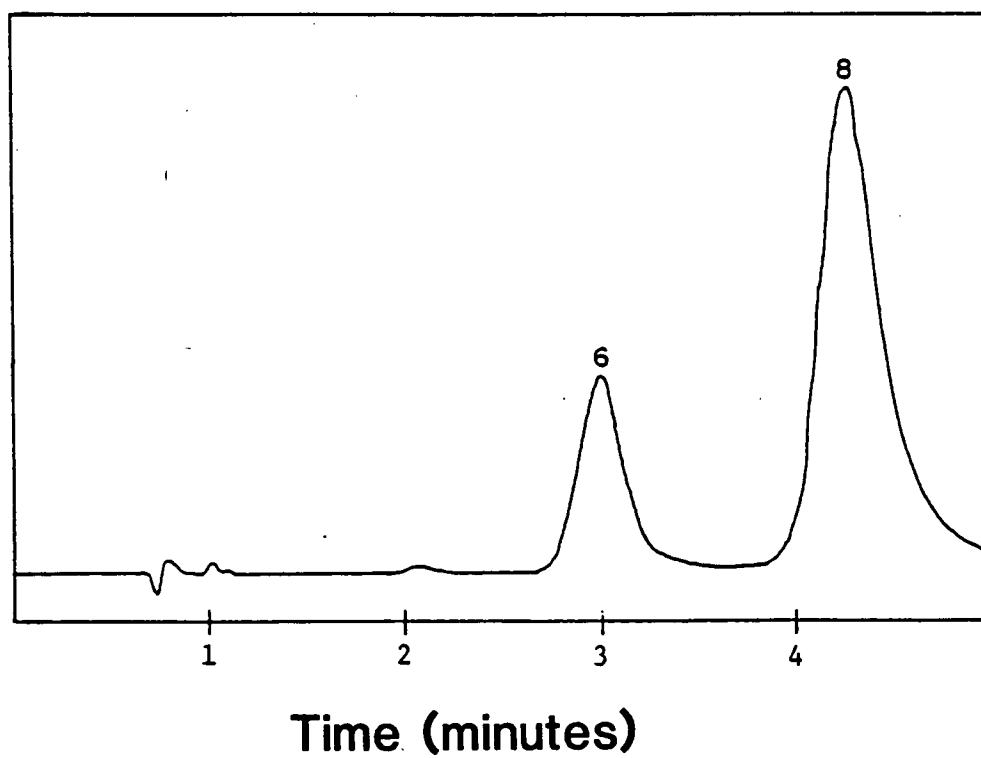
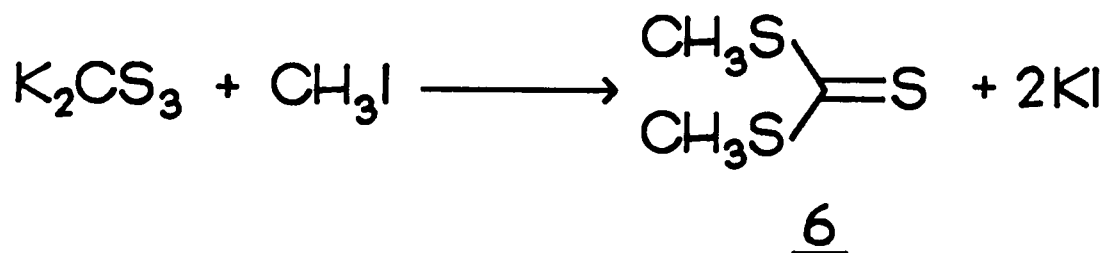


Figure 5. Chromatogram of CS_2 reduction solution at 412 nm. Flow rate 5.0 ml min^{-1} , 50:50 methanol/water, 1.0 absorbance full scale.

reduction⁴ or by electrochemical reduction in DMF or acetonitrile at a platinum working electrode.¹⁴ Indeed peaks #4 and #8 (p. 57) were assigned to species 1 and 2 using standards. Potassium trithiocarbonate in DMF was methylated with CH₃I to generate the standard for peak #4, while an independent synthesis of thione 10 provided the standard for peak #8.

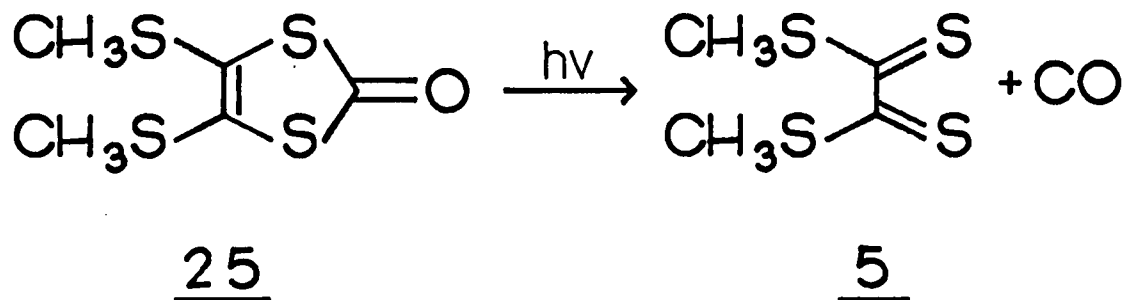


Dimethyltrithiocarbonate (peak #4) is a major electrolysis product at more negative potentials and longer electrolysis times, but is not present in the solutions sampled early in the electrolysis. Peak #8, corresponding to compound 10 is shown in Figure 5 to dominate the chromatogram at 412 nm.

An outstanding feature of both Figures 4 and 5 is the appearance of peak #6 which apparently represents a major, if not the principal electrolysis product under these conditions. In assigning the species responsible for peak #6 several likely species were ruled out as electrolysis products by analyzing standards of the suspected compounds. Neither methyl disulfide nor dimethylsulfide gave peaks which matched those of Figure 4 or 5. Therefore S₂²⁻ and S₂²⁻ can be eliminated as possible electrolysis products under these conditions.⁹ Likewise S₈ was analyzed and found not to absorb light in this area of the visible spectrum, indicating that none of the unassigned peaks, including peak #6

were due to elemental sulfur. Interestingly, some S_8 is usually obtained in the work-up of preparative scale electrolysis solutions, even though S_8 is reduced at the electrolysis potential used in these experiments.

Peak #6 was assigned as the dimethyl ester of tetrathiooxalaic acid (compound 5). This assignment was established by an independent synthesis of compound 5 using photolytic decarbonylation of 4,5-dimercapto-2-oxo-1,3-dithiophene (compound 25) following the procedure reported by Kissel et al.¹¹



A chromatogram of the photolysis product obtained at the absorption maximum of compound 5 (362 nm) is shown in Figure 6. The retention volume (V_R) for dimethyltetrathiooxalate is within 2% of the V_R for peak #6. Further support for this assignment is made by running the chromatograms of the electrolysis solution at varying wavelengths close to the maximum wavelength in the absorption spectrum of compound 5 (362 nm). As expected, peak #6 had an absorption maximum consistent with that of the known compound of 5.

Important information regarding the role of the species assigned to peak #6 is obtained from chromatograms of electrolysis solutions

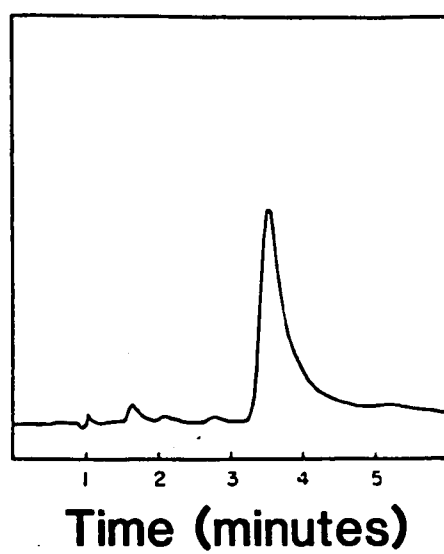
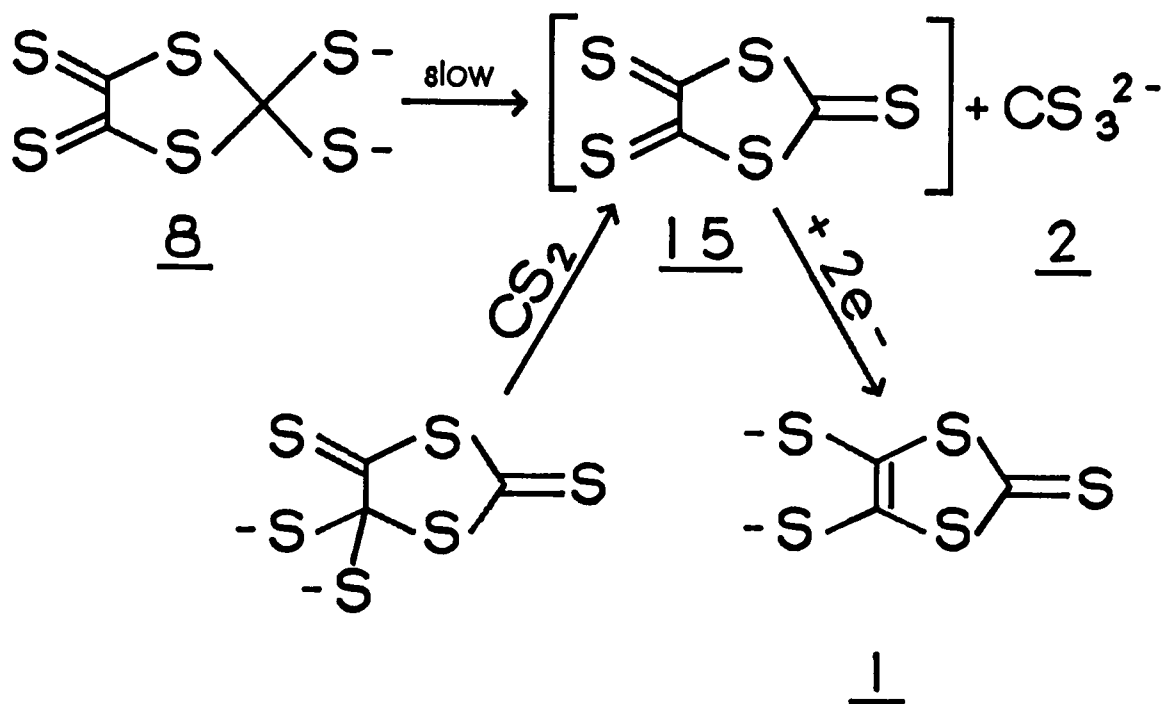


Figure 6. Chromatogram of dimethyltetraathiooxalate at 362 nm. Flow rate 4.0 ml min^{-1} , 50:50 methanol/water, 0.5 absorbance full scale.

obtained over a period of time after disconnecting the working electrode. Figure 7 shows a chromatogram of the same electrolysis solution as in Figure 4, obtained more than 24 hours after the electrolysis was stopped. Peak #6 has disappeared completely, while peak #4 assigned to compound 6 has increased. This observation further indicates that the trithiocarbonate dianion is not formed directly in the electrode reaction, but arises from a slow follow-up reaction involving the species which gives rise to peak #6 in the chromatogram. Reaction schemes consistent with this behavior have been suggested previously^{4,5} (Scheme 12).



SCHEME 12

Mass spectrometry was also used to analyze the methylated syringe contents after evaporation of the solvent. Tables I and II show the

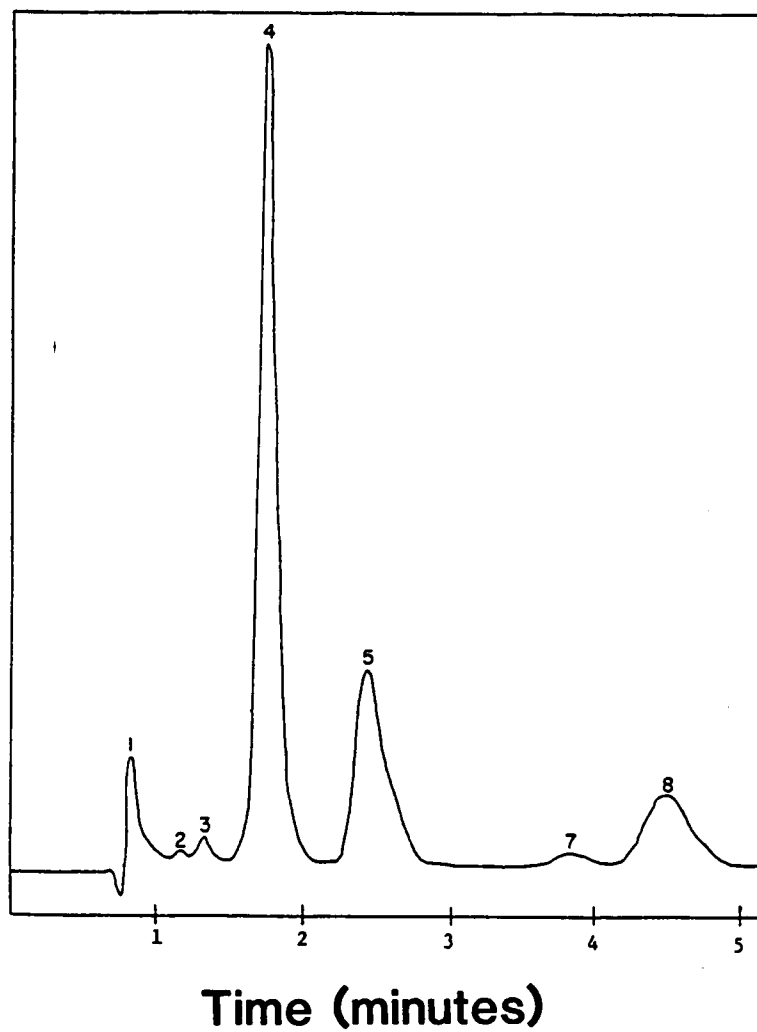
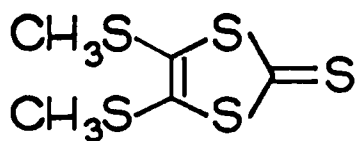
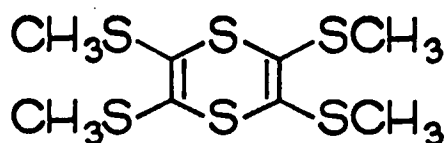


Figure 7. Chromatogram of CS_2 reduction solution more than 24 hours after disconnecting the working electrode at 330 nm. Flow rate 5.0 ml min^{-1} , 50:50 methanol/water, 1.0 absorbance full scale.

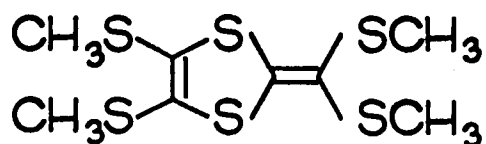
Table I. CS₂ Electrolysis Solution
 Parent Ion Assignments for the Molecular Weights (MW) and
 Detector Intensities (I) Shown Under Each Structure



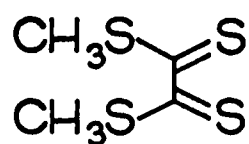
M.W. = 226
 I = 82.6%



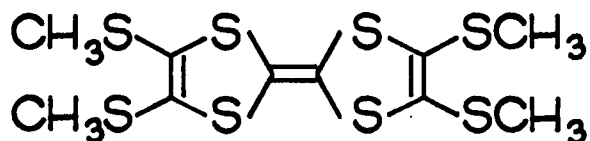
M.W. = 300
 I = 21.4%



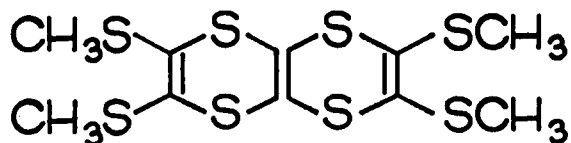
M.W. = 300
 I = 21.4%



M.W. = 182
 I = 16.4%



M.W. = 388
 I = 6.4%

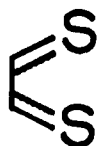


M.W. = 388
 I = 6.4%

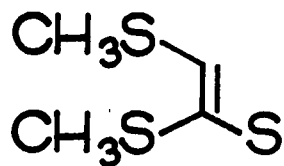
Table II. Fragment Ions Assignments Consistent with Parent
Ions in Table I



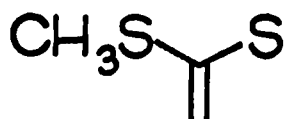
M.W. = 91
I = 100%



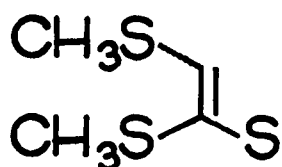
M.W. = 88
I = 47.8%



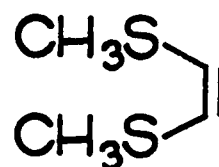
M.W. = 135
I = 36.8%



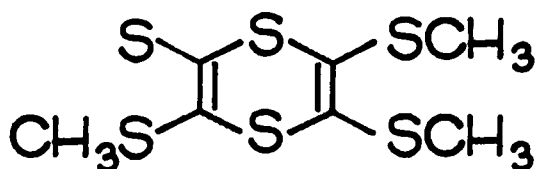
M.W. = 103
I = 33.1%



M.W. = 150
I = 31.4%



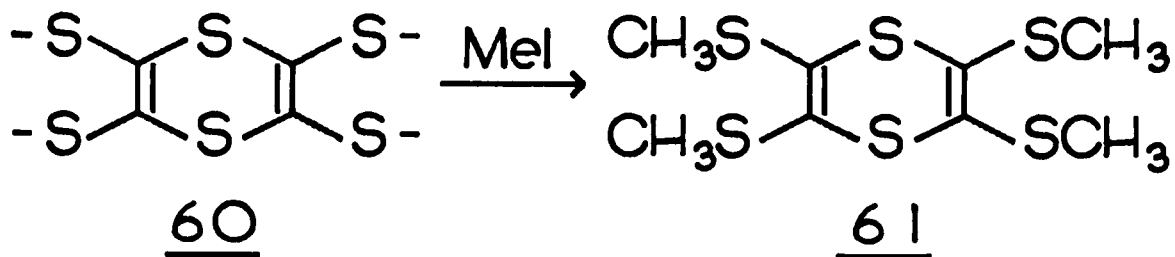
M.W. = 118
I = 24%



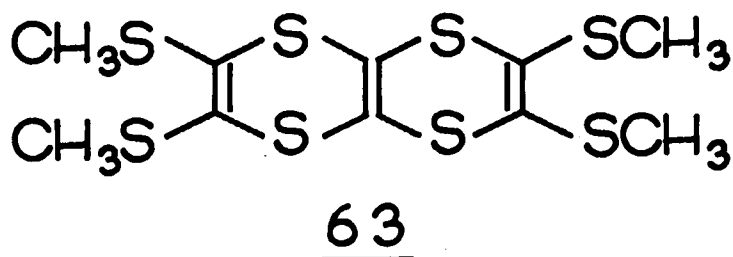
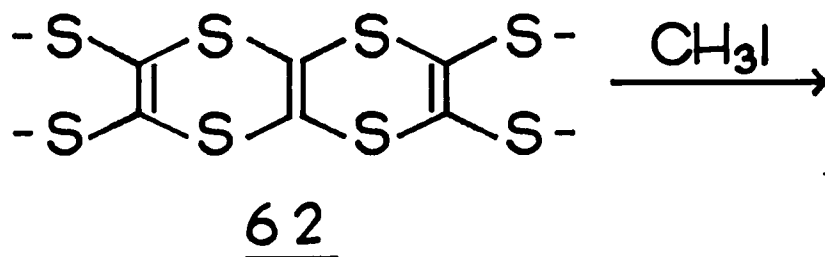
M.W. = 285
I = 30.1%

most probable parent ion species and ensuing fragment ions observed when a methylated sample from the electrolysis is ionized by electron impact (70 eV) and its mass spectrum recorded. While there were several m/e ions with values less than 100, the predominant m/e values can be assigned to fragment structures consistent with those expected. All ions in Tables I and II are assumed to be singly charged cations. In addition to the expected product ion peaks for compounds 1 and 2, the mass spectra indicated that the electrolysis solutions contain significant amounts of carbon-sulfide anions with molecular weights greater than that of compound 1.

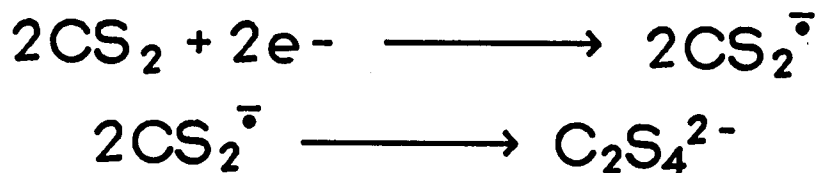
Specifically, a relatively intense peak at $m/z = 300$ (21.4%) indicates a $C_4S_6^{4-}$ electrolysis product for which the tetraanion 60 is a possible structure.



Furthermore, the small m/z peak at 388 suggests the existence of the next oligomeric species in the series (tetraanion 62).



These results demonstrate that the tetrathiooxalate dianion has an intermediary role in the CS_2 reduction process, which strongly implies that the electrode reaction proceeds via coupling of CS_2 radical anions¹⁰:

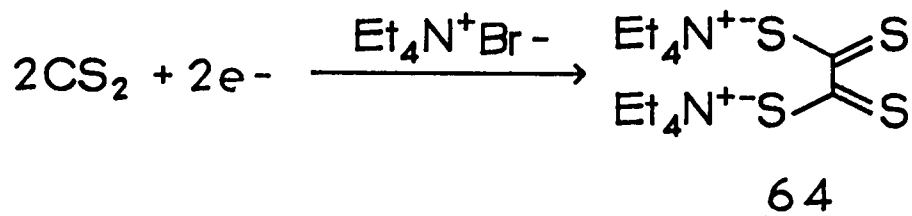


SCHEME 13

The $\text{C}_2\text{S}_4^{2-}$ species is not stable, but reacts further to give trithio-carbonate dianion and other species of undetermined nature. The sequence of steps leading to compound 1 in the reduction process remains to be elucidated, but it can be inferred from Figure 7 (p. 63), which shows that the peak corresponding to 10 does not increase as peak #4 disappears, that decomposition of $\text{C}_2\text{S}_4^{2-}$ does not lead directly to the

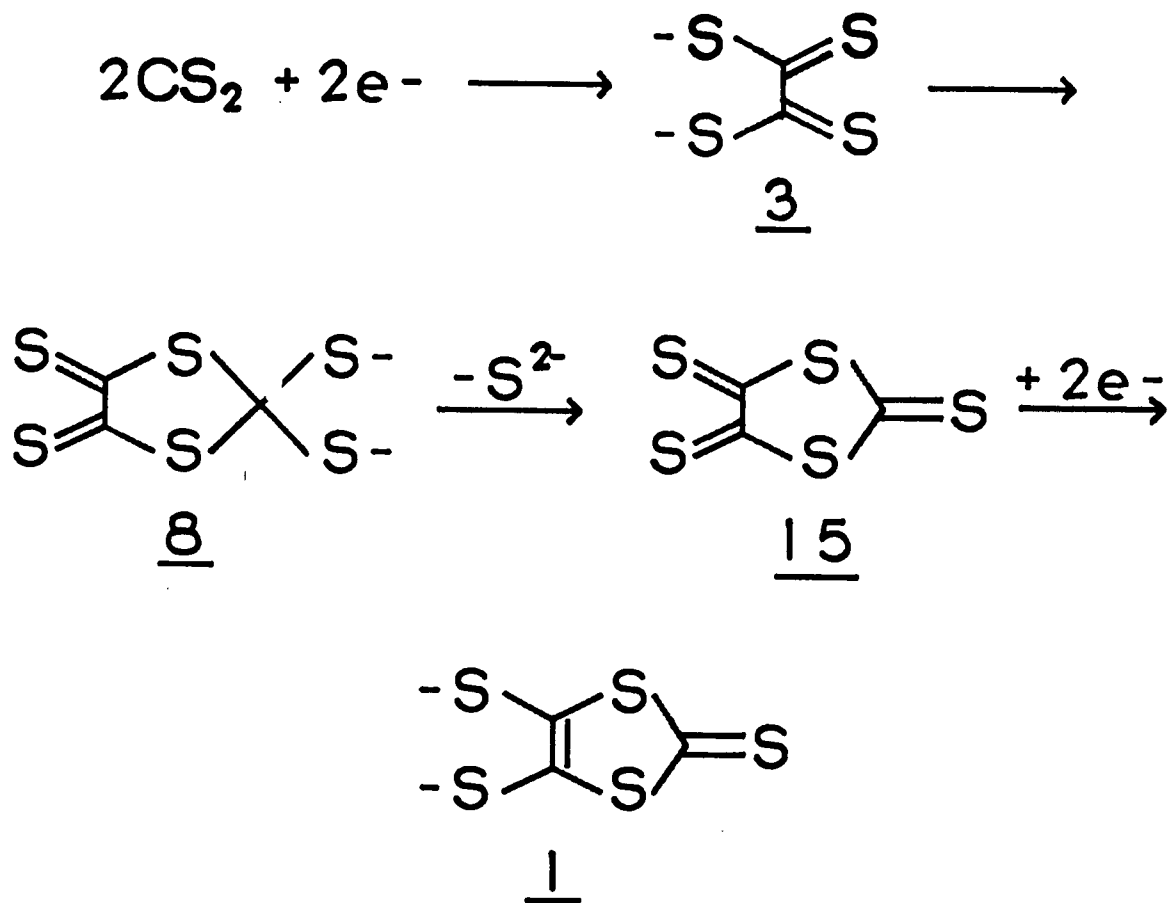
1,3-dithiole ring system of 1. These results are not consistent with the suggested mechanisms put forth by Bontempelli et al.,⁷ or Jeroschewski,⁶ but corroborates the suggested intermediate step of Wawzonek and Heilmann.⁵ The CS₂ coupling appears to be directly analogous to CO₂ anion radicals which couple in nonaqueous solvents to give the oxalate dianion.¹⁰⁵

Subsequent to the publication of Lodmell et al.,¹⁰ Jeroschewski found that the C₂S₄²⁻ dianion could be electrocrystallized out of solution by reducing CS₂ in acetonitrile using tetraethylammonium bromide and a mercury cathode.¹⁰³



SCHEME 14

Lund and coworkers later found that by treating the tetrathiooxalate salt (64) with excess CS₂ in acetonitrile followed by methylation, compound 10 could be formed in 75-90% yield and dimethyl trithiocarbonate in 10-25% yield.²⁸ No 10 was isolated, however, by the treatment of CS₃²⁻ with CS in cold methanol followed by methylation. In fact, Lund showed that CS was incorrectly reported by Bontempelli et al. to be involved in the mechanistic scheme of CS₂ reduction. He reported Scheme 15, which is like Scheme 2, p. 9, to be the most likely pathway for the formation of 10, consistent with the research from this laboratory.



SCHEME 15

B. Oxidation of 4,5-Bis(Methylthio)-1,3-Dithiole-2-One (Compound 25)

The synthesis of compound 5 according to Kissel et al. involved the photolytic decarbonylation of 25 (p. 45) using ultraviolet light.¹¹ Mass spectral data obtained on the crude product from this process indicate that a complex mixture of carbon and sulfur containing products was formed in addition to the desired product, dimethyltetrathiooxalate.

Product isolation from this process afforded an oil which matched spectral characteristics with literature data for 5, but never afforded crystalline material. Often the product mixture was viewed as intractable. As an alternative approach, methylation of Jeroschewski's tetraethylammonium salt of tetrathiooxalate (compound 64, p. 68) seemed promising. But as we noted, and he later reported, methylation of 64 rendered the same complex mixture of products obtained via the photolysis of 25.¹⁰⁴ This difficulty, coupled with the problem that CS₂ is reduced very slowly in the presence of tetraethylammonium salts as opposed to tetrabutylammonium salts, suggests that synthesis of 5 via 64 will not be successful. In seeking an alternative route for the preparation of 5, electrochemical oxidation and reduction of compound 25 were investigated. Perhaps a simpler electrochemical route existed.

Figure 8 shows a typical cyclic voltammogram of 25 in acetonitrile and TEAP. Scanning in the anodic direction the CV exhibits a reversible oxidation compatible with other 1,3-dithiolene ring systems.^{106,107} The $E_{1/2}$ for the first oxidation falls around 0.99 V vs Ag/Ag⁺. The first wave shows some reversible behavior, but the radical cation is apparently consumed by the more anodic oxidation processes occurring in the second wave.

This conclusion is drawn from the observation that the peak current at the reduction peak at +0.95 V is significantly lowered by scanning past ox₁ through ox₂. In view of the fact that a well defined ESR spectrum was obtained using the flow cell arrangement described on page 39, ox₁ is probably a one-electron process. A seven line ESR spectrum ($a_H =$

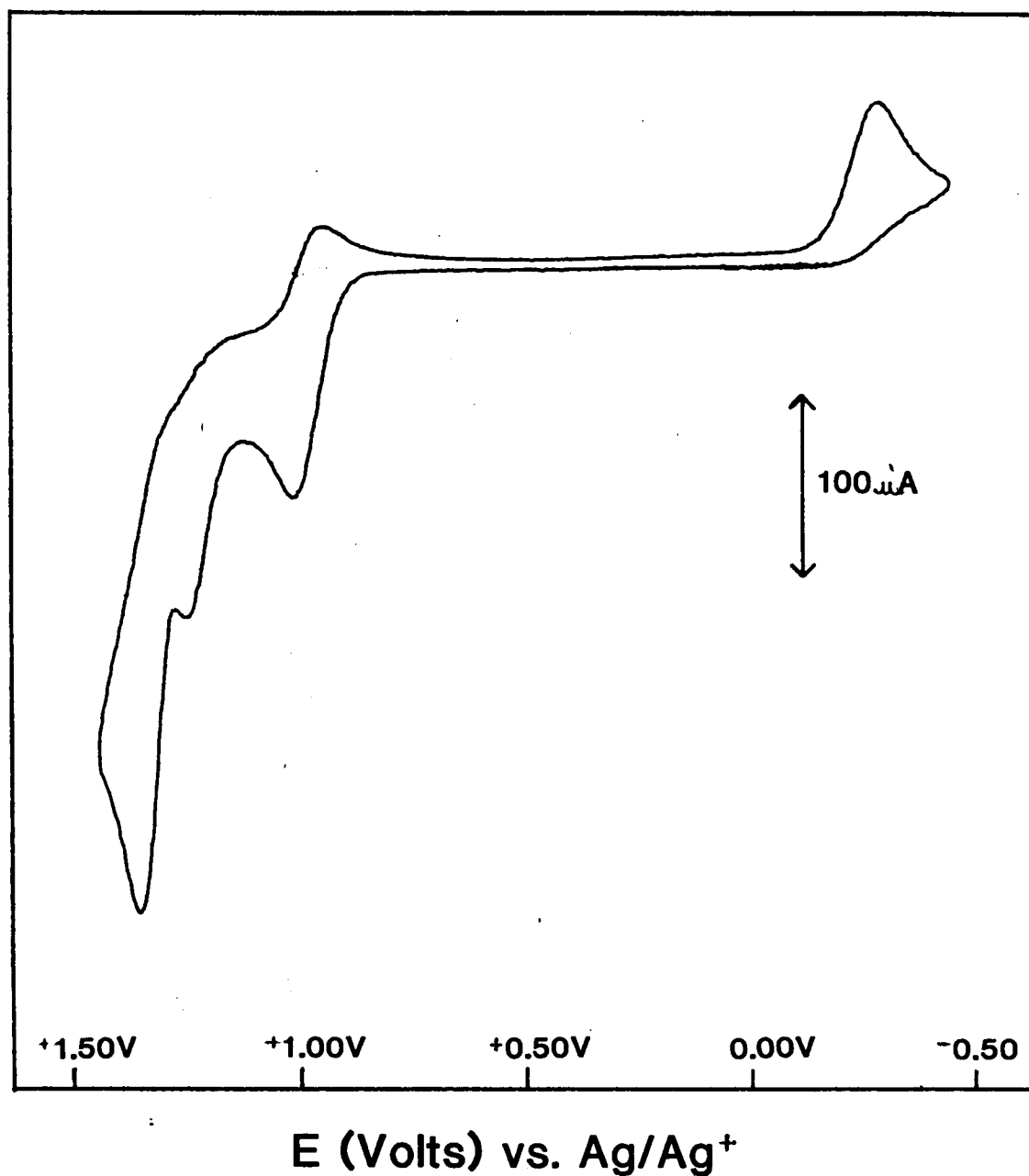


Figure 8. Cyclic voltammogram of 4,5-bis(methylthio)-1,3-dithiole-2-one in 0.1 M TEAP/CH₃CN. Platinum electrode, scan rate 100 mV sec⁻¹, neutral alumina added, initial potential 0.0 V, initial sweep positive.

4.5 gauss, $g = 2.0076$) was observed by setting the potential of the working electrode anywhere on the rising portion of the first voltammetric wave. The indication is that the cationic charge is well delocalized across the molecule causing the radical to be relatively stable under these conditions. However, coulometric analysis carried out at $E \approx +0.99V$ indicated that $n = 2$ Faradays per mole was required for this oxidation process. Exhaustive electrolysis however, typically took several hours to complete, and while the lime green radical cation persisted initially, the green color faded to a light yellow towards the end of the electrolysis. Figure 9 shows that after completion of electrolysis, no starting compound remained, and that the new product cannot be reduced back to the starting products. The shoulder occurring on the second wave at $+1.27 V$ also disappears after electrolysis.

Liquid chromatography was also used to monitor the progress of the electrolysis. The starting compound (25) has a λ_{max} at 330 nm and a retention volume of 17.0 mL while the product shows a λ_{max} at 273 nm and a much smaller retention volume (6.0 mL). The peak at 6.0 mL is the only one occurring after the electrolysis is completed, indicating that only a single product is formed, and that no detectable starting product remains.

Mass spectral data indicated that several of the fragments previously observed for the parent compound (25) had an additional 16 amu in the electrolysis product suggesting possible sulfoxide formation on the 1,3-dithiole ring.¹⁰⁸ The infrared spectrum (KBr) of the electrolysis product showed a strong band in the 9.7-9.9 μm region, attesting to the presence of the sulfoxide function.¹⁰⁹⁻¹¹¹

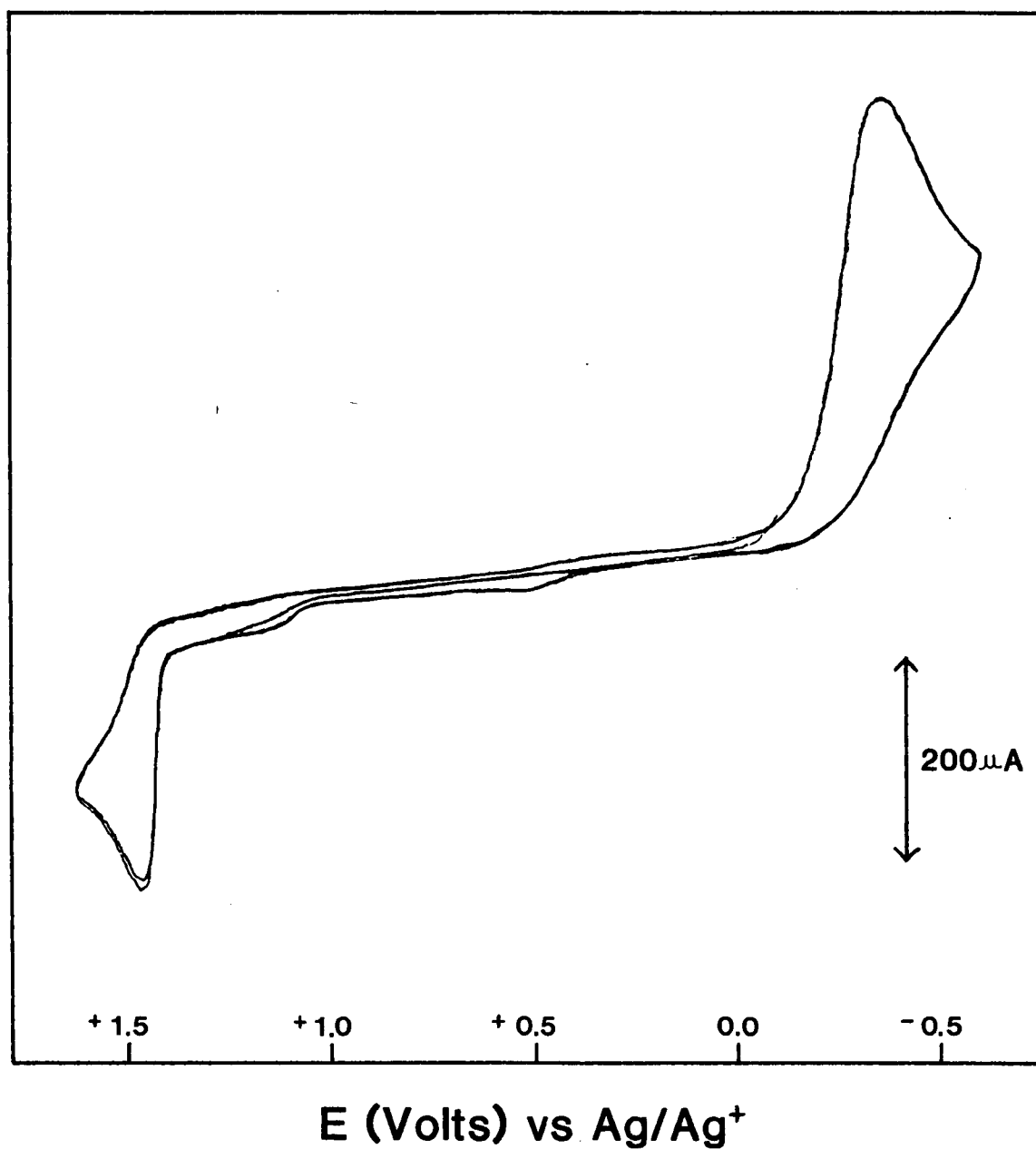
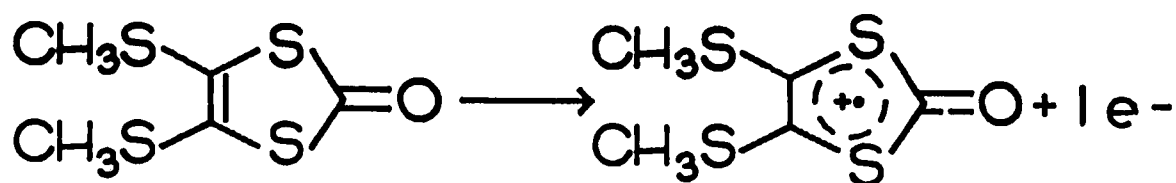
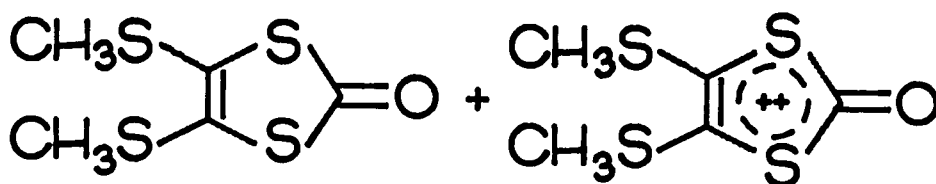
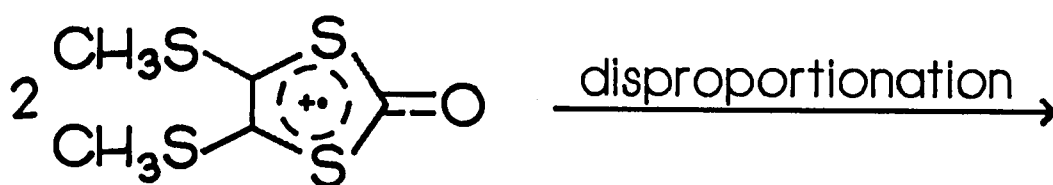


Figure 9. Cyclic voltammogram of 4,5-bis(methylthio)-1,3-dithiole-2-one after exhaustive electrolysis at +1.0 V in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 200 mV sec⁻¹.

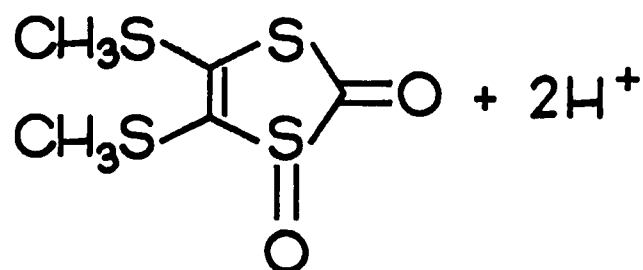
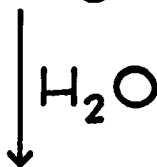
An ECCC scheme which fits the observed data is shown below. The heterogeneous formation of a radical cation is followed by a disproportionation reaction reforming the neutral substrate and a dication. The dication reacts further to scavenge the residual water in the



25



25



SCHEME 16

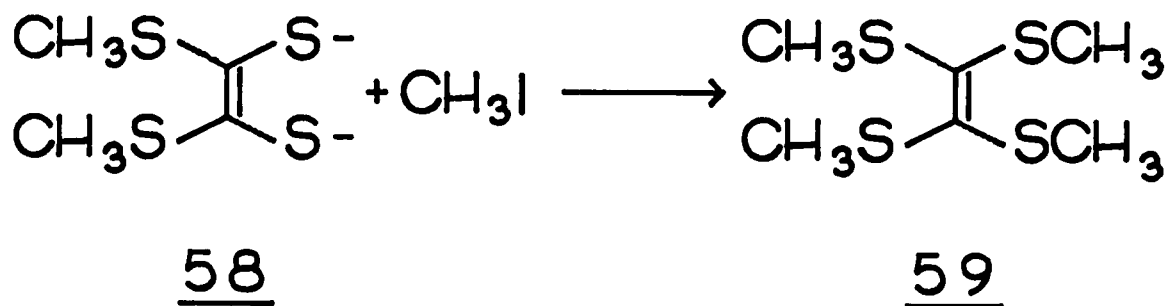
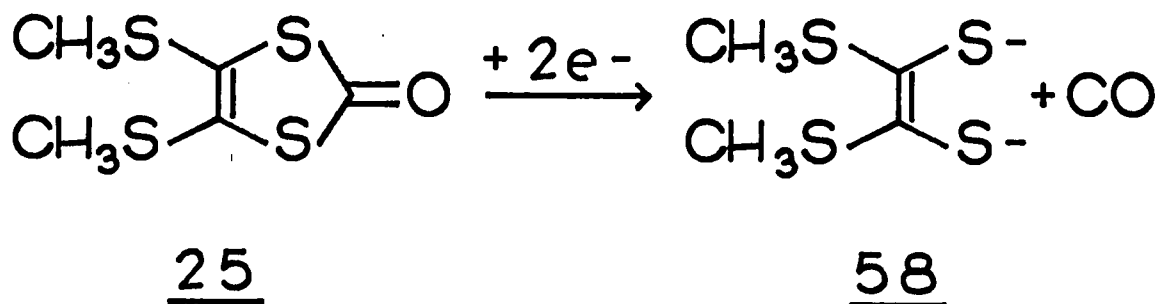
acetonitrile to form the sulfoxide upon deprotonation. Assignment of the reduction wave at -0.42 V on platinum is made to the reduction of protons (H^+) released in the reaction and is consistent with this scheme. Credibility is added to this assignment in view of the enhancement observed for the wave at -0.42 V by the addition of perchloric acid to the CV cell. The shoulder at $+1.27$ V can be tentatively assigned to formation of the dication based on its disappearance after exhaustive coulometry which also causes the net decrease in current at the second oxidation wave.

Information was sought regarding the oxidation products of the second ox_2 wave using fast sweep cyclic voltammetry and ultra-dry conditions.^{112,113} Cyclic voltammograms run over a broad range of sweep rates (0.10 - 50.0 V/sec) in dry acetonitrile with neutral alumina added¹¹⁴ to scavenge nucleophiles failed to show signs of reversibility for this wave. Even at suppressed temperatures reversibility was never detected at any sweep rate for this wave. A technique demonstrated by Parker to "tie up" nucleophiles was also attempted without success.¹¹⁵ Trifluoroacetic acid (1 - 2 mL) was added to the electrolysis cell, but no change in reversibility was noted in the voltammogram. This wave can tentatively be assigned to the sulfoxide oxidation which perhaps leads to a second sulfoxide formation at the second sulfur atom in the ring.

Thioanthrene has also been shown to react with residual water through its dication to form the thioanthrene 5-oxide in acetonitrile.¹¹⁶⁻¹¹⁸ Disproportionation reactions of this kind were shown to be involved in a similar role in the studies of the radical cations of chlorpromazine¹¹⁹, and 9,10-diphenylanthracene.¹²⁰

C. Reduction of 4,5-Bis(Methylthio)-1,3-Dithiole-2-One (25)

Compound 25 undergoes a two electron reduction at -2.41 V vs Ag/Ag^+ which is coupled with the loss of CO to form dianion 58.¹²¹ Figure 10 shows the reductive cyclic voltammetry of 25 in $\text{CH}_3\text{CN}/\text{TEAP}$ vs. Ag/Ag^+ .



Methylation of dianion 58 gives the corresponding tetrathioethylene (59) in good yield (~75%).¹²¹ Verification of tetrakis(methylthio)ethylene (59) was carried out by several methods. Liquid chromatograms of a known solution of 59 matched retention volumes (9.6 mL) with those of a methylated sample of the electrolysis solution. Mass spectral data on the isolated product also indicate strong ion currents for the fragment ions expected for this compound. Also, NMR, ESR, and $E_{1/2}$ determination gave satisfactory results for the product.

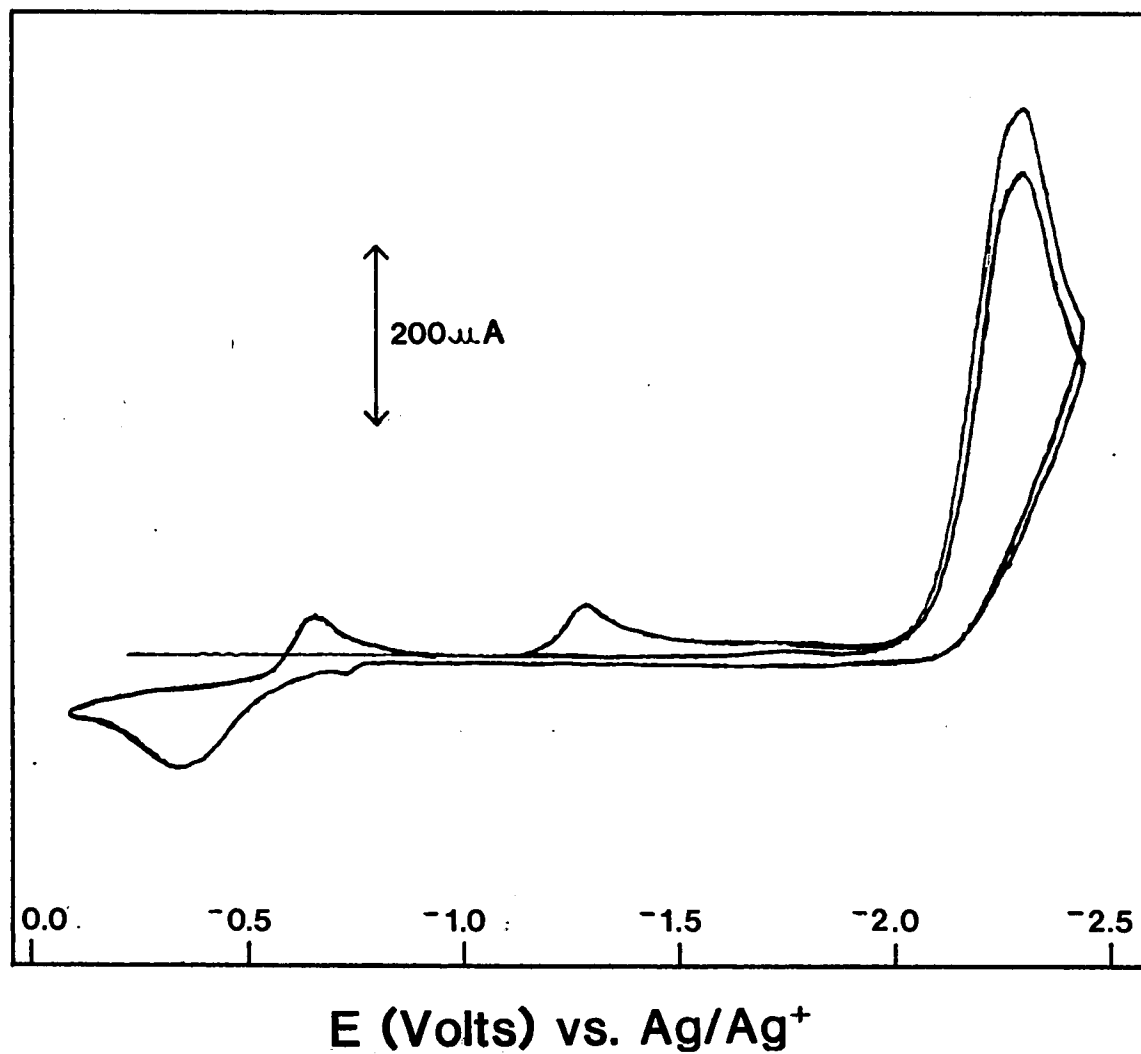
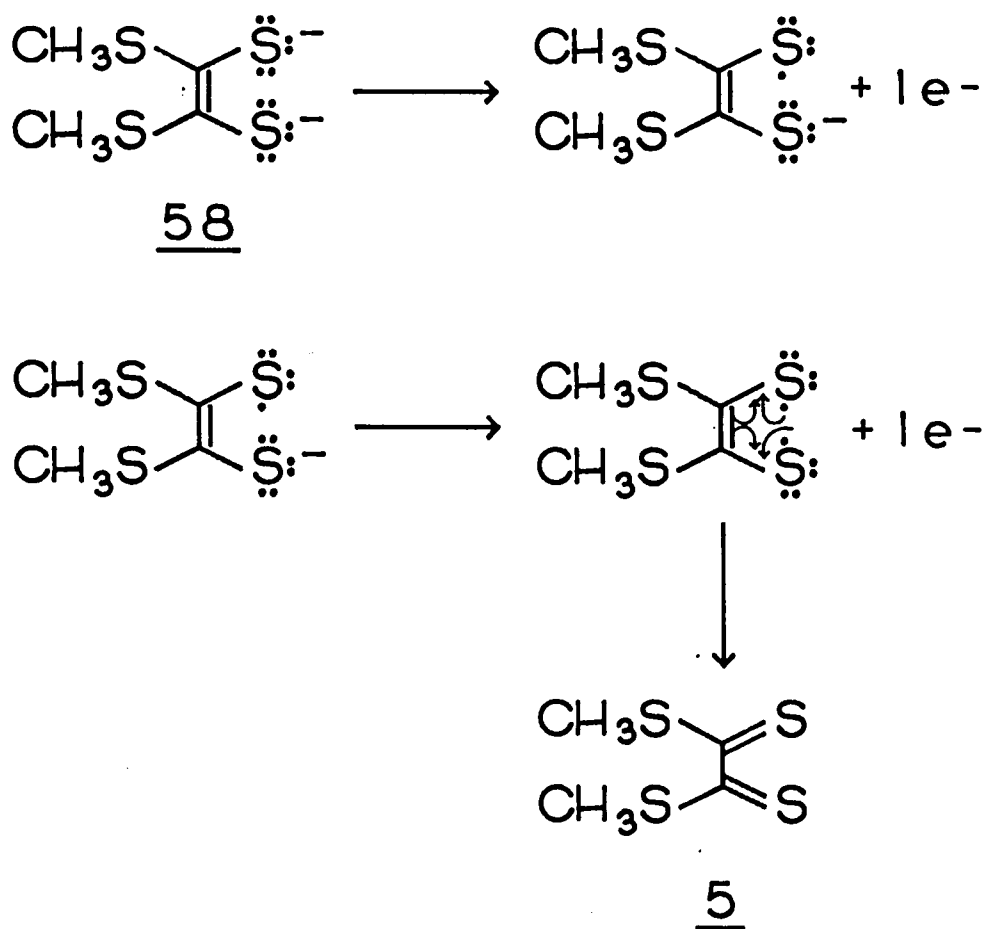


Figure 10. Cyclic voltammogram of the reduction of 4,5-bis(methylthio)-1,3-dithiole-2-one in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 200 mV sec⁻¹.

A cyclic voltammogram of compound 25 at fast sweep, is shown in Figure 11. The only current observed during the first potential scan is a broad irreversible reduction at -2.41 vs Ag/Ag^+ , presumably forming the dianion 58. On reverse scan, small reversible anodic currents are seen in the vicinities of -1.45 V and -0.69 V at 5 V per second. These currents suggest that the oxidation of the tetrathioethylene dianion 58 occurs by two one-electron steps and perhaps leads to the formation of dimethyltetrathiooxalate.



SCHEME 17

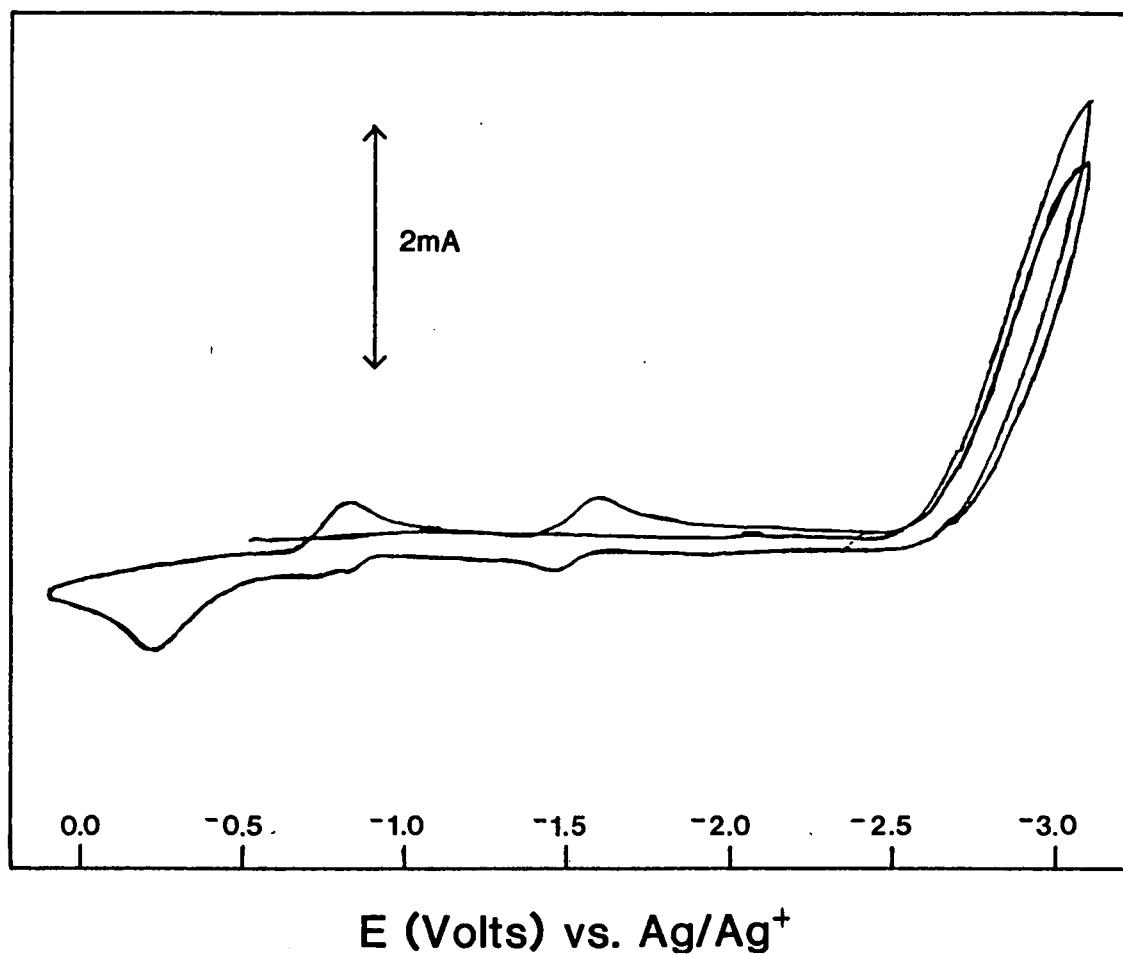


Figure 11. Cyclic voltammogram of 4,5-bis(methylthio)-1,3-dithiole-2-one at fast sweep rate in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 5.0 volts sec⁻¹.

Further support for this hypothesis is given by voltammograms taken of dimethyltetrathiooxalate in acetonitrile (Figure 12). Two reversible reduction peaks are noted which, indicate that dimethyltetrathiooxalate converts into the dianion and reversibly back to dimethyltetrathiooxalate. To test the ability of 25 to form dimethyltetrathiooxalate a sample of 25 was reduced at -2.41 V, and then was oxidized at 0.0 V vs Ag/Ag^+ and analyses carried out in attempt to detect the formation of dimethyl tetrathiooxalate. Electrolysis proceeded very slowly in both directions. Complete reduction of 25 took ~4 hours to complete, and a subsequent oxidation proceeded even slower (>24 hours). Liquid chromatographs of the oxidized solution failed to show evidence for the formation of 5 at 362 nm; nor could m/e fragments be conclusively assigned in mass spectra of the electrolysis solution.

Reversing the scheme, however, showed that using the tetrathiooxalate 5 as the starting product, tetrathioethylene (59) was obtained by reducing the substrate at -1.5 V vs Ag/Ag^+ followed by methylation. Mass spectral and liquid chromatographic data confirmed the assignment of the methylated product. N-value determinations on the reduction of 5 to the dianion were precluded by the lack of pure crystalline 5 for which a known amount could be electrolyzed. Likewise the n-value for the oxidation of dianion 58 (p. 76) was not successfully recorded due to the slowness by which the electrolysis proceeded. While these data suggest that an electrochemical connection exists between dianion 58 and dimethyl tetrathiooxalate, utility of this procedure is a very limited option for the generation of synthetically useful quantities of product.

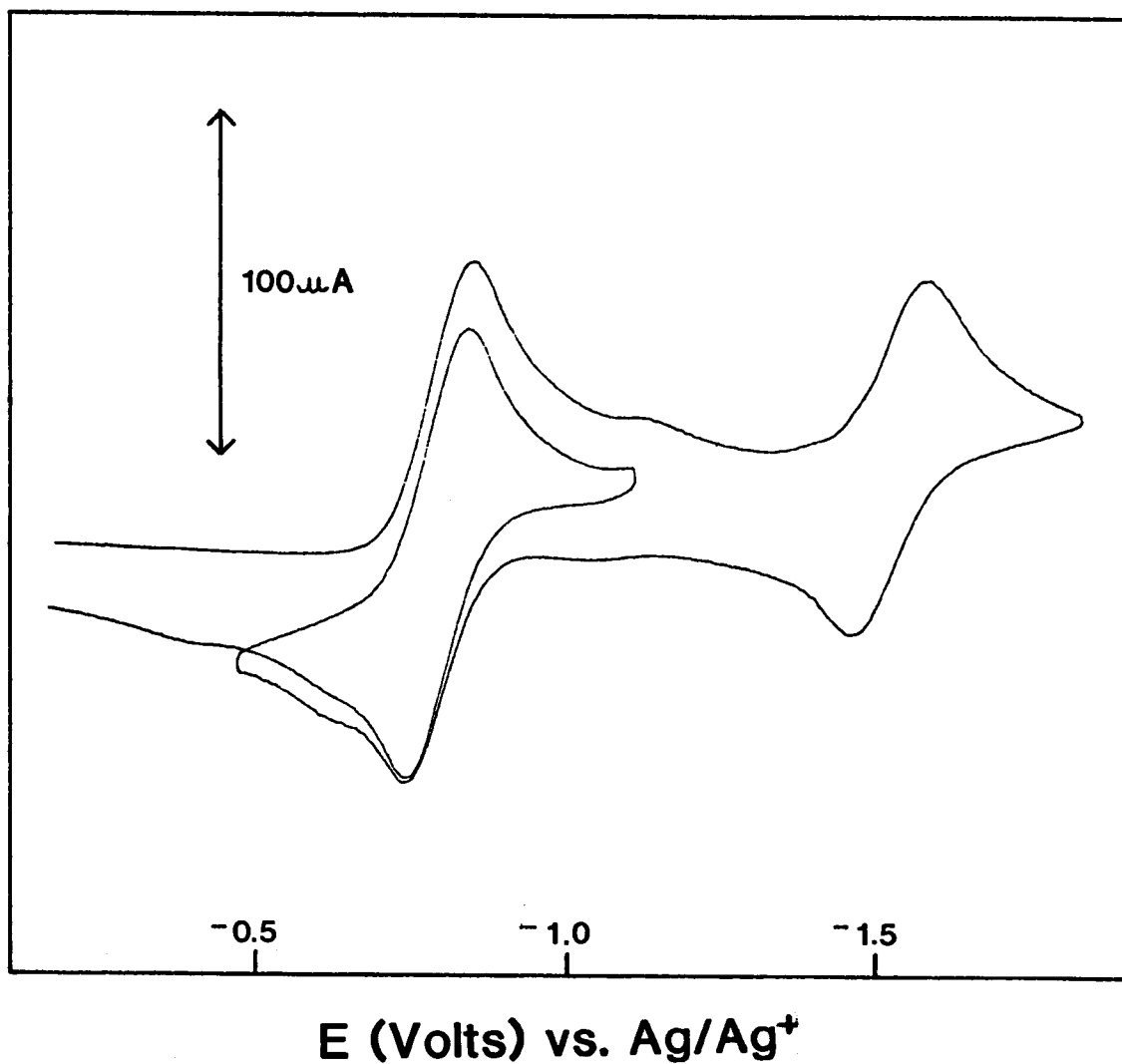
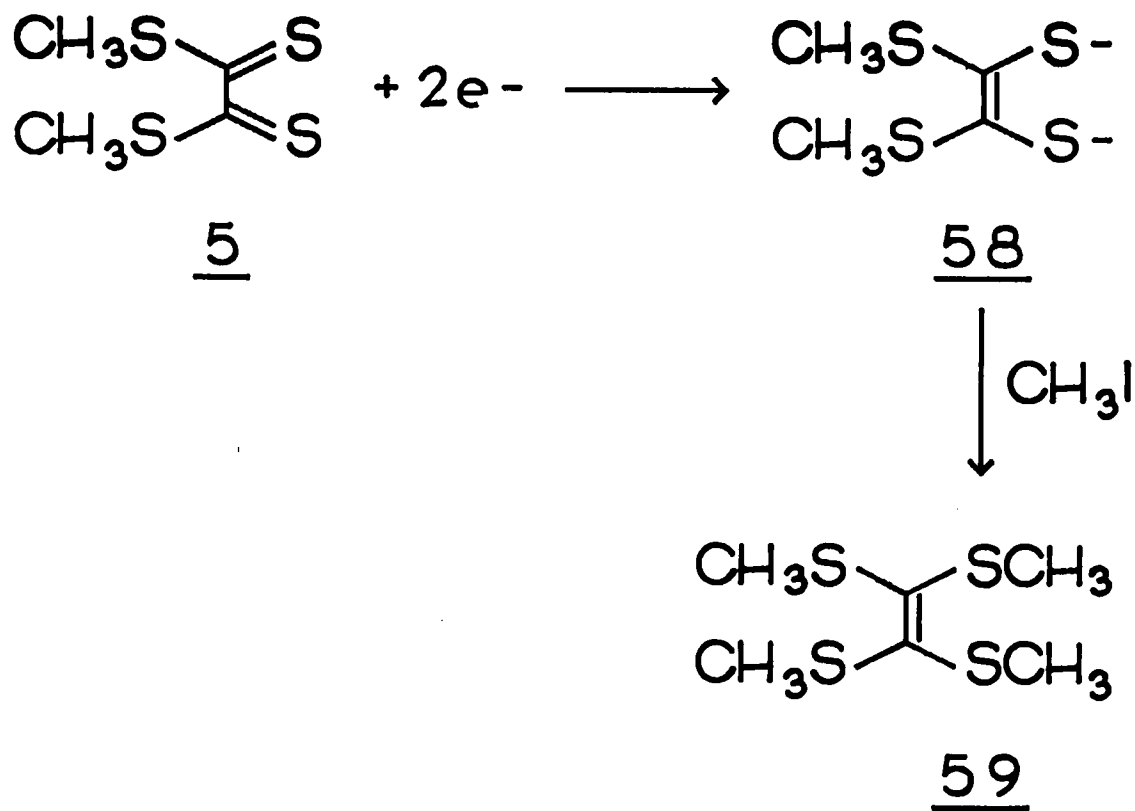


Figure 12. Cyclic voltammogram of the reduction of dimethyltetrathiooxalate in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 200 mV sec⁻¹.



SCHEME 18

D. Photolysis of 4,5-Bis(Methylthio)-1,3-Dithiole-2-One, (25)

As discussed in Section B, the product mixture from the photolysis of compound 25 is very complex. Dimethyltetrathiooxalate is obtained as the primary product, but in the crude form, 5 is mixed with several other carbon-sulfur species with similar characteristics. Separation of 5 was carried out using several different column and solvent variations, attempting to obtain crystalline material. No crystalline sample was ever obtained from these efforts, even though dark brown, foul smelling

crystals were reported by Kissel et al.¹¹ Interesting observations, however, were made on the data from the viscous brown oil routinely obtained from this reaction.

Figure 12 (p. 81) shows a typical voltammogram of the isolated tetrathiooxalate oil. The product was only slightly soluble in CH_3CN , so Figure 12 represents a saturated solution.

The waveform closely resembles those obtained for elemental sulfur dissolved in CH_3CN ¹²² (Figure 13). The two voltammograms were assigned to different compounds based on their different $E_{1/2}$ and ΔE_p values. The tetrathiooxalate sample gave $E_{1/2}$ values of -0.798 V and -1.512 V vs. Ag/Ag^+ for the first and second reduction steps, respectively. The $E_{1/2}$ values for the reduction of S_8 under the same conditions were -0.871 V and -1.562 V. A large difference in the ΔE_p 's for the two compounds' reduction steps further support this argument. The ΔE_p for the tetrathiooxalate's reduction steps was 79 mV, while S_8 gave 235 mV. Both Figures 12 and 13 are voltammograms of saturated solutions in CH_3CN . The peak currents of Figure 13 in one electroactive region are three times as large as the same region of Figure 12, indicating further that Figure 12 does not represent S_8 .

Compound 5 is unstable in DMF based on the fact that cyclic voltammograms taken immediately after the compound was dissolved in the solvent displayed the same current features like those in Figure 12. These currents quickly faded to unresolved background. Also, liquid chromatograms taken on the DMF/tetrathiooxalate solutions failed to show the peak for compound 5.

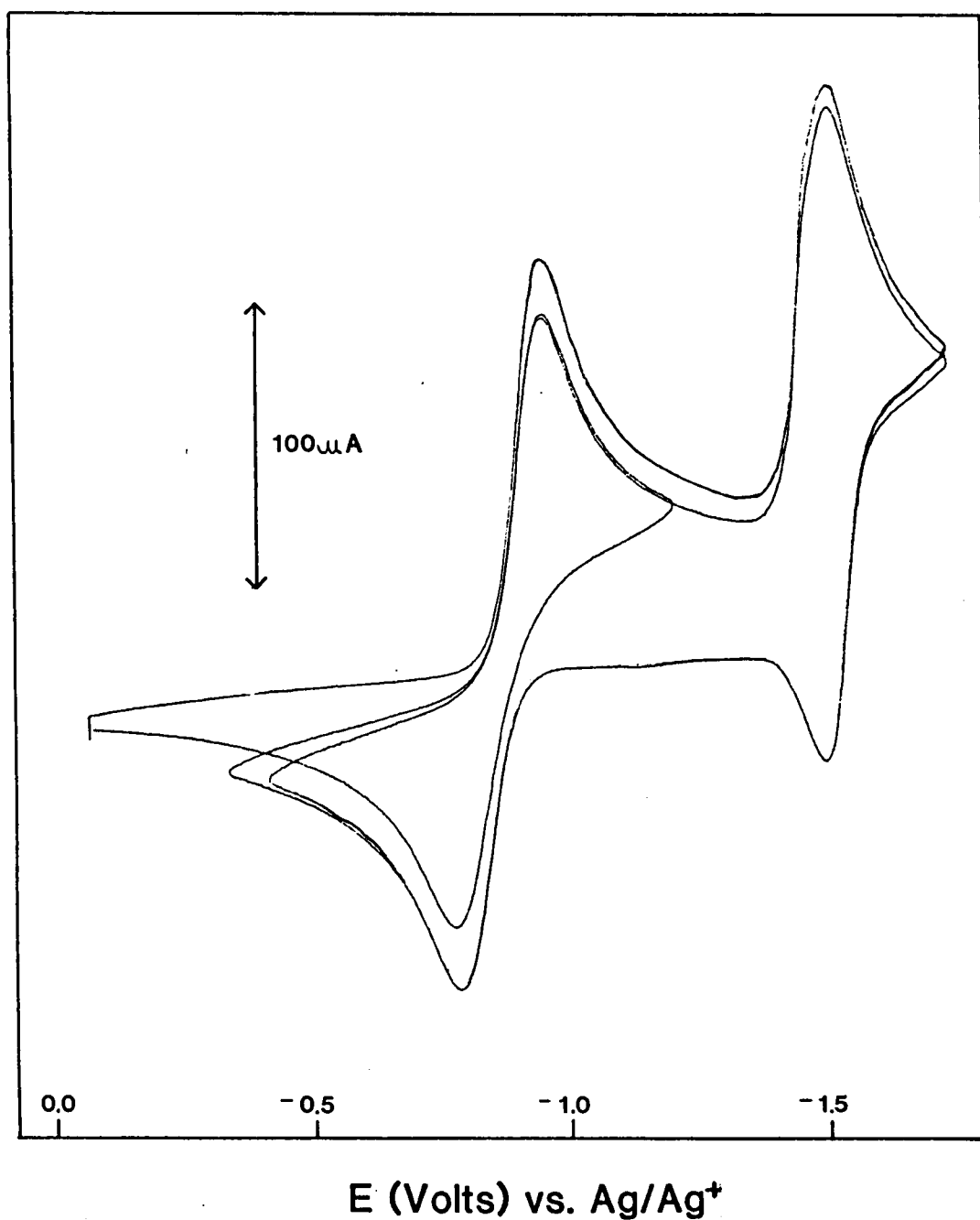
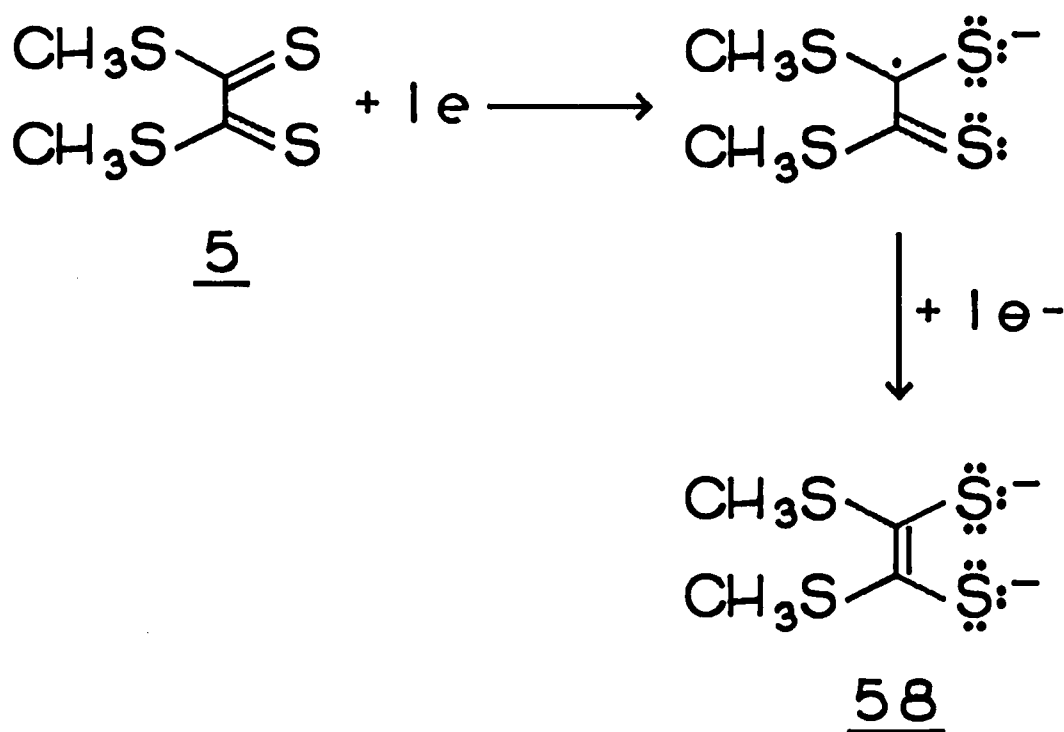


Figure 13. Cyclic voltammogram of sulfur in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 100 mV sec⁻¹.

The cyclic voltammogram in Figure 12 shows two reversible reductions. As discussed in Section C, the product of electrochemical reduction of 5 at -1.8 V vs Ag/Ag^+ followed by methylation is tetrathioethylene, 57. Also, reduction of 5 at -1.2 volts vs Ag/Ag^+ in the cavity of the ESR gave a seven line spectrum in which the first and seventh lines were almost invisible ($g = 2.0073$ $a_{\text{H}} = 2.75$ Gauss). These facts suggest that the tetrathioethylene anion is formed by two successive one-electron transfers (Scheme 19).^{123,124}



SCHEME 19

The reduction pattern for tetrathiooxalate closely resembles the one obtained for dithiooxamide 65. Figure 14 shows two one-electron

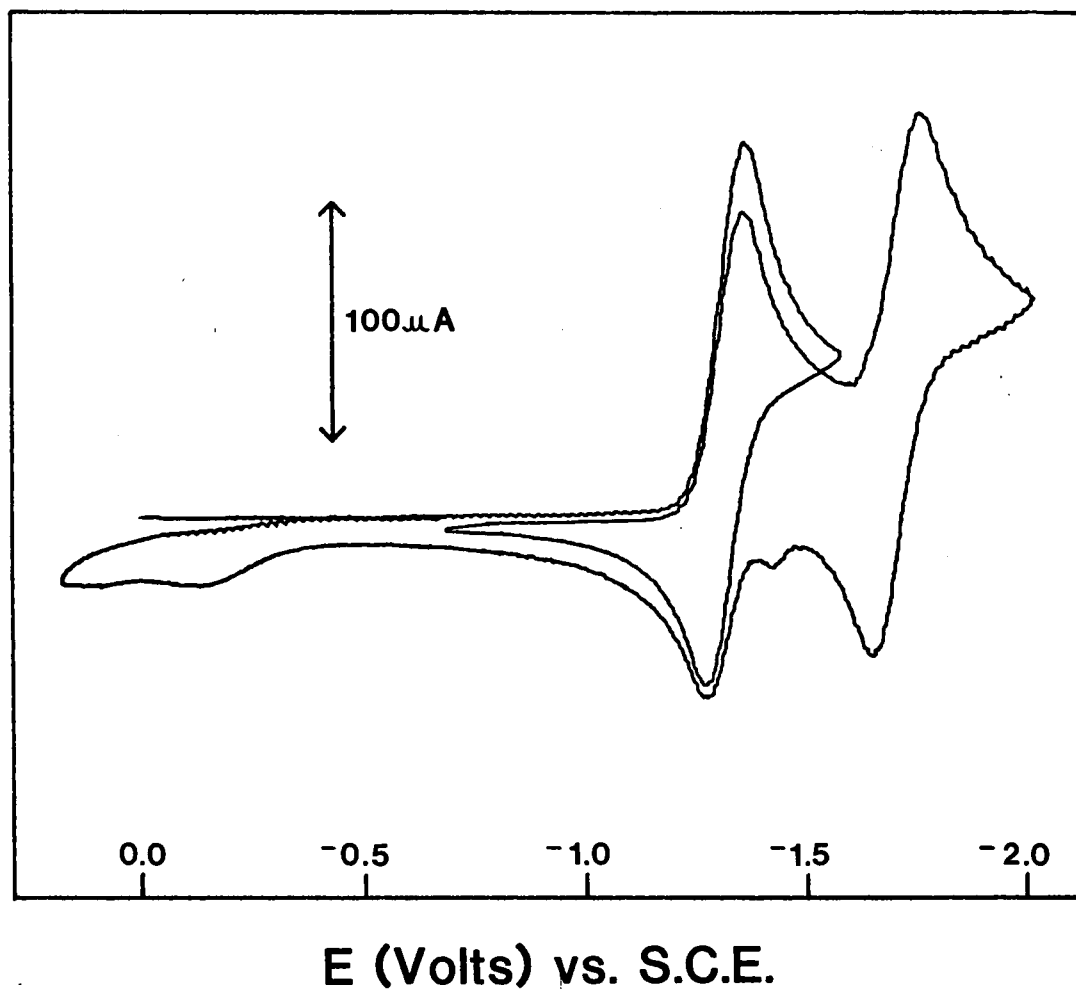
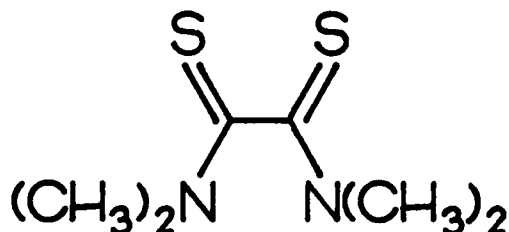


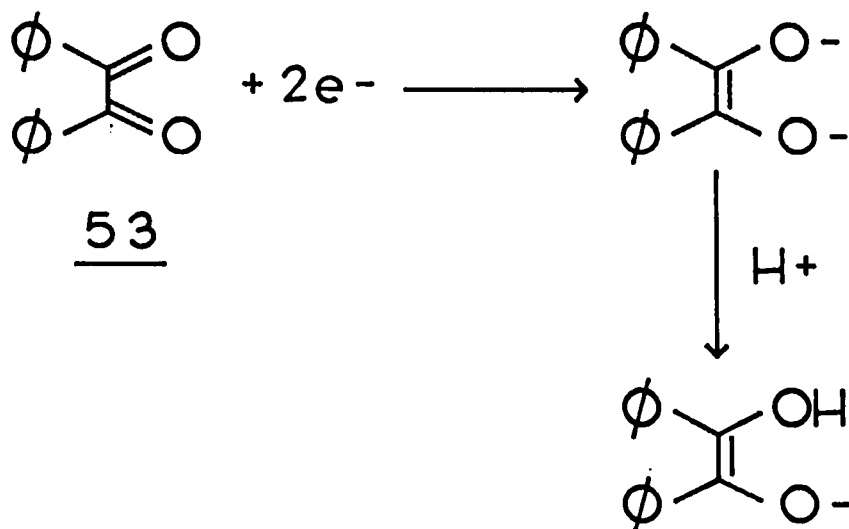
Figure 14. Cyclic voltammogram of the dimethyl adduct of dithiooxamide in 0.1 M TEAP/ CH_3CN . Platinum electrode, sweep rate 200 mV sec^{-1} , temperature -10°C .

reduction steps for this α -dithione adduct. Coulometric determinations and ESR data at 1.3 V were consistent with the one-electron assignments for 65.



65

The behavior of tetrathiooxalate at an electrode also resembles in some ways that of the electrochemical reduction of benzil, 33, in methanol-water solutions. Stapelfeldt and Perone showed that benzil is reversibly reduced at pH >11 to a stilbenediolate intermediate, which rearranges to the benzoin anion.^{125,126}



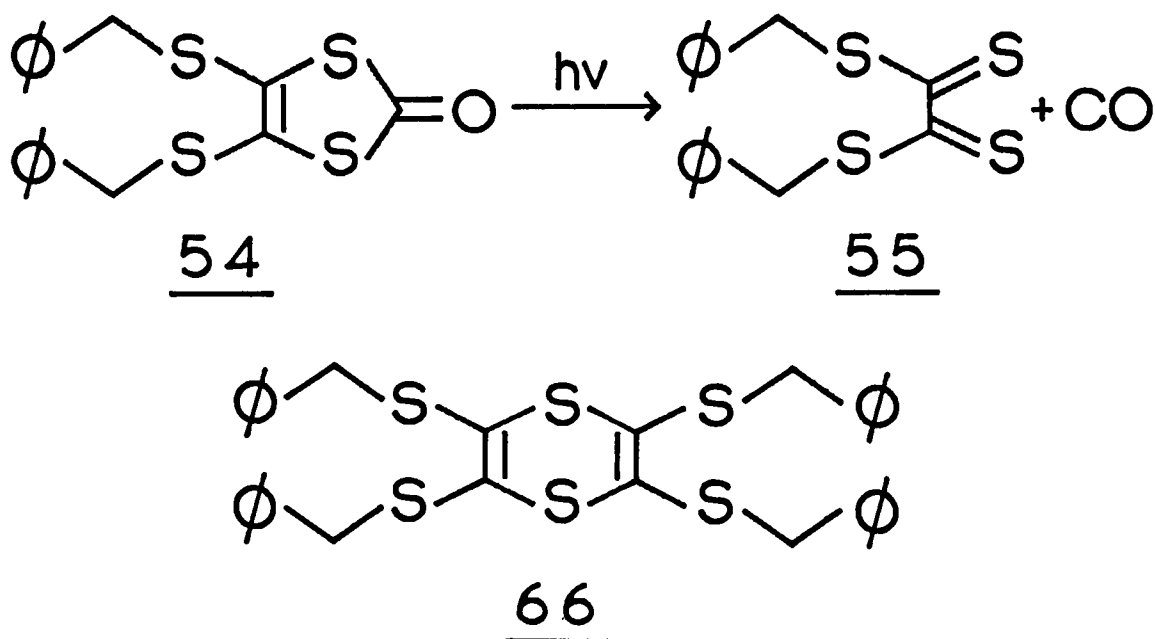
SCHEME 20

Benzil undergoes one two-electron reduction, however, at ~ -0.8 V vs SCE to the dianion, instead of two discrete reductions.

The crude product mixture from the photolysis reaction was analyzed by GC/MS. using direct probe injection. The parent and expected fragment peaks for compound 5 were observed in addition to higher molecular weight analogues with the same m/e values as those observed earlier for CS_2 reduction products (Tables I and II, pp. 64 and 65).¹⁰ Another citing of this phenomenon to generate high molecular weight oligomers came from experiments by Jeroschewski and Hansen which involved methylation of the TEA^+ salt (64).¹⁰⁴ Many of these same products were reported, suggesting that some species common to all these experimental conditions is responsible for this behavior.

Solid state photolyses were attempted in an effort to increase the yield of higher molecular weight components. Needles of compound 25 were photolyzed in capillary tubes, followed by mass spectral analysis. No notable increases were observed for fragment ion intensities of the higher molecular weight species. For some fragments the intensity decreased.

By changing the methyl groups to benzyl groups on compound 25 it was hoped that the products from the photolysis would more readily crystallize. Synthesis of dibenzyltetraathiooxalate (55) was attempted by the photolysis of compound 54. Mass spectral data indicate that a small fraction of the photolysis mixture contained a higher molecular weight compound at $m/e = 604$ for which 66 is a possible structure.

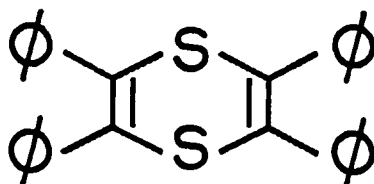


Little evidence was observed for the formation of α -dithione 55, however. Low intensities for m/e values expected for benzyltetraethiooxalate were present, but also present were a large number of additional product peaks outside the expected pattern. Analysis by HPLC failed to show any resolved product peaks. The appearance of the chromatogram was a broad increase in the background absorbance at higher retention volumes (>20 mL).

Treatment of the tetrathiooxalate salt 64 (p. 51) with benzylchloride and benzylbromide also failed to give the α -dithione. Mass spectral data for this reaction product showed no peak at $m/e = 334$, but like the photolysis reaction, there were many fragments outside the expected pattern.

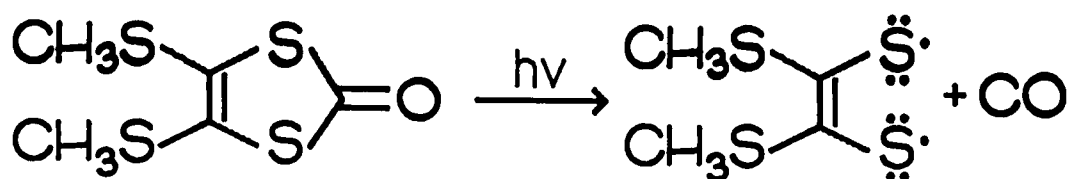
Photolysed products of 25, which were shown by the mass spectra to contain high molecular weight species, failed to yield crystals when

attempts at electrocrystallization were carried out. The potential selection for cation formation was based on the position of the first oxidation wave in Figures 15 and 16 ($E_p = +1.00$ V vs. SCE) for the dithiacyclohexadiene compound, (57).

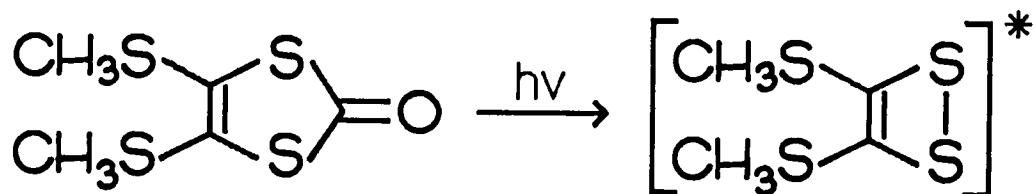


57

The product variety observed from the photolysis of 25 indicates that a complex reaction is taking place. A possible explanation for this behavior is that the initial decarbonylation step forms a highly



labile diradical species which can further react in several ways, including coupling of the radical electrons with the vinylene π electrons to form the α -dithione. While the interatomic distance may be too large to favor formation of the 1,2-dithiete,⁸⁹ it is possible that this structure forms as a labile intermediate giving different products on further reaction. Intermediates of these kinds are probably



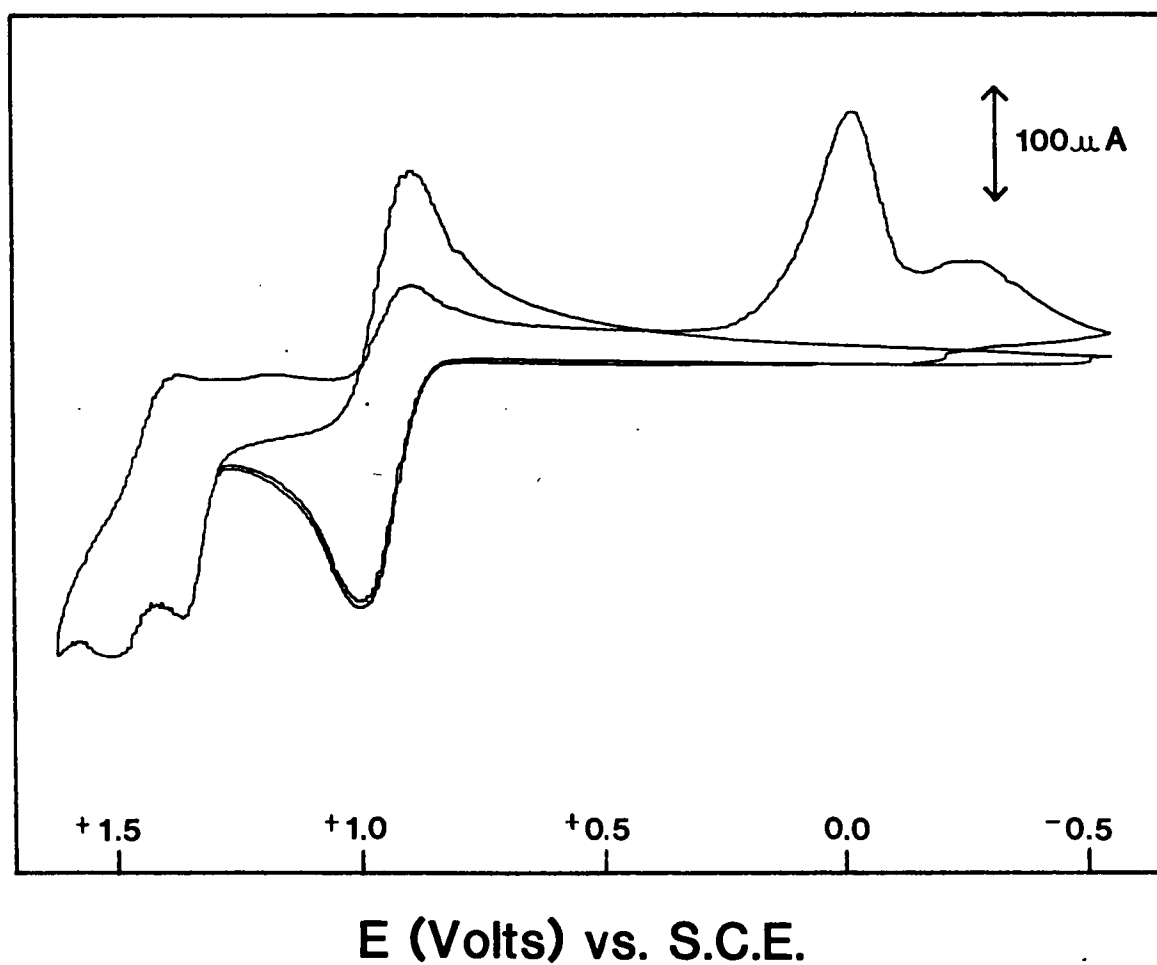


Figure 15. Cyclic voltammogram of tetraphenyldithiacyclohexadiene in 0.1 M TEAP/ CH_2Cl_2 . Platinum electrode, sweep rate 200 mV sec^{-1} .

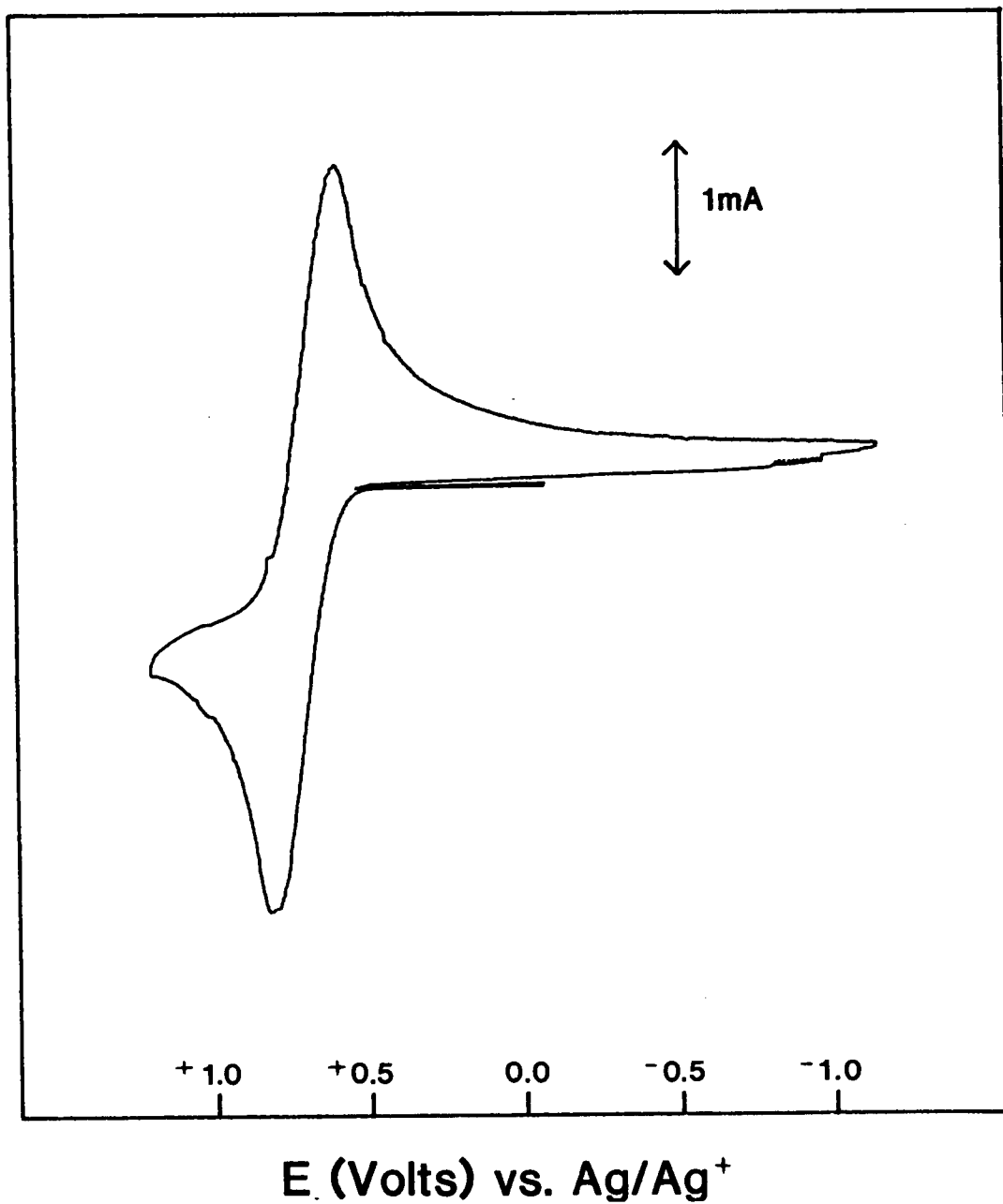
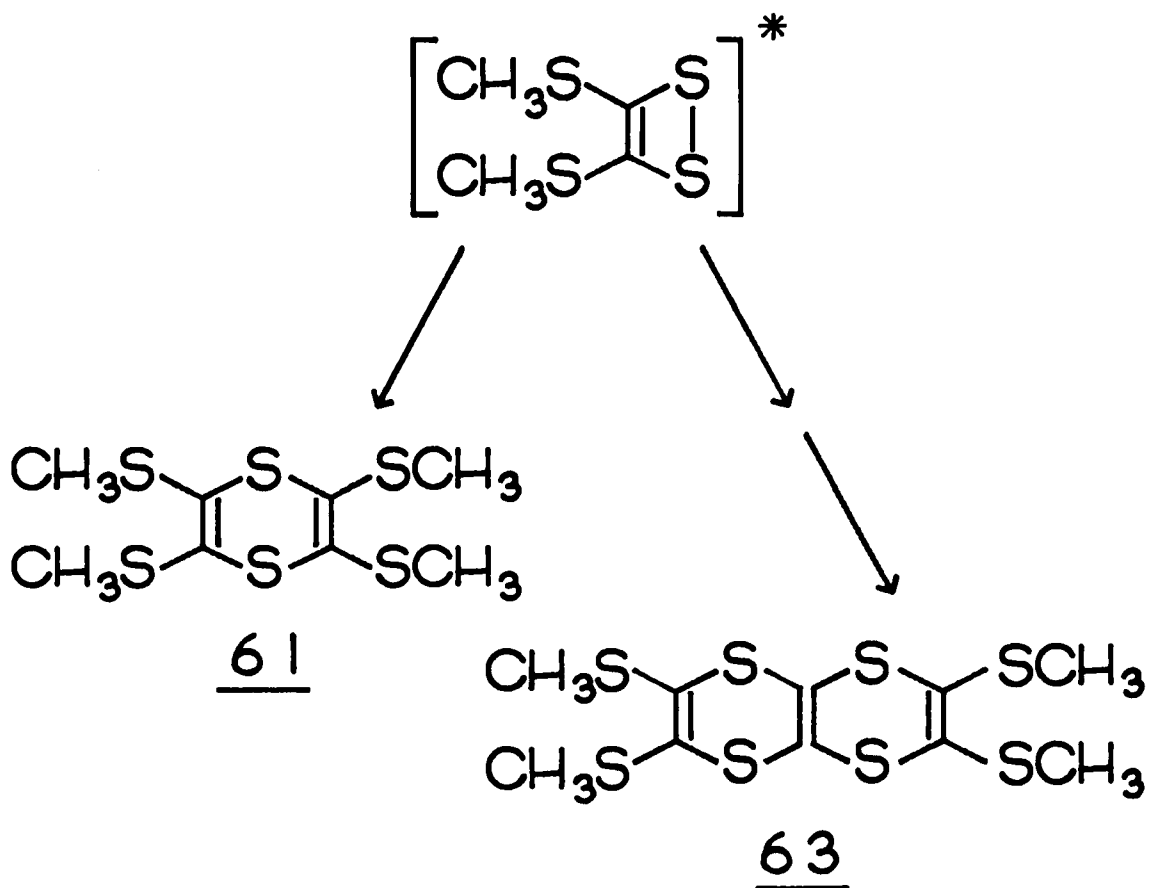
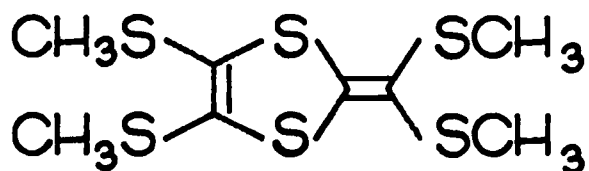


Figure 16. Cyclic voltammogram of tetraphenyldithiacyclohexadiene in 0.1 M TEAP/C₆H₅CN. Platinum electrode, sweep rate 200 mV sec⁻¹, neutral alumina added.

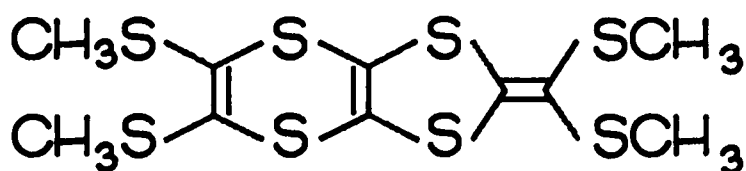
responsible for the appearance of high molecular weight adducts in the mass spectra of the photolysis solution.



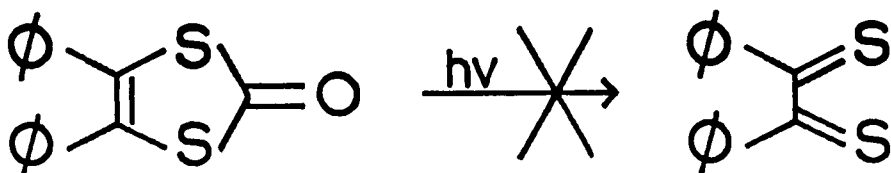
The structure assignments for compounds 61 and 63 from the photolysis of 25 are tentative, since pure crystalline samples were not obtained. Alternative structural isomers with m/e values of 300 and 388 amu can be drawn for the parent ions. Kusters and de Mayo¹⁵ studied a photolysis system similar to this one in an attempt to synthesize dithiabenzil, (20) (p. 16).

66

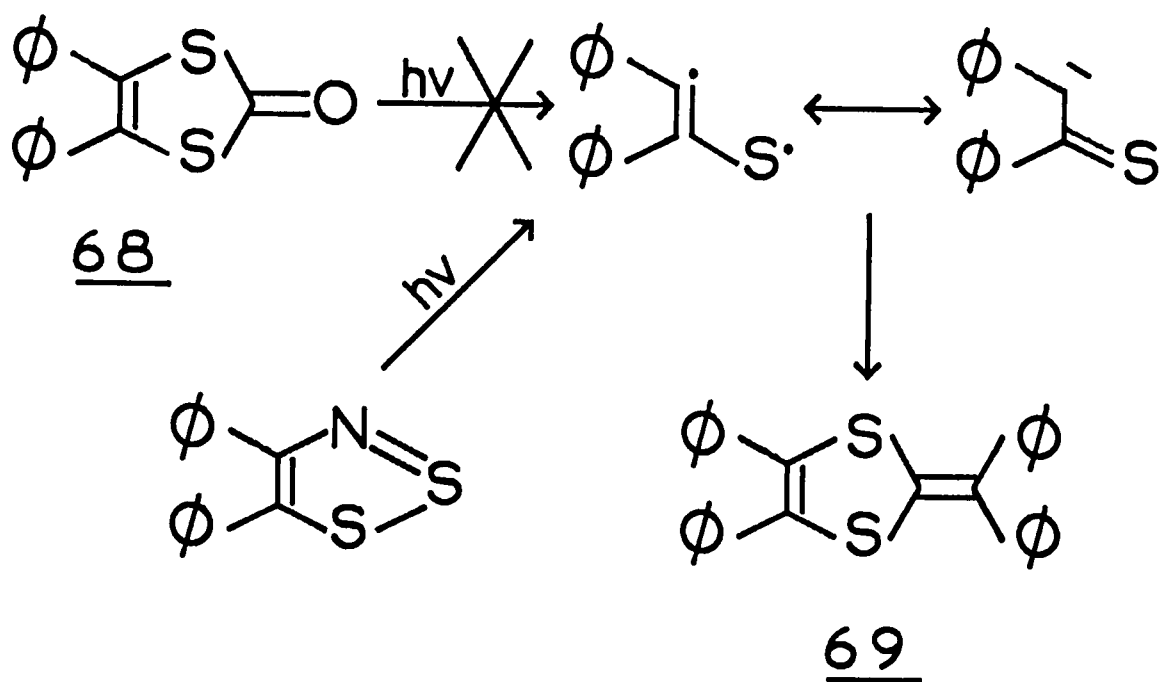
M. W. = 300

67

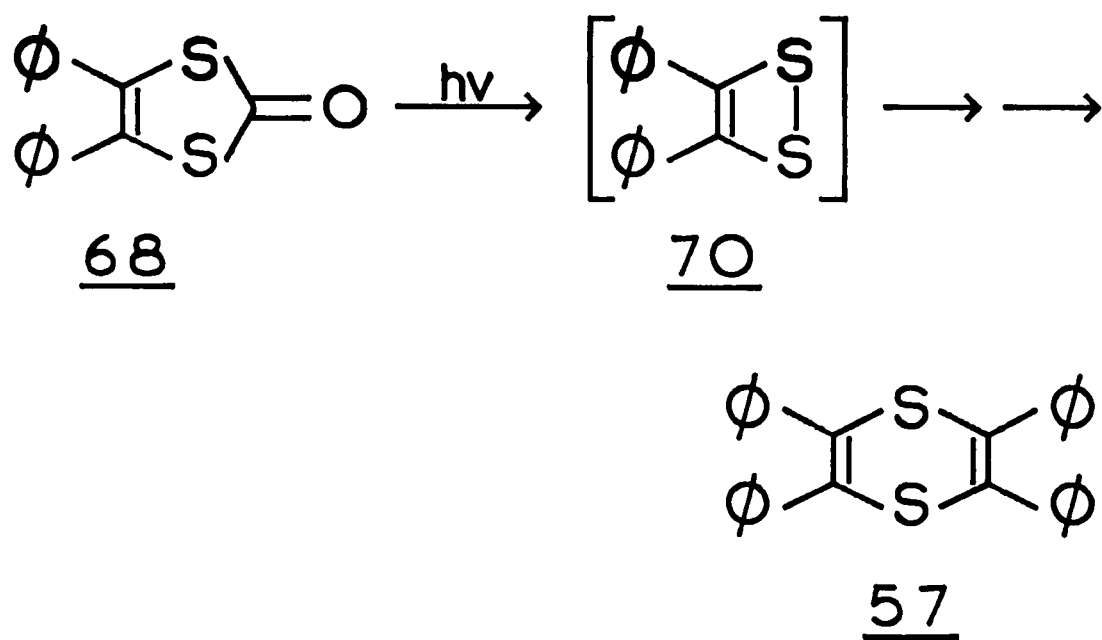
M. W. = 388

6820

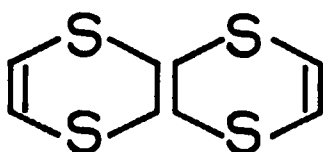
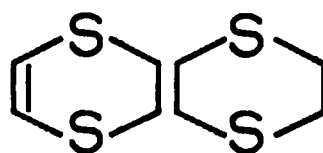
Scheme 21 shows the pathway not followed by the photolysis of compound 68. Instead of the elimination of carbonyl sulfide, carbon monoxide is evolved, followed by the formation of 57. Based on the similarities of compounds 68 and 25, structures 61 and 63 seem like reasonable assignments.



SCHEME 21



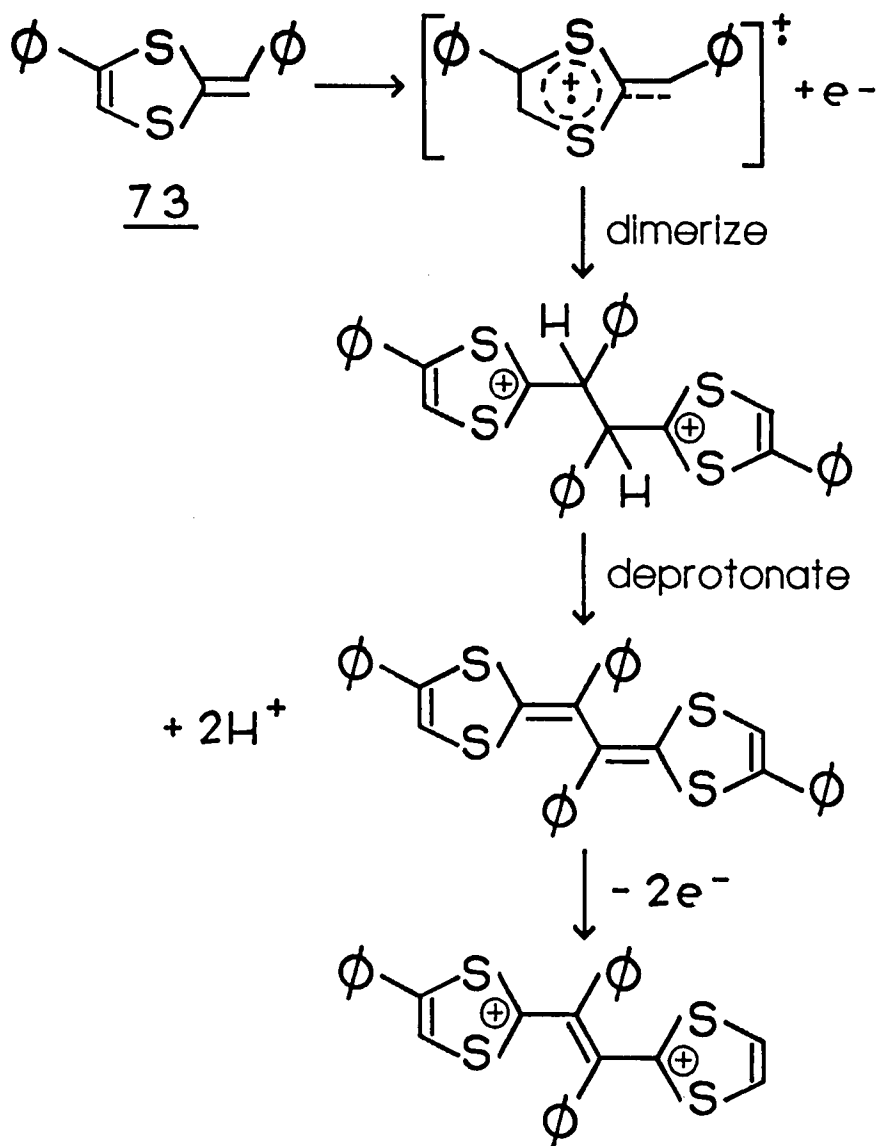
Because of the implied similarities between the high molecular weight multisulfur cations suggested by the mass spectra and the TTF cations in many organic metals, consideration could be given to their possible use as donor cations in conducting organic metals. Cava and coworkers¹²⁷ reported the synthesis of 1,4,5,8-tetrathiatetralin, 71, which was viewed as a potentially aromatic 14- π -electron system. However, the NMR spectrum of 71 showed a singlet at $\delta = 6.46$, very close to the olefinic proton signal observed for the dihydro derivative, 72.

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Based on this observation, Cava suggested that 71 lacks aromatic stabilization and therefore possesses a nonplanar configuration. Additionally, compound 71 lacked the relative ease of oxidation seen for TTF. The $E_{1/2}$ values for the first and second oxidations of 71 are 0.561 V and 0.965 V vs Ag/Ag^+ , and the second step is irreversible. TTF oxidizes relatively easily and reversibly at $E_{1/2}$ values of 0.006 V and 0.385 V vs Ag/Ag^+ . If compounds 61 and 63 also suffer from the same difficulty of oxidation and possess nonplanar geometry, their use as donor cations in highly conducting organic metals would be expected to be hindered.

E. The Electrochemical Behavior of 4-Phenyl-2-Benzylidene-1,3-Dithiole, (73)

A study of the chemical oxidation of compound 73 reported that dimerization of radical cations occurred followed by a deprotonation

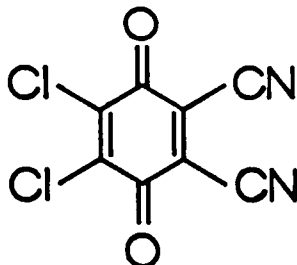


SCHEME 21

step and a second redox step.¹²⁸ The electrochemical oxidation of 73 was examined to see if the same mechanism could be observed. A cyclic voltammogram of 73 is shown in Figure 17. Beginning in the anodic direction, an irreversible oxidation is first encountered in the region of +0.31 V vs Ag/Ag⁺ which is assigned as the formation of radical cation.



ESR spectra of 73 in situ exhibited a one line resonance, ($g = 2.0079$). This g -value matched the value obtained when 73 was chemically oxidized with DDQ (74) in CH₃CN by a procedure similar to the one used by Mayer



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and Kröber.¹²⁸ On reverse scan, a new couple appears whose $E_{1/2} = +0.12$ V, and is assigned to the reduction of dimer dication formed subsequent to the radical generation at ox_1 . A deprotonation step immediately following the dimerization step is consistent with Mayer's chemical oxidation mechanism. The actual formation of dimer and the departure of protons apparently is kinetically fast, allowing for the formation of the final product and a heterogeneous oxidation on the voltammetric time scale.

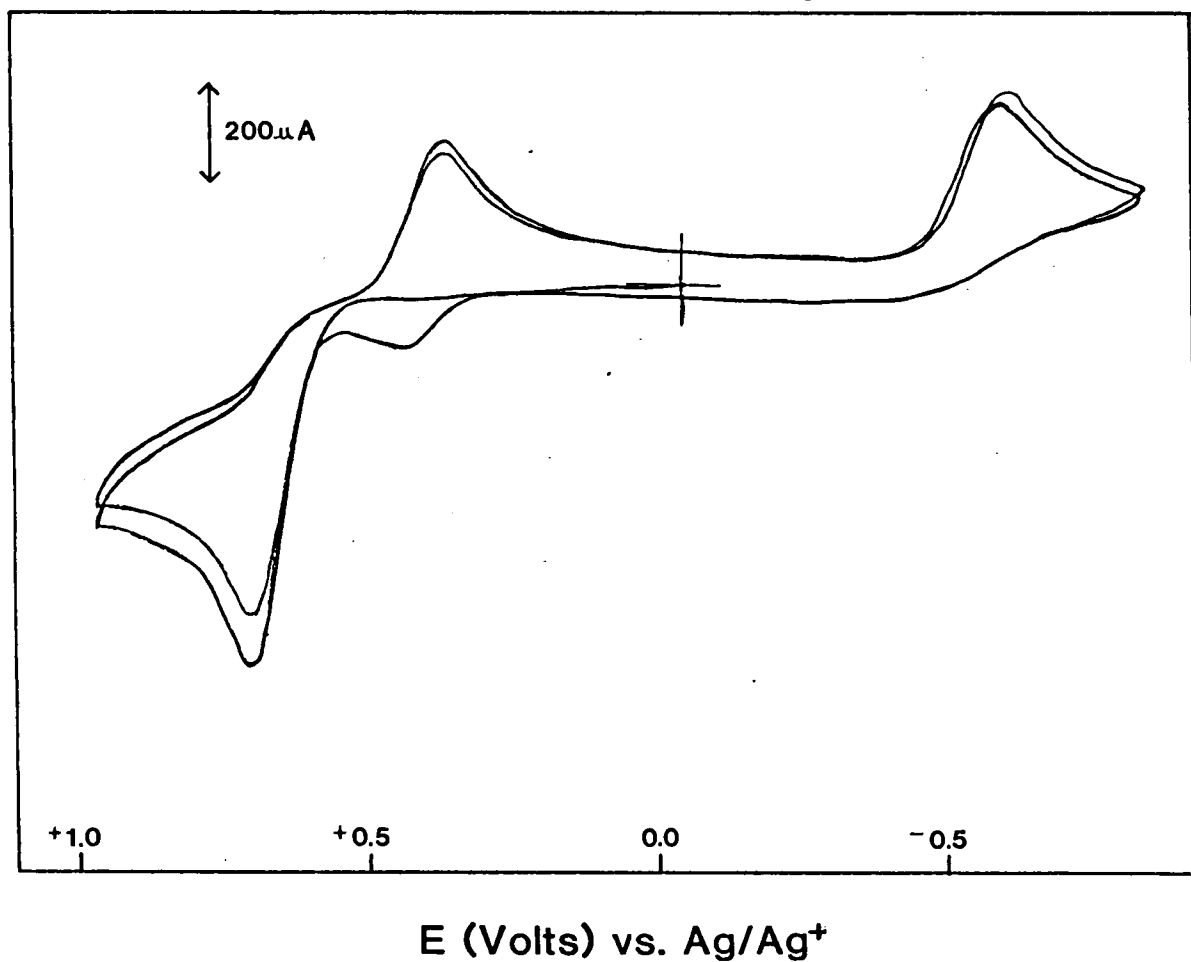
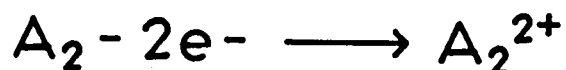
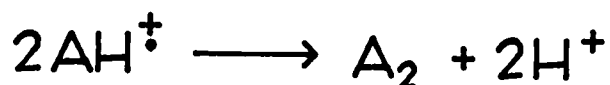


Figure 17. Cyclic voltammogram of 4-phenyl-2-benzylidene-1,3-dithiole in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 121 mV sec⁻¹.



Fast sweep rates applied at suppressed temperatures failed to reveal reversibility of the wave. As expected the irreversible reduction appearing at -0.52 V is heightened by the addition of perchloric acid, and diminished by added pyridine, (Figures 18 and 19). Therefore, the reduction of H^+ is assigned to this wave.

Coulometry carried out at +0.50 V gave an n-value of 2. Rereducing the dimer dication to the neutral dimer was also a two-electron process. UV-visible spectra of both the chemically oxidized compound and the electrolysed sample had $\lambda_{\max} = 520$ nm.

The conclusion was drawn that the electrochemical mechanism is the same as the mechanism reported by Mayer for the chemical oxidation of 73.^{128,129} The nitro benzylidene adduct exhibits the same voltammetric pattern as seen for 73, (Figure 20). The stability of the dimer dication and its reversible reduction to the neutral dimer are implied by the well defined shape of Figure 21. The neutral dimer carries a pair of nitro groups which apparently reduce separately as shown by the two reduction waves at around -1.3 V to 1.5 V (Figure 22).

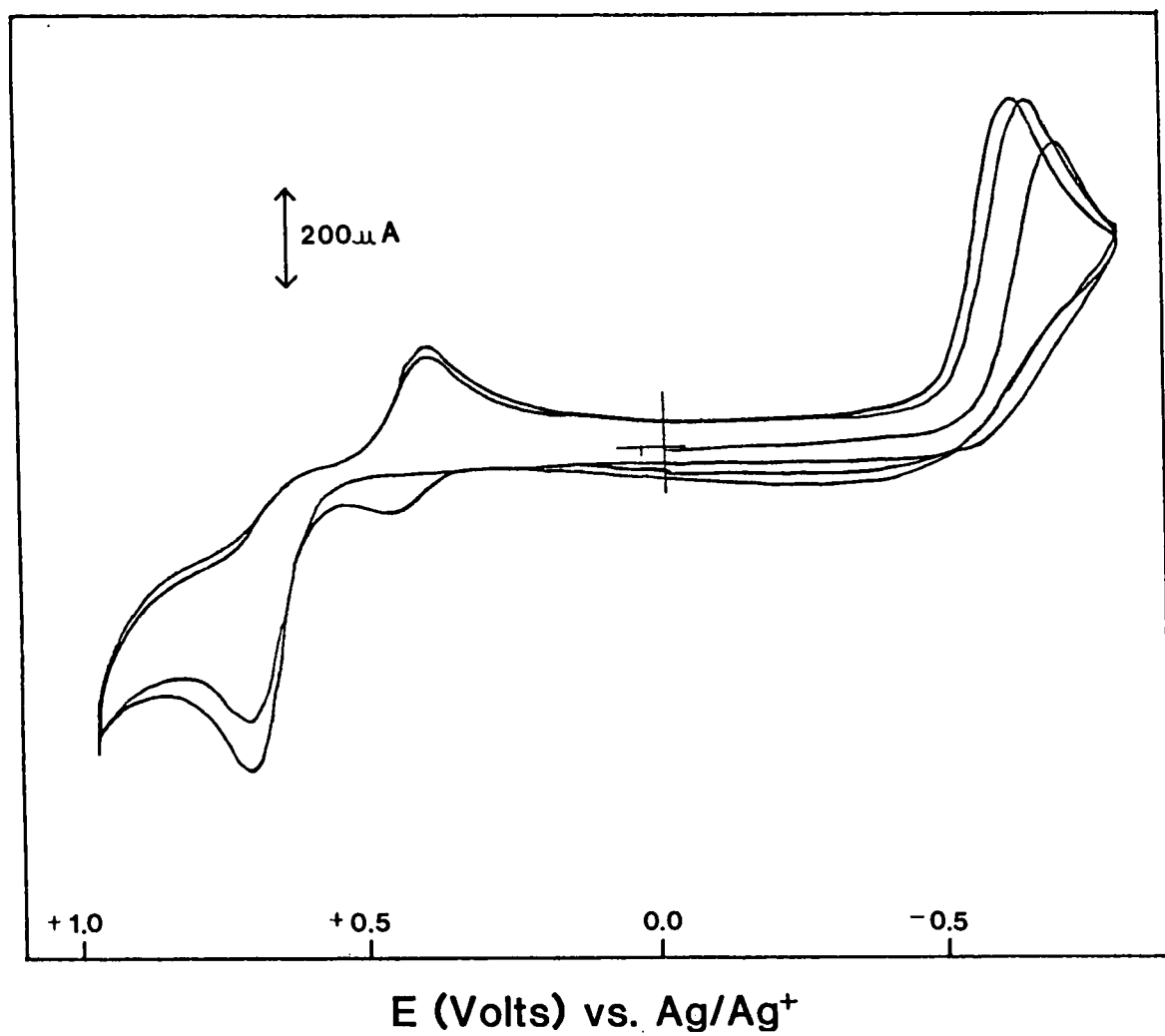


Figure 18. Cyclic voltammogram of 4-phenyl-2-benzylidene-1,3-dithiole plus 1.0 ml of perchloric acid in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 121 mV sec⁻¹.

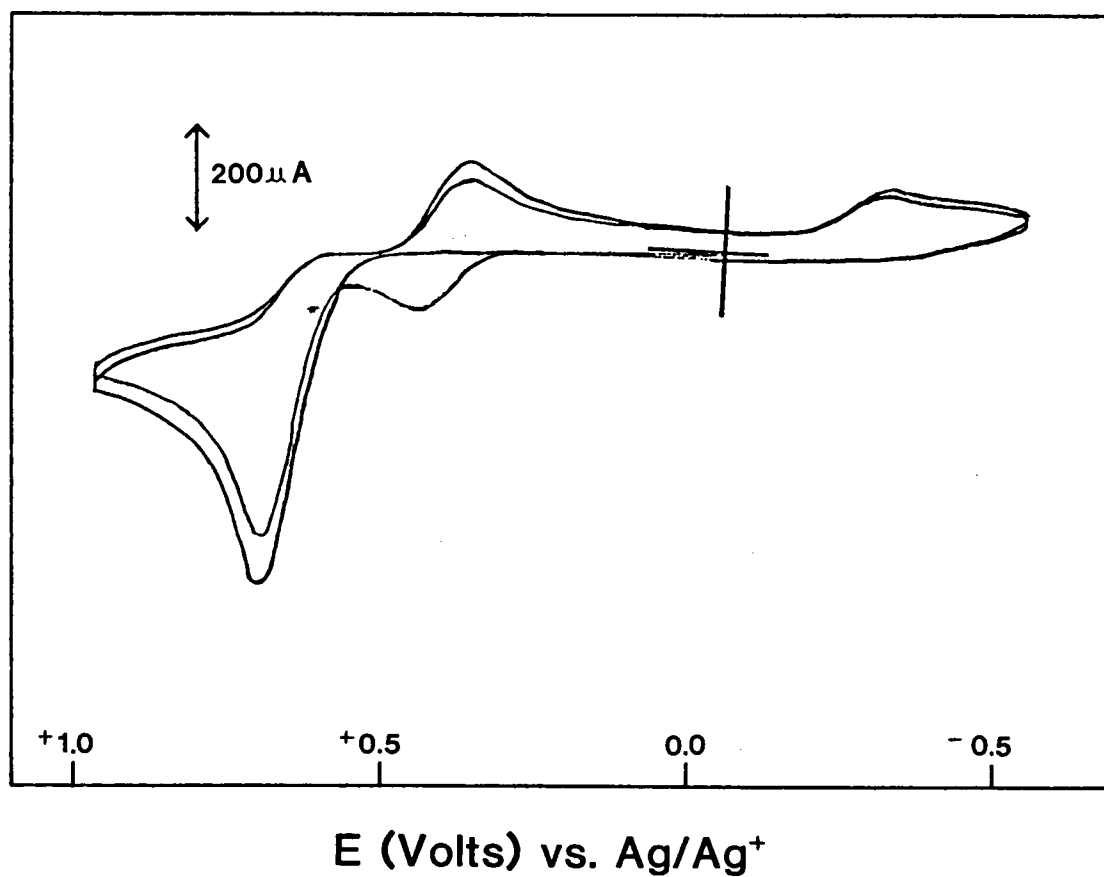


Figure 19. Cyclic voltammogram of 4-phenyl-2-benzylidene-1,3-dithiole plus 1.0 ml of pyridine in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 121 mV sec⁻¹.

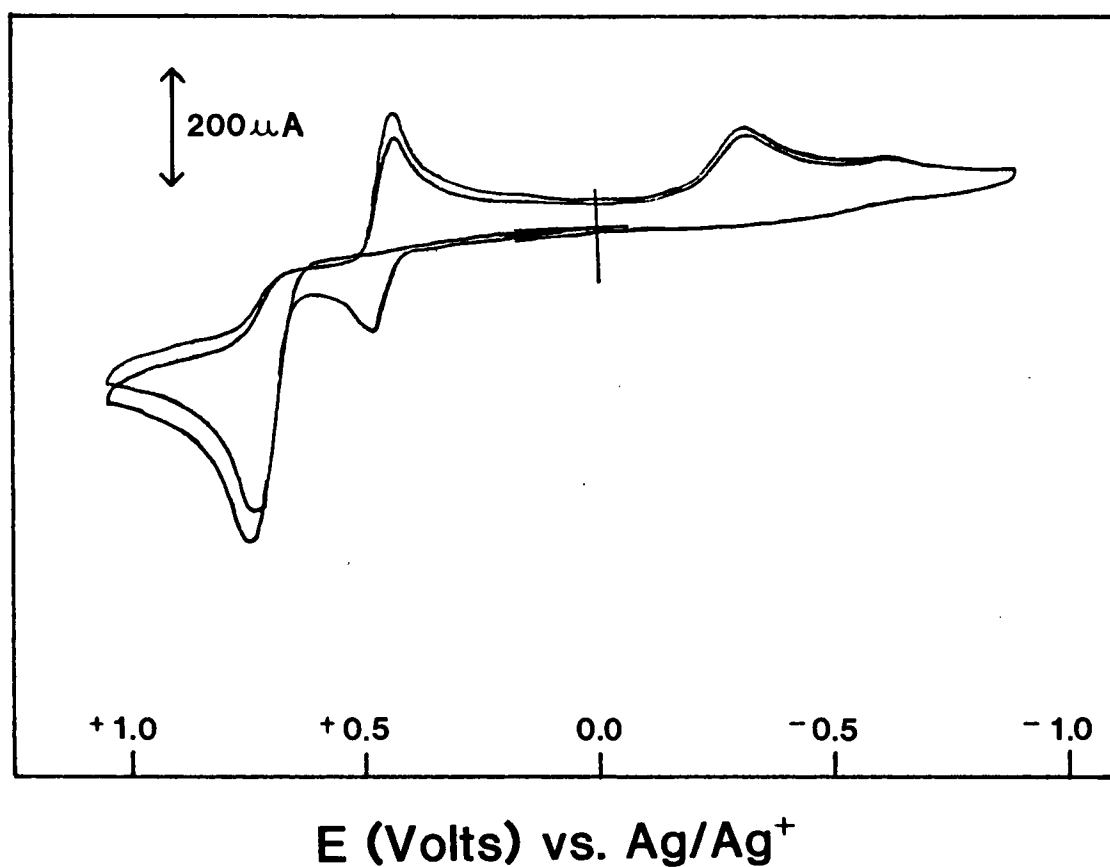


Figure 20. Cyclic voltammogram of the nitro-adduct of 4-phenyl-2-benzylidene-1,3-dithiophene in 0.1 M TEAP/CH₃CN. Platinum electrode, sweep rate 121 mV sec⁻¹.

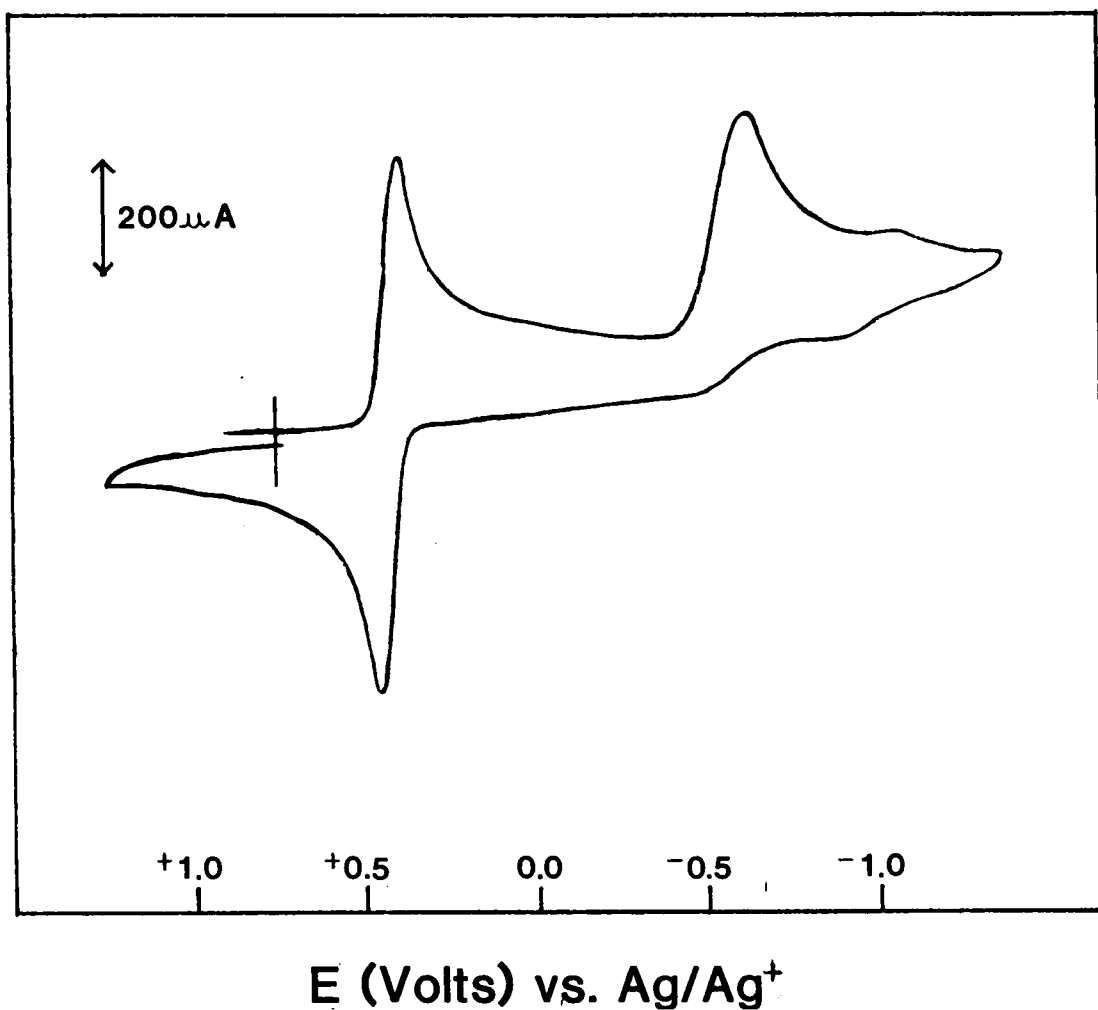


Figure 21. Cyclic voltammogram of the nitro-adduct of 4-phenyl-2-benzylidene-1,3-dithiole after electrolysis at +1.15 volts. Platinum electrode, sweep rate 121 mV sec^{-1} .

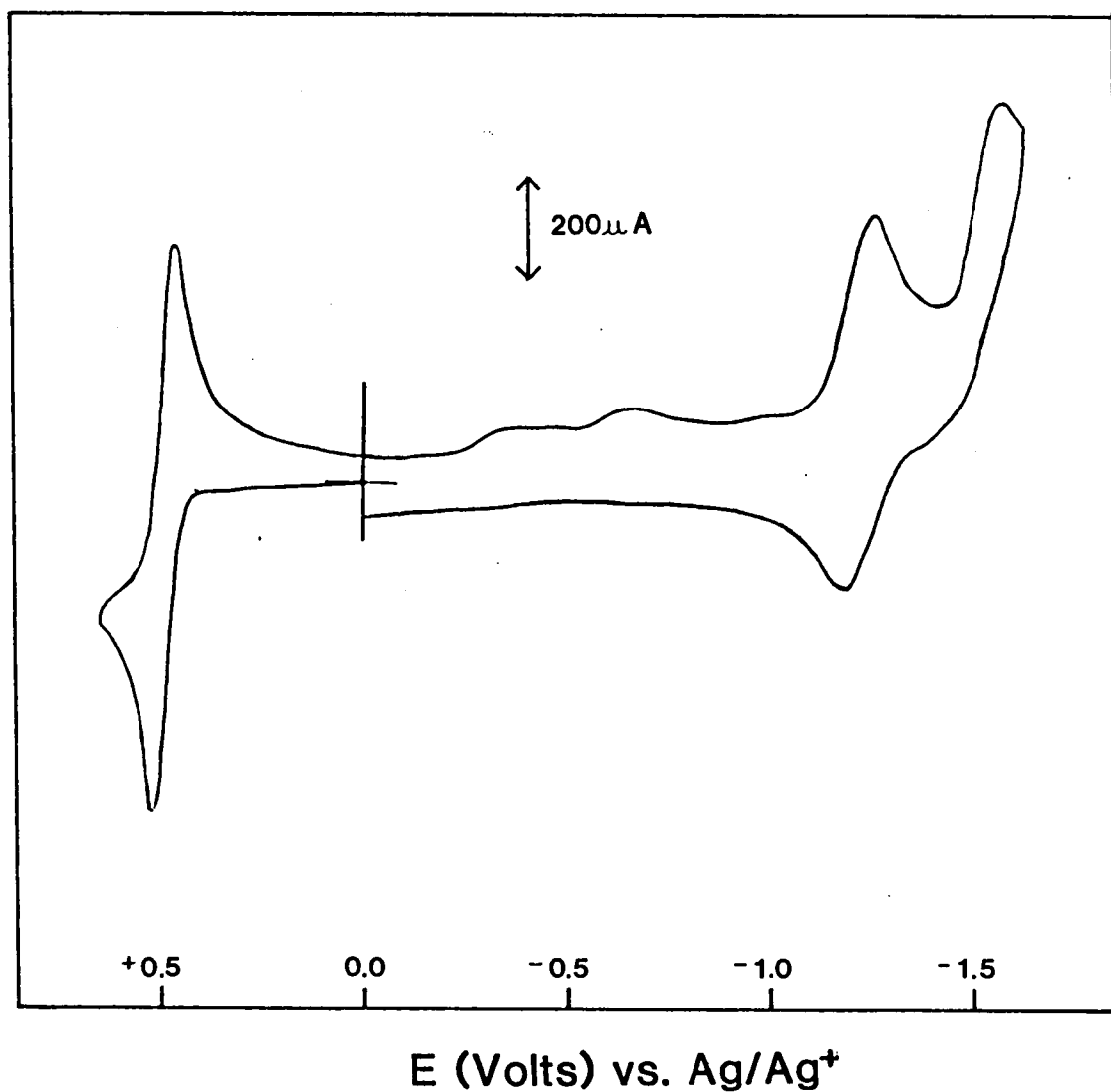


Figure 22. Cyclic voltammogram of the nitro-adduct of 4-phenyl-2-benzylidene-1,3-dithiole after rereducing at -1.58 volts to remove H⁺ ions. Platinum electrode, sweep rate 121 mV sec⁻¹.

CHAPTER IV

CONCLUSIONS

The electrochemical characterization of CS_2 and some related sulfur-containing compounds has contributed to the understanding of the redox mechanisms for these compounds. Often, a thorough understanding of a reaction mechanism leads to more versatile uses of a reaction for broader synthetic application. CS_2 was shown to initially form tetrathiooxalate dianions (3, p. 2) when reduced at -2.0 V, which was followed by further chemical reactions leading to the final product (1, p. 2). The tetrathiooxalate was identified by h.p.l.c. methods, which also indicated the presence of five other species in the reduction solution. Assignment of peaks for (1) and trithiocarbonate (2, p. 2) were made based on the retention times of these compounds versus the retention times of standards and the known wavelength maxima of the UV-visible absorption bands. Tetrathiooxalate can apparently undergo complex reactions in the electrolysis solutions leading to high molecular weight species. The tendency to form the compounds was first observed in the mass spectra of CS_2 reduction solutions. Later, the same species were discovered in the photolysis products of compound 25 (p. 18). It is implied by these results that the tetrathiooxalate functionality can be activated in such a way as to form a higher analogue series of compounds. Refinement of the factors which initiate and control this behavior may lead to useful quantities of these interesting species.

The reduction of compound 25 is a useful method for the preparation of tetrakis (methylthio) ethylene (59, p. 50), but it is not useful as a reactant in the electrochemical preparation of dimethyltetrathiooxalate (5, p. 6). However, the reduction of tetrathiooxalate to its dianion, followed by methylation gives 59. The electrochemical oxidation of 25 in acetonitrile does not lead to decarbonylation which would leave the tetrathiooxalate framework; instead, this oxidation leads to sulfoxide formation on the 1,3-dithiole ring.

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