INVESTIGATION OF ELECTROCHEMISTRY

OF

HIGH ENERGY COMPOUNDS IN ORGANIC ELECTROLYTES

FINAL REPORT

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by

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Abstract

This investigation has dealt with the electrochemistry of high energy compounds in organic electrolytes, specifically organic compounds of high capacity capable of being reduced at high potential.

The contributions made to the field of non-aqueous electrochemistry discussed in previous reports are briefly reviewed. These include the introduction of a special gas chromatographic technique for the analysis of the cyclic ester solvents, the clarification of the term "range of electrolysis" and the demonstration of its usefulness as a significant parameter in the analysis of non-aqueous battery systems, the appraisal of reference electrodes and the selection of the Ag/Ag^+ electrode as the most stable, and the compilation of the literature on the chemical properties of the cyclic esters.

The chronopotentiometric investigation of type organic compounds suitable for cathode depolarizers has been continued. On the basis of potential and capacity nitro compounds are of most interest; m-dinitrobenzene has a high relative capacity. The introduction of chlorine groups onto the aromatic ring allows the acceptance of four electrons. Steric factors are important in the adsorption and electrode reaction. Sulfonyl-bis-benzofurazan-dioxide exhibits reversibility and offers the possibility of developing a rechargeable system. Positive chlorine compounds are relatively unstable in the organic solvents and their electroreduction is controlled by an insoluble product.

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I. INTRODUCTION

This investigation has dealt with the electrochemistry of high energy compounds in organic electrolytes, specifically organic compounds of high capacity capable of being reduced at high potential (1-6).

This report has three objectives. The first is to summarize the work up to the last reporting period. This is done on the assumption that the first five progress reports and the supplement to the third progress report are available to the reader. Thus, the results are discussed in a broad way and the general implications of the results in terms of energy conversion or battery development are stated.

The second objective is to describe in detail recent chronopotentiometric investigations on the reduction of organic compounds. Four type compounds have been investigated and the rate determining step in each of the electrode processes is determined.

Finally - the third objective - an attempt is made to summarize the research in terms of what these findings mean regarding the possibility of developing a high energy primary or secondary battery. The technical problems associated with the utilization of high energy organic compounds are cited.

II. REVIEW OF PREVIOUS RESEARCH

Selection of Solvent

In the earliest stage of the project the open literature and reports of government contract work were studied to select the most suitable solvent system (1). This survey considered many solvents from the viewpoint of their chemical and physical properties. Six solvents, acetonitrile, dimethylformamide, α-picoline, propylene carbonate, γ-butyrolactone, and γ-valerolactone were included in the investigation. All of these solvents possessed long liquid ranges, high dielectric constants, the ability to dissolve many inorganic salts in high concentrations, and generally were chemically stable. As the work progressed, γ-butyrolactone and propylene carbonate were given more attention and the final work dealt mainly with systems comprised of γ-butyrolactone as the solvent.

Bibliographic Survey of Literature on Cyclic Esters

It was recognized that, for the successful employment of cyclic esters, such as butyrolactone and propylene carbonate, as solvents in electrochemical systems, a rather complete knowledge of their chemical, physical and electrochemical properties was required. The requirement with regard to their physical characteristics, e.g. freezing point, boiling point, viscosity, etc., and electrochemical behavior, e.g. decomposition potentials, is obvious. The need to know about their chemical reactions, such as hydrolysis, condensations and couplings arise when these solvents are used with organic depolarizers or are subjected to various electrode processes generating protons or hydroxyl ions. To have available the research previously done and reported in the literature an extensive survey of the literature was conducted. From this survey, 423 pertinent references were selected and reported as "Bibliography on Propylene Carbonate, γ-Butyrolactone, and Related Subjects," Supplement to Third Progress Report, dated September 12, 1966 (4). The references were grouped under the following headings:

I. Lactones

II. Butyrolactones

  A. Purification and Properties

  B. Preparation of γ-Butyrolactone

  C. Synthesis of Substituted γ-Butyrolactones

  D. Reactions of Unsubstituted γ-Butyrolactones

  E. Reactions of Substituted γ-Butyrolactones

  F. Hydrolysis

    (a) General

    (b) γ-Butyrolactone

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    (a) General

    (b) γ-Butyrolactone

  H. Miscellaneous

III. Metal-Organic Reactions

IV. Cyclic Carbonates

V. Propylene Carbonate

The need to have a detailed knowledge of the chemical reactions of these organic solvents is not fully appreciated. However, many of the problems encountered in non-aqueous electrochemical investigations have stemmed from oversight of a basic chemical reaction reported in the literature.

Solvent Properties

Solvent Purification and Analysis

All of the solvents were purified by fractional distillation under reduced pressure (1). The γ-butyrolactone used in most of the work was commercial grade material fractionally distilled at 2 mm. Hg through a 17-inch Vigreux column. A center cut was taken at 69°C. The distilled cut was collected and transferred in dry nitrogen to a dry box in which the experiments were conducted. A number of physical properties or analytical techniques were used to establish the solvent purity (6). Much of the problem involved the detection of water contents in the ppm range.

Techniques based on the following were used:

refractive index
density
electrical conductivity
reaction with Karl Fischer reagent
gas phase chromatography
reaction with calcium hydride

A considerable number of measurements were made which are of value in the handbook sense and provide a means for detecting gross contamination. The measurements of refractive index, density, and electrical conductivity fall into this category. The Karl Fischer method for water analysis is the accepted technique for the analysis for water in organic solvents and apparently is used successfully in many laboratories. However our experience has shown that the technique is not satisfactory for the water range in which we were working. The direct reaction is sluggish, suggesting that the water is bound in a complex with the solvent with the dissociation of the complex being a slow step. The most suitable analytical technique is gas chromatography with a special column material called Poropak Q (6). Under proper conditions water concentrations in the 10-100 ppm range can be measured quantitatively, and as low as 2 ppm can be detected. The introduction and application of gas chromatographic techniques to this field has made available a powerful tool toward the attainment of pure systems free of contaminants in the ppm range.

Chemical Properties of Solvent

When the organic solvent is considered as a component in an electrolytic system two important reactions are those the solvent undergoes with metals and halogens (3). The metals of interest in this project are those that would provide active anode materials. The reactions of Li, Na, K, Ca, and Mg with butyrolactone and propylene carbonate were investigated at 100°C. Weighed quantities of the metals and purified solvents were refluxed at 100°C while nitrogen gas, dried over P_2O_5, was passed over the reaction mixture. Following the 100-hr reaction time the metals were reweighed and the solid and solution products were separated and examined by chemical methods, infrared absorption, thin layer chromatography and gas chromatography. Na and K react almost completely with butyrolactone whereas Li, Ca and Mg are unreactive. The best explanation for the reactivity of Na and K in the anhydrous system involves a complicated mechanism with the major product being the sodium (or potassium) salt of the hydroxy carboxylic acid. These experiments were repeated recently using purified Na and K and butyrolactone with a water content not greater than 2 ppm. The same result was obtained so it is concluded that the reaction is one with Na or K metal rather than their oxides or hydroxides. The presence of NaOH is known to cause the ring opening observed and for this reason great care was taken to eliminate this possibility. Further, if water and hydroxide impurities were involved in these reactions it would be expected that Li would also react. Li is quite stable in the anhydrous system.

In propylene carbonate under similar conditions Na, K, and Ca were reactive whereas Li and Mg were unreactive.

There are certain implications applicable to electrochemical systems to be drawn from these experiments. The use of sodium or potassium salts in rechargeable systems should be carefully studied. The probable charging voltage for a non-aqueous system, over 3 volts, would be expected to deposit Na or K. This deposit would react with the solvent, appreciably at elevated temperature, but significantly at room temperature. Li and Mg are stable in these solvents. Li, of course, is used as an anode material but Mg is not, presumably due to its lower voltage. Further, if excessive reaction of Li in the system is observed it would be expected that the system is contaminated with water or some other acid material.

The reactions of γ-butyrolactone and propylene carbonate with chlorine gas were studied briefly at 100°C and at room temperature (3). Chlorine apparently dissolves in γ-butyrolactone but does not react in 2.5 hours at 100°C as shown by refractive index and infrared absorption measurements. Chlorine gas dissolves in propylene carbonate and upon standing reacts as indicated by new absorption maxima produced in the UV region. These experiments are not detailed enough to be conclusive. They do, however, indicate the possibility of a reaction that might compete with certain electrode reactions and chlorine should be viewed in that light.

Range of Electrolysis

The "range of electrolysis" is a measure of the electrochemical stability of the solute-solvent system (2). It is defined as the voltage that must be applied across smooth platinum electrodes before a sensible faradaic current flows in the cell. The voltage is measured at the arbitrarily chosen current density of 0.10 ma/cm^2.

Considerable confusion has arisen in connection with the use of the terms "range of electrolysis" or "decomposition voltage" because this quantity is not amenable to precise thermodynamic treatment. Analogous to most electrode processes the actual voltage measured is dependent on current density, electrode material, surface area, impurities in solute, etc. All of the comments that are applicable to overvoltage phenomena apply to these measurements. Thus, it is necessary to define the conditions under which the measurements are made. However, once the experimental conditions are defined, and it is understood that the results refer to a solute-solvent system rather than the solvent itself, it must be concluded that these values are the most significant parameters available to evaluate any new system under consideration as an electrochemical energy conversion system.

Within this framework the range of electrolysis of a number of solutions were measured. The values for the $LiClO_4$ solutions of primary interest were:

Butyrolactone	5.78 v.
Propylene carbonate	5.25 v.
Valerolactone	6.82 v.

To obtain these values polarizations were conducted in both the anodic and the cathodic directions. The limit in the anodic direction for specific anions, in comparison with a silver reference, were as follows:

ClO_4^-	= 2.40 v.
PF_6^-	= 2.47 v.
Cl^-	= 1.41 v.
BF_4^-	= 2.51 v.

The cathodic potential limits as established by cations is as follows:

Li^+	= 3.44 v.
K^+	= 1.65 v.
Na^+	= 1.08 v.
$(CH_3)_4N^+$	= 0.92 v.
Al^{+++}	= 0.21 v.
Morpholinium	= 0.40 v.

In the last three cases the cathodic reaction is not known but it very likely does not involve the discharge of the cation specified.

The net conclusion to be drawn from these experiments is that an electrolyte system such as a 1.0M solution of lithium perchlorate in butyrolactone can potentially support a 5-6 volt galvanic cell. To utilize this range a lithium anode is required and a cathode reaction approaching 2.5 v. All of the known cathode materials have relatively low potentials so the problem of utilizing the 5-6 volt capability of the solute-solvent system becomes one of finding a high energy cathode compound.

Reference Electrode

In the field of non-aqueous electrochemistry considerable attention has been devoted to the selection of appropriate reference electrodes (3). One type has been based on a conventional aqueous type electrode, such as a saturated calomel electrode, connected to the non-aqueous solution through a non-aqueous salt bridge which presumably prevents water contamination. Another type is the Ag-AgCl type, useful in those solutions containing the anion to which the electrode is reversible. Two other types of considerable experimental value are the Ag/Ag^+ type and the Ag metal type. The stability and reversibility of these two electrodes were studied. In investigating the stability of these electrodes the experimental problem arises regarding what electrode is to be used for comparison. In our work a large platinum electrode was used. The Ag/Ag^+ electrode is the more stable of the two varying ± 8 mv. over 60 hours. It also follows Nernst law behavior with regard to the Ag^+ concentration. The Ag wire after equilibration varies only a few mv. over a several hour duration and is, therefore, very useful from an experimental standpoint. A practical solution to the reference electrode question is to use a silver wire in close proximity to the working electrode (low IR drop) and to check this reference against a Ag/Ag^+ reference separated from the solution by a porous glass frit.

High Energy Organic Compounds

The initial work on high energy organic compounds involved reviewing the literature to attempt to develop some correlation between reduction potential, capacity and efficiency (1). Then, on the basis of this correlation, compounds could be selected for experimental study. Practically all of the pertinent work that has been reported in the literature has dealt with aqueous systems. Nitrogen-halogen compounds or compounds containing a "positive" halogen group were of significance because of their high potentials -- in the neighborhood of 1.0 volt and their high capacity. The mechanism of reduction has not been elucidated and this has been a crucial question. If, as postulated, a hydrolysis step must proceed reduction, then the reduction would depend on the water content of the "non-aqueous" solution.

Aromatic nitro compounds have also been useful depolarizers. In the reduction of the $-NO_2$ group, as generally written, protons are required. If a similar mechanism operates in the organic electrolytes then protons or a proton substitute would have to be supplied. Of the organic compounds previously investigated one of the few classes to exhibit reversibility are the quinones. Most quinones have low potentials however. Within all these classes of compounds it is possible to write rules governing the effect of substituents on the potential or discharge characteristics of the compound. These rules would be applicable, if and when, parent compounds were found that exhibited desirable electrochemical properties. They would provide an addition 0.1-0.[illegible] v. potential in a compound that yielded a suitable capacity. The work reported in the literature in aqueous system has influenced our choice of organic compounds as described below.

III. KINETICS OF REDUCTION OF ORGANIC COMPOUNDS

Preliminary Experiments

Various electrochemical techniques to study the kinetics of reduction of high energy organic compounds were surveyed and of the accepted procedures chronopotentiometry was selected. Recent theoretical treatments have made it possible to determine the rate determining step in a series of steps associated with an electrode reaction (7-10). Also the instrumentation used in chronopotentiometry has been well developed.

The preliminary experiments, previously reported, dealt with the reduction of certain type compounds such as nitrobenzene, m-dinitrobenzene, and trichloromelamine. These experiments demonstrated that it was possible to get chronopotentiometric waves for reductions in organic solvents that could be analyzed by conventional methods.

The use of thin-layer chronopotentiometry had been reported in the literature as a technique for improving the definition of the reduction waves in organic solvents (11). A thin-layer cell of this type reported in the literature was built and considerable effort was expended in attempting to get data with it. However, the difficulty in filling the cell and manipulating to achieve a precise known value of the diffusion layer thickness was such that work on this technique was dropped.

The project was continued using conventional chronopotentiometric techniques and the accuracy and precision was such that it was possible to identify the rate determining step in the reduction of several <u>type</u> organic compounds.

Experimental

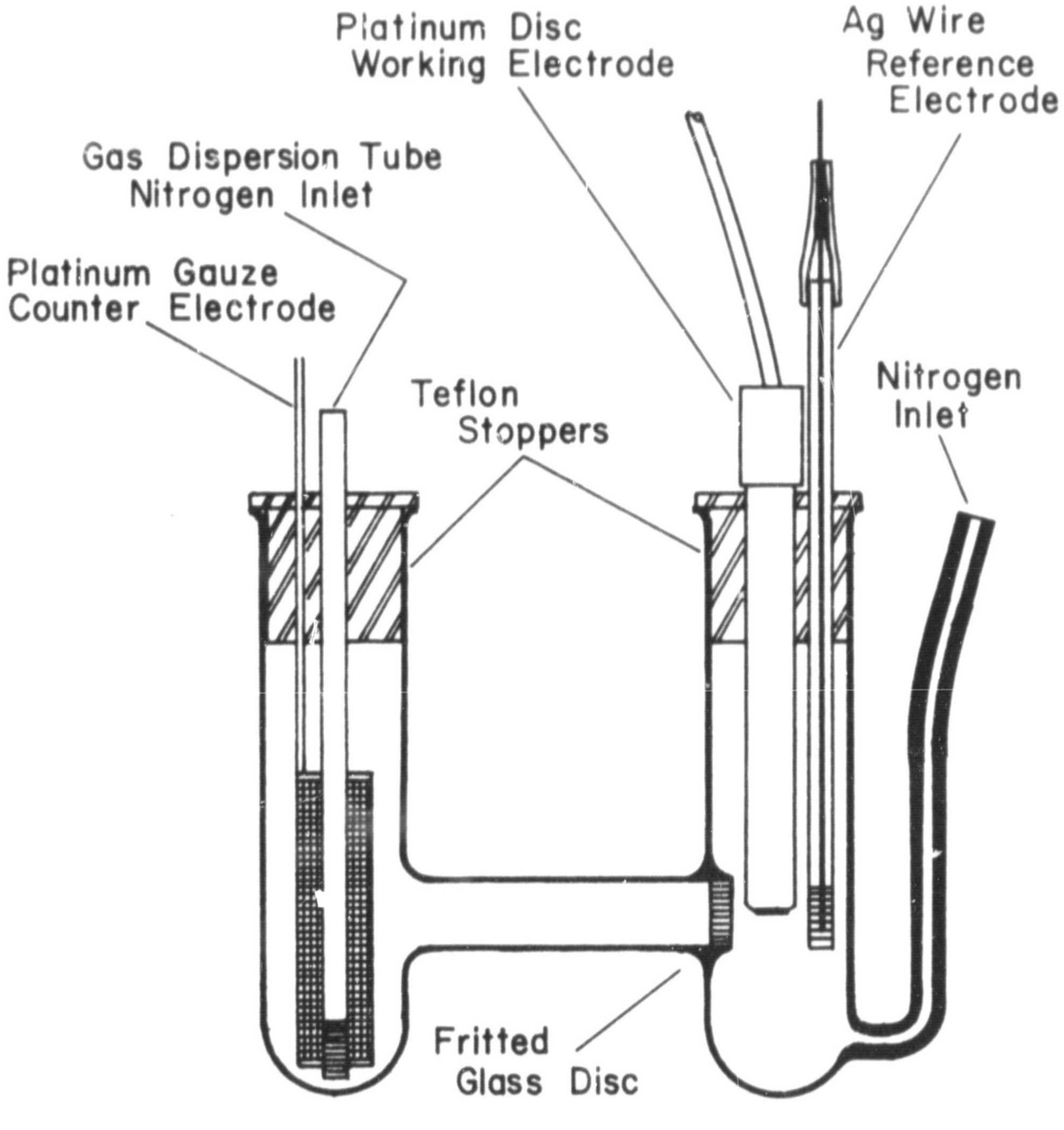
The greater part of the apparatus was similar to that previously described in other chronopotentiometric investigations. A conventional glass electrolysis H-cell was used as depicted in figure 1. A fritted glass disc separated the anode and cathode compartments. The cell was stoppered with Teflon plugs machined to fit the cell closely. A large platinum anode (counter electrode) of approximately 57 cm^2 area was employed and both compartments were provided with gas dispersion tubes so that the solution could be swept free of dissolved oxygen which was reduced at polarizing potentials less than those of interest. The cathode (working electrode) was a Beckman Platinum Disc Electrode of an area of 0.196 cm^2. The reference electrode was a silver wire electrode mounted adjacent to the working electrode.

The schematic diagram of the electrical set up is very close to that previously reported and is shown in figure 2. The major change was in the power supply which was replaced with a North Hills Electronics Model CS-11, Series R. This is a precision unit designed to deliver 0 to 100 milliamperes in steps of 1 microampere by means of five decade switches. The terminal voltage capacity is 0 to 100 volts at any setting. Current regulation is rated as 0.002% for load voltage change from 0 to 100 volts and for line voltage change from 105 to 125 volts rms.

The potential of the working electrode was measured with a Keithley Model 600 A Electrometer representing a high impedance source of greater than 10^{14} ohms. The plot was recorded on a Sargent Model MR Recorder.

FIGURE I

ELECTROLYSIS CELL FOR CHRONOPOTENTIOMETRY



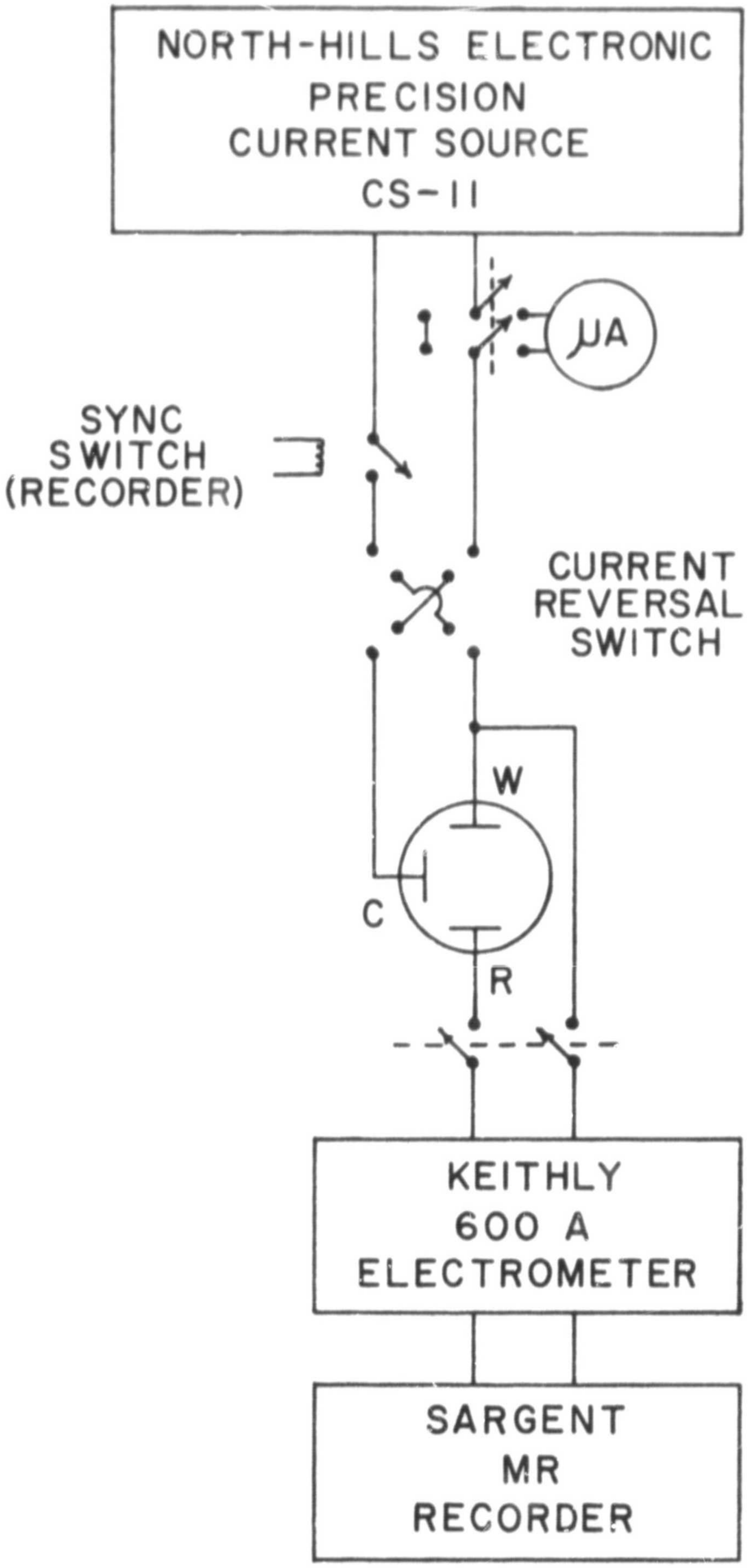


FIGURE 2

INSTRUMENTATION FOR CHRONOPOTENTIOMETRY

The following compounds were investigated:

1. Potassium dichloro-s-triazinetrione. This compound was obtained from FMC Corporation (CDB-59M) with a listed impurity of 100%.

2. Sodium dichloro-s-triazinetrione was also obtained from FMC Corporation (their compound CDB-63M).

3. m-Dinitrobenzene. This compound was Eastman (P 99) practical grade m-dinitrobenzene. It was recrystallized from methanol using activated charcoal. The recrystallized material had a melting point of 89.6°C.

4. 1,3-dinitro-2,4,5-trichloro-benzene. This compound was obtained from the Aldrich Chemical Co. (D 20,080) and recrystallized from either ethanol or hexane. Both recrystallized products had the same melting point, 101.5-102.5°C.

5. 5,5' - Sulfonyl-bis-benzofurazan-3,3'-dioxide obtained from the American Cyanamid Co. through the courtesy of Dr. S. M. Davis and Dr. R. Bruce Van Order. This compound was used as received.

Procedure

The procedures used were similar to those previously reported. Solutions were prepared and transferred in a dry box under an argon atmosphere. The supporting electrolyte was a solution 0.3 to 1.0M $LiClO_4$ in γ-butyrolactone. Lithium perchlorate obtained from Foote Mineral was recrystallized from water to obtain the trihydrate. The trihydrate was heated at 180°C under vacuum for 24 hours. The dried lithium perchlorate had a well defined melting point of 235-236°C which agreed with the handbook value. The dried lithium perchlorate was stored in small weighing dishes over phosphorus pentoxide in a vacuum desiccator.

Butyrolactone was purified by redistilling at 69°C and 2 mm. mercury through a 17-inch Vigreux column. The middle fraction was collected in a dry nitrogen atmosphere and transferred in that atmosphere to the dry box with the dry argon atmosphere. The butyrolactone so prepared contained less than 10 ppm of water when analyzed by the gas chromatographic methods described above (6).

Properties of $LiClO_4$-butyrolactone solutions prepared in this manner had the properties indicated in table 1. The density and viscosity were measured for use in the calculation of the diffusion constants in the rate equations.

Treatment of data

Certain basic equations have been developed for the treatment of the data accumulated during a chronopotentiometric investigation (12). The first of these is the Sand equation which defines the transition time, τ.

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n \ FAD^{\frac{1}{2}} C}{2i}$$

in which C is the concentration of the electroactive species in solution, i is the current which is kept constant during the run, D is the diffusion coefficient, F, the Faraday, A is the electrode area and n is the number of electrons involved in the reaction. This equation was developed on the basis that linear diffusion to the electrode controlled the current (the electrode reaction) so that if the product

$$\frac{i\tau^{\frac{1}{2}}}{C}$$

calculated from the experimental data is constant then the rate determining factor is diffusion.

TABLE 1

PROPERTIES OF $LiClO_4$ - BUTYROLACTONE SOLUTIONS

Molarity (M)	Density (g/ml)	Specific Conductivity ($ohm^{-1}cm^{-1}$)	Viscosity (cp)
0.00	1.1254	4.97×10^{-8}	1.98
0.10	1.132	1.82×10^{-3}	2.15
0.50	1.153	4.60×10^{-3}	3.17
1.00	1.183	5.69×10^{-3}	5.34
2.00	1.238	3.04×10^{-3}	20.20

The potential-time relationship in chronopotentiometry is represented by the Karaoglanoff equation (12)

$$E = E_{\frac{1}{4}} - \frac{RT}{nF} \ln \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}$$

Here $E_{\frac{1}{4}}$ is the potential when the time, t, is $\frac{\tau}{4}$, τ being the transition time defined above.

Based on these equations many investigators have developed criteria for analyzing data. Reinmuth has worked out a whole series of relationships (7) that are too detailed to be reproduced here but have been used in the analysis of our data and have been helpful in establishing the rate determining process. The experimental data for each compound are discussed separately.

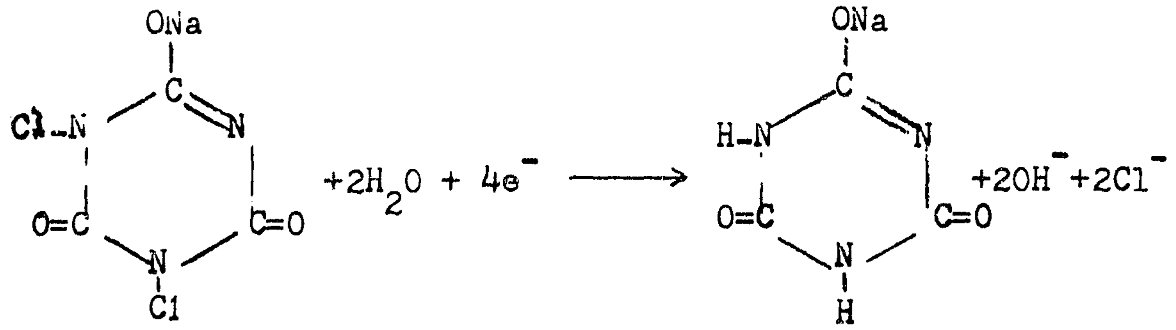
Results and Discussion

Potassium and Sodium Dichloroisocyanurate

In preliminary experiments with aqueous solutions containing 1 M potassium nitrate supporting electrolyte, the potassium dichloroisocyanurate was found to be unstable with respect to decomposition to chlorine gas and water soluble products. The overall reaction which occurred at a potential of +0.25 v. (vs. S.C.E.) was attributed to either hydrolysis and reduction, or direct reduction, or a combination of both mechanisms.

In the aqueous potassium nitrate solutions it was observed that the sodium dichloroisocyanurate, CDB-63M (FMC-703505), was more stable with respect to spontaneous decomposition. For the sodium salt, two distinct chronopotentiometric waves were observed. The first wave, $E_{\frac{1}{4}}$ = -0.08v.(vs. S.C.E.), had a transition time constant, $i\tau^{\frac{1}{2}}$, which was independent of current density at constant concentration of electroactive species. The electron change for this irreversible wave was calculated from the Sand equation to be 4.0 as shown in table 2.

This reaction was believed to be:



The second reduction wave, $E_{\frac{1}{4}}$ = -0.34v.(vs. S.C.E.), was found to be independent of the concentration of the sodium salt, but directly proportional to the concentration of the supporting electrolyte - this wave was attributed to an impurity in the potassium nitrate.

TABLE 2

CHRONOPOTENTIOMETRIC DATA FOR THE FIRST REDUCTION WAVE OF SODIUM DICHLOROISOCYANURATE IN AQUEOUS KNO_3

Concentration M/ml	Current Amps	Transition Time Sec	$i\tau^{\frac{1}{2}}$ $Amp \cdot sec^{\frac{1}{2}}$	Electron Change N
1.82×10^{-6}	1.5×10^{-4}	6.60	3.86×10^{-4}	4.0
1.82×10^{-6}	2.0×10^{-4}	3.54	3.76×10^{-4}	3.9
1.82×10^{-6}	2.5×10^{-4}	2.36	3.85×10^{-4}	4.0
1.82×10^{-6}	3.0×10^{-4}	1.65	3.84×10^{-4}	4.0
1.82×10^{-6}	3.5×10^{-4}	1.18	3.82×10^{-4}	3.9

Average Electron Change = 4.0

The solubility of the alkali dichloroisocyanurates in v-butyrolactone solutions was small. The potassium salt was more soluble than the sodium salt. A saturated solution of the potassium dichloroisocyanurate was prepared in 0.43 M $LiClO_4$- butyrolactone solution. The concentration of the potassium salt was less than 5.4×10^{-5} M/ml. The transition time constant, $i\tau^{\frac{1}{2}}$, was not constant with respect to increasing current density for the irreversible wave at +0.25v.(vs. Ag Wire). As the current increased, the transition time constant also increased, that is, the $\frac{\partial i\tau^{\frac{1}{2}}}{\partial i}$ was positive. From Reinmuth's criteria (7) and from the identical quarter-wave potentials of both the aqueous and non-aqueous chronopotentiograms, the reaction was believed to be identical in both solvents. It was postulated that the solvent served as a source of protons in the non-aqueous solution. The product of the postulated reaction, potassium isocyanurate was believed to be even less soluble than the reactant; the potassium isocyanurate was thought to be precipitated on the electrode surface. If the electrode were covered with an insoluble layer, then the electrode would act as if it were adsorption controlled. In support of this assumption, the transition time constant increased with increasing current density, and quarter-wave potential decreased with increasing current density (table 3). Further, the transfer coefficient, α , obtained from the plot of potential, E, versus log $[(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}]$ shown in figure 3 was extremely low. The reduction of potassium dichloroisocyanurate in v-butyrolactone is thought to occur in the following manner:

$$O + 4e^{-} \longrightarrow R_{(\text{Insoluble})}$$

where O is the oxidized species and R is the reduced species.

TABLE 3

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF POTASSIUM DICHLOROISOCYANURATE IN 0.4 M $LiClO_4$-γ- BUTYROLACTONE

Current Amps	Transition Time Sec	$I\tau^{\frac{1}{2}}$ Amp·sec$^{\frac{1}{2}}$	$E_{\frac{1}{4}}$ Volts vs. Ag Wire
3.0×10^{-5}	23.7	1.46×10^{-4}	+0.25
3.5×10^{-5}	17.1	1.45×10^{-4}	+0.19
4.0×10^{-5}	13.4	1.46×10^{-4}	+0.23
4.5×10^{-5}	11.0	1.49×10^{-4}	+0.24
5.0×10^{-5}	8.9	1.49×10^{-4}	+0.22
5.5×10^{-5}	7.7	1.52×10^{-4}	+0.21
6.0×10^{-5}	6.1	1.48×10^{-4}	+0.19
6.5×10^{-5}	5.8	1.57×10^{-4}	+0.14
7.0×10^{-5}	4.7	1.52×10^{-4}	+0.13

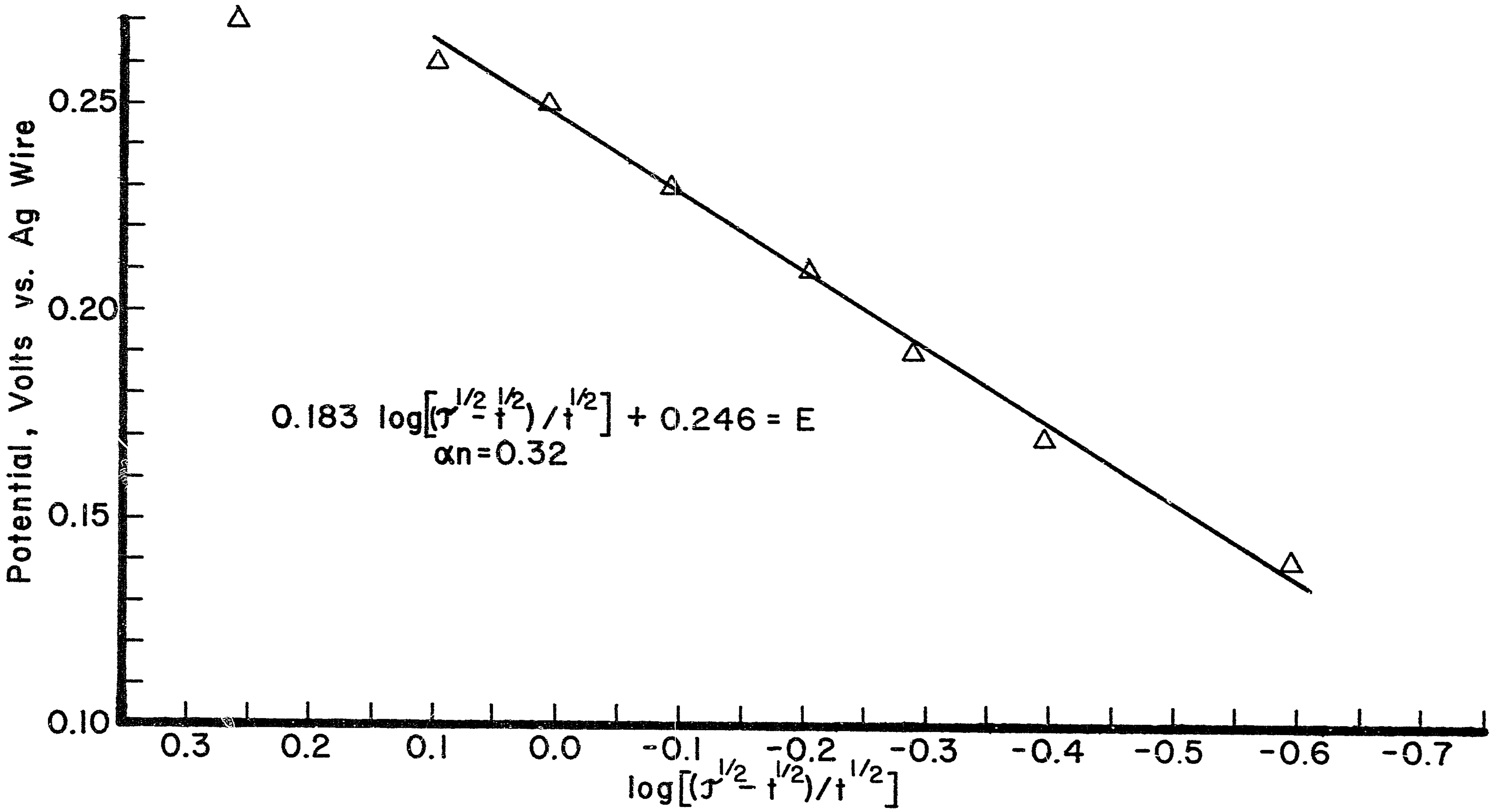


FIGURE 3

KARAOGLANOFF PLOT FOR POTASSIUM DICHLOROISOCYANURATE

m-DINITROBENZENE

A solution of γ-butyrolactone containing 0.43 M $LiClO_4$ as supporting electrolyte was used in the reduction of m-dinitrobenzene. The date for the irreversible chronopotentiometric cathodic wave was observed with a quarter-wave potential of -0.69 v. vs. Ag. From the data of Table 4, it is obvious that there is a distinct tendency for the transition time constant, $i\tau^{\frac{1}{2}}$, to decrease with increasing current density at constant concentration. The quarter-wave potential, $E_{\frac{1}{4}}$, also exhibits this decreasing trend with increasing current density. In fact, for a plot of the logarithim of the current versus the quarter-wave potential, as in Figure 4, a negative slope of -0.067 is obtained. Only three concentrations of m-dinitrobenzene were investigated; however, even with this limited data plotted in figure 5 it appears that both the quarter-wave potential and the transition time constant increases with increasing concentration. See Figure 5. The log $[(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}]$ is plotted versus the potential in Figure 6. From the slope of this plot, $\alpha n = 0.93$. Although the differences between observations are slight, a convincing argument for a slower step than linear diffusion should be inferred from the preceding statements. If α is assumed to be 0.5, the number of electrons involved in the electrochemical reaction is approximately 2.0.

The reduction of m-dinitrobenzene under these conditions is thought to occur via the following steps:

$$BH \rightleftharpoons H^{+} + B^{-}$$

$$2H^{+} + Ph(NO_2)_2 + 2e \longrightarrow Ph(NO_2)NO + H_2O$$

where BH is either the solvent or trace water in the solvent. Water

TABLE 4

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF m-DINITROBENZENE IN 0.43 M $LiClO_4$-γ-BUTYROLACTONE

Concentration M/ml	Current Amps	Transition Time Sec	$E_{\frac{1}{4}}$ Volts	$i\tau^{\frac{1}{2}}$ Amp·sec$^{\frac{1}{2}}$
3.45×10^{-6}	5.0×10^{-5}	77.1	-0.68	4.39×10^{-4}
3.45×10^{-6}	6.0×10^{-5}	49.2	-0.69	4.21×10^{-4}
3.45×10^{-6}	7.0×10^{-5}	34.7	-0.69	4.12×10^{-4}
3.45×10^{-6}	8.0×10^{-5}	23.6	-0.70	3.89×10^{-4}
3.45×10^{-6}	9.0×10^{-5}	16.8	-0.71	3.68×10^{-4}
3.45×10^{-6}	10.0×10^{-5}	13.5	-0.72	3.67×10^{-4}
3.45×10^{-6}	11.0×10^{-5}	11.1	-0.72	3.66×10^{-4}
3.45×10^{-6}	12.0×10^{-5}	8.7	-0.73	3.55×10^{-4}
3.45×10^{-6}	11.0×10^{-5}	11.1	-0.72	3.66×10^{-4}
7.45×10^{-6}	11.0×10^{-5}	21.7	-0.69	5.13×10^{-4}
11.06×10^{-6}	11.0×10^{-5}	25.8	-0.68	5.59×10^{-4}

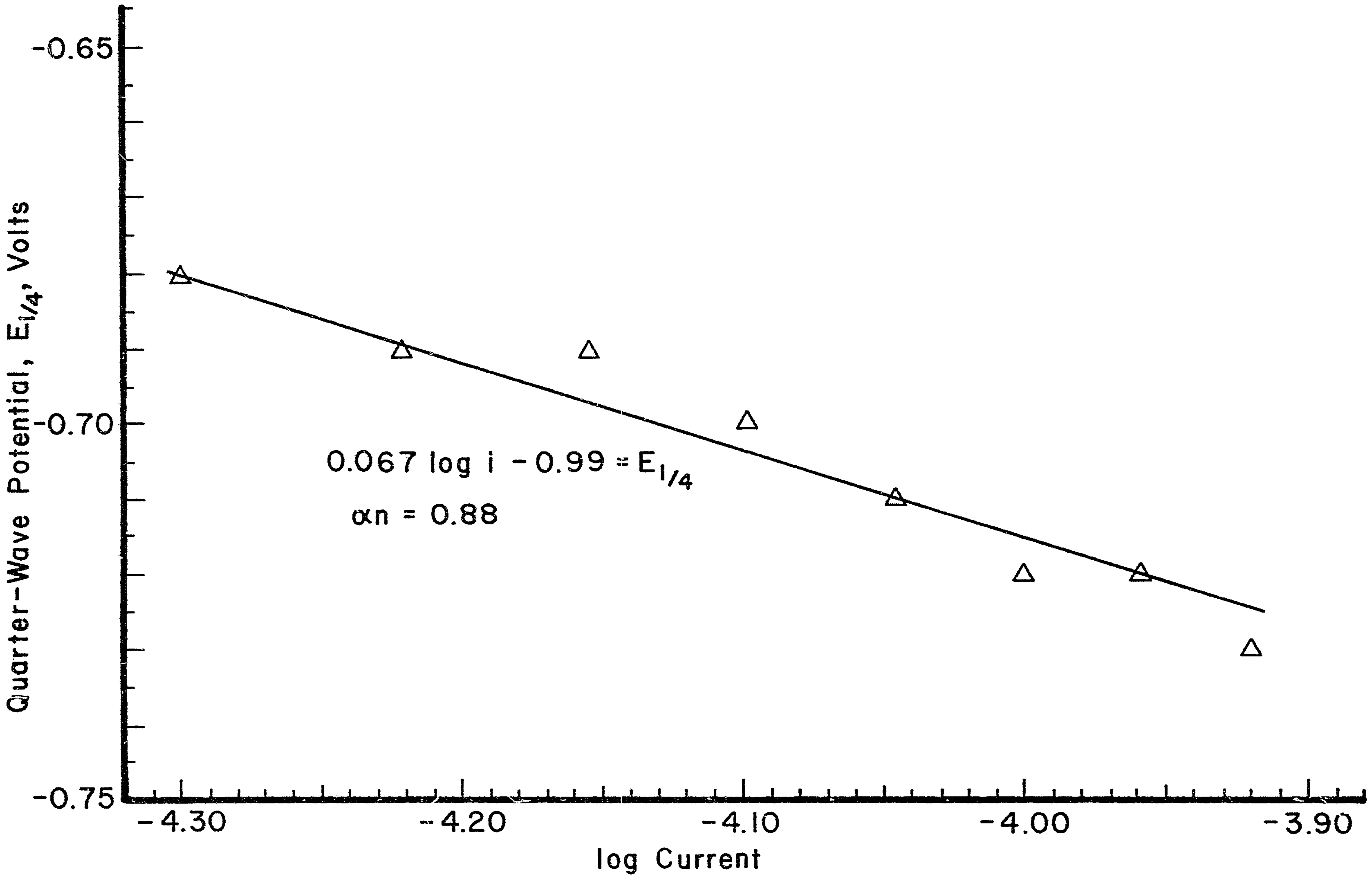


FIGURE 4
LOG CURRENT vs. $E_{1/4}$ FOR m-DINITROBENZENE

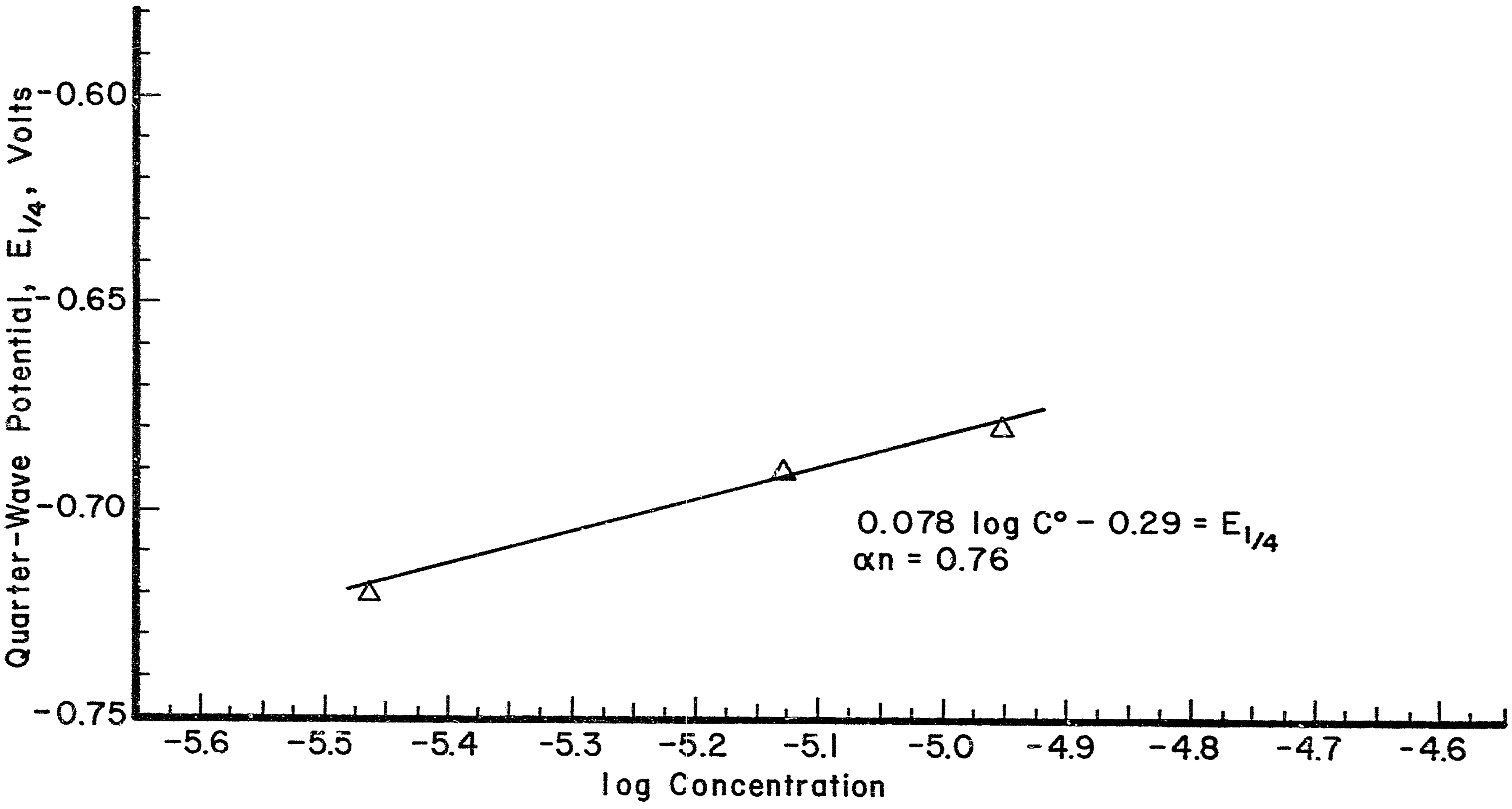


FIGURE 5

LOG CONCENTRATION vs. $E_{1/4}$ FOR m-DINITROBENZENE

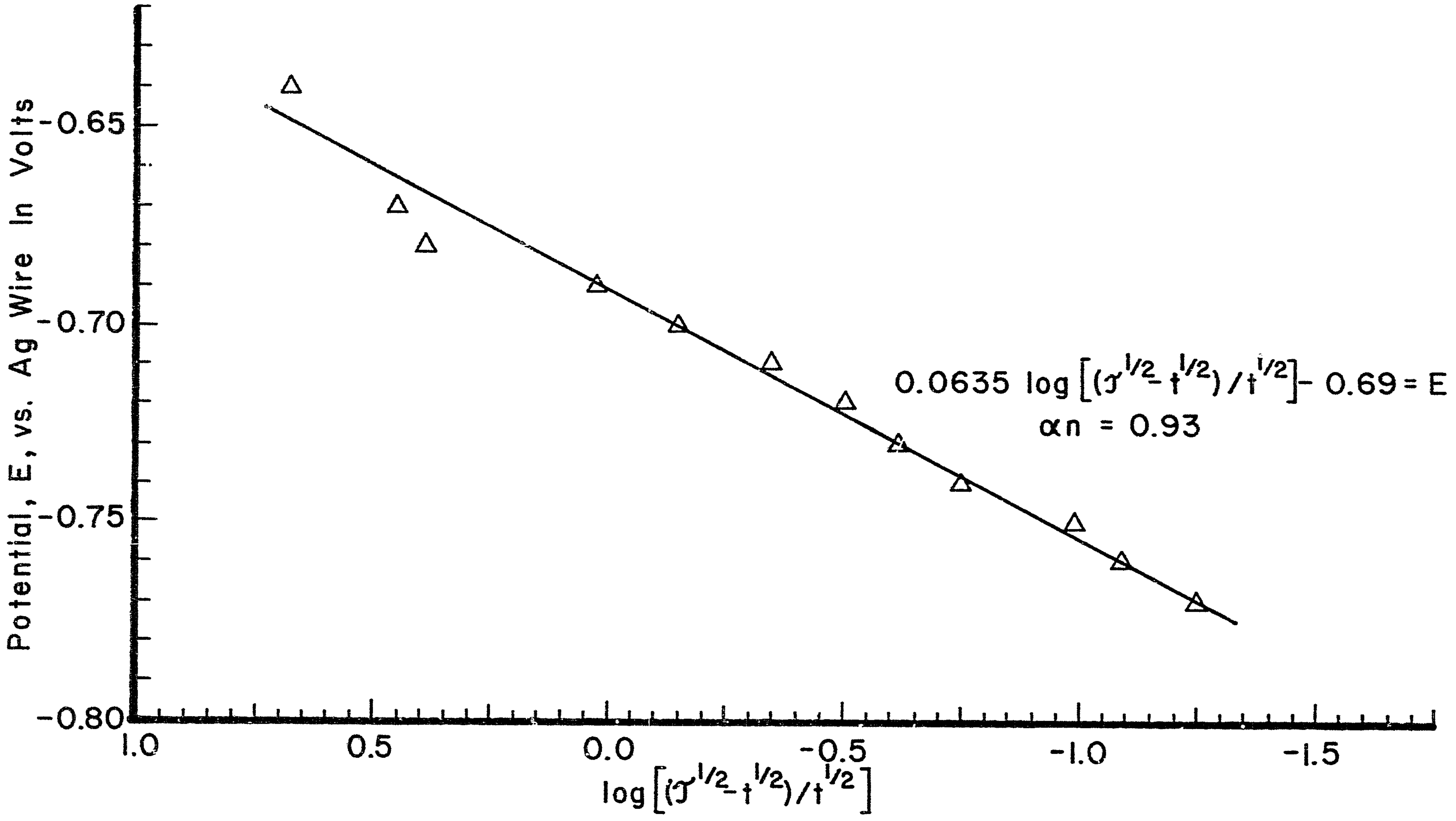


FIGURE 6
KARAOGLANOFF PLOT FOR m-DINITROBENZENE

in gamma butyrolactone in amounts less than 100 ppm is known to not behave as a solvent, but it appears to be bound to butyrolactone much like a complex. Thus, the first reaction above may be the slow breakdown of the water-butyrolactone complex with the subsequent ionization of the water. An alternative source of protons may be from the alpha hydrogens of gamma butyrolactone. These protons may be released by a mechanism not unlike the acid-catalyzed enolization of esters where the acid is replaced by the lithium ion of the supporting electrolyte. Protons may be supplied from either water as a trace contaminant, the solvent, or a combination of both wherein the equilibrium represents a competition between the two sources. In any case, the release of protons is thought to be the rate determining step of the reaction. That a slow rate-determining step exists is inferred from the negative slope of a plot of the transition time constant as a function of current at constant concentration of the m-dinitrobenzene as in Column 5 of Table 4. Without further evidence, it is not possible to determine the chemical nature of the product; however, from the ease of reduction of nitroso groups in aqueous solution it is probable that a four electron change occurs to yield either the phenylhydroxylamine or the azoxybenzene derivatives.

1,3-DINITRO-2,4,5-TRICHLOROBENZENE

The chronopotentiometric data for the reduction of 1,3-dinitro-2,4,5-trichlorobenzene are presented in Table 5. In 0.25 M $LiClO_4$ γ-butyrolactone solution, the dinitrotrichloro-compound appears to exhibit all the properties of an adsorption controlled species. The irreversible reaction yields a value of 1.73 for αn from the Karaoglanoff plot. See Figure 7. That αn is considerably higher for this compound than for m-dinitrobenzene may be anticipated by the presence

TABLE 5

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION OF 1,3-DINITRO-2,4,5-TRICHLOROBENZENE IN 0.25 M $LiClO_4$-γ-BUTYROLACTONE

Concentration M/ml	Current Amps	Transition Time Sec	$E_{1/4}$ Volts	$i\tau^{1/2}$ Amp·sec$^{1/2}$
5.24×10^{-5}	1.50×10^{-4}	29.3	-0.56	8.1×10^{-4}
5.24×10^{-5}	1.75×10^{-4}	21.9	-0.57	8.2×10^{-4}
5.24×10^{-5}	2.00×10^{-4}	21.2	-0.58	9.2×10^{-4}
5.24×10^{-5}	2.50×10^{-4}	16.1	-0.57	10.0×10^{-4}
5.24×10^{-5}	3.00×10^{-4}	12.0	-0.58	10.4×10^{-4}
5.24×10^{-5}	4.00×10^{-4}	8.0	-0.60	11.3×10^{-4}
5.24×10^{-5}	4.50×10^{-4}	7.6	-0.61	12.3×10^{-4}
6.47×10^{-5}	2.00×10^{-4}	24.5	-0.54	9.9×10^{-4}
6.47×10^{-5}	3.00×10^{-4}	14.8	-0.58	11.5×10^{-4}
6.47×10^{-5}	4.00×10^{-4}	8.0	-0.60	12.3×10^{-4}
8.96×10^{-5}	3.00×10^{-4}	14.3	-0.59	11.3×10^{-4}

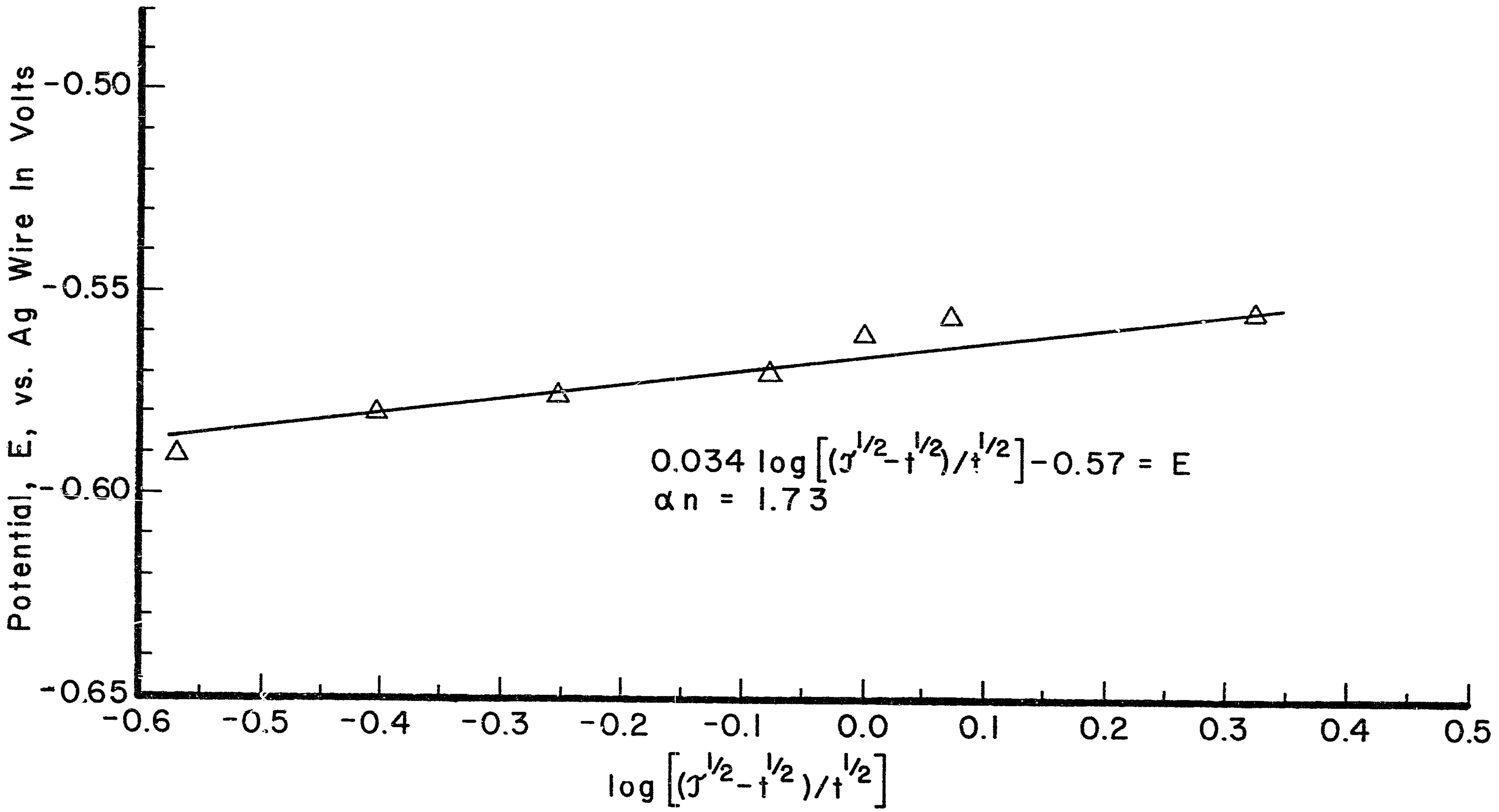


FIGURE 7

KARAOGLANOFF PLOT FOR 1,3-DINITRO-2,4,5-TRICHLOROBENZENE of the three chlorine substituents. The effect of the chlorine substituents is to increase the electron density of the ring; thus, less energy is needed to remove the oxygen from the compound. The ease of reduction of this compound compared to m-dinitrobenzene is reflected in the higher quarter-wave potential, $E_{\frac{1}{4}} = -0.57$ v., and in the higher value of αn. In this case, a red precipitate was formed on the electrode surface during preliminary experiments at high current densities. This compound , then, exhibits an electrochemical reaction which is adsorption controlled.

5,5'-SULFONYL-BIS-BENZOFURAZAN-3,3'-DIOXIDE

Of the compounds studied in this research, 5,5'-sulfonyl-bis-benzofurazan-3,3'-dioxide was unique in that an anodic wave was observed upon current reversal. In Figure 8, a typical chronopotentiogram with current reversal is presented. It should be noted that the current was reversed prior to the transition time, τ. Under these conditions, if one assumes the current efficiencies of the forward and reverse processes to be the same, the overall reverse transition time should be one-third the forward transition time. A series of experiments were performed where the forward transition time was exceeded, and then the current was reversed. The data from these experiments are presented in Table 6. Four concentrations were investigated. As the current was increased at constant concentration of the bis compound, the transition time constant was indeed a constant, as is shown in Column 4. The only inconstancy of the transition time constant occurred for short transition times where the accuracy of the measurement is subject to large error or for long transition times where a break-down of the diffusion layer by convection increases the error. It is the break-down of the diffusion layer which is primarily responsible for large scatter of values for

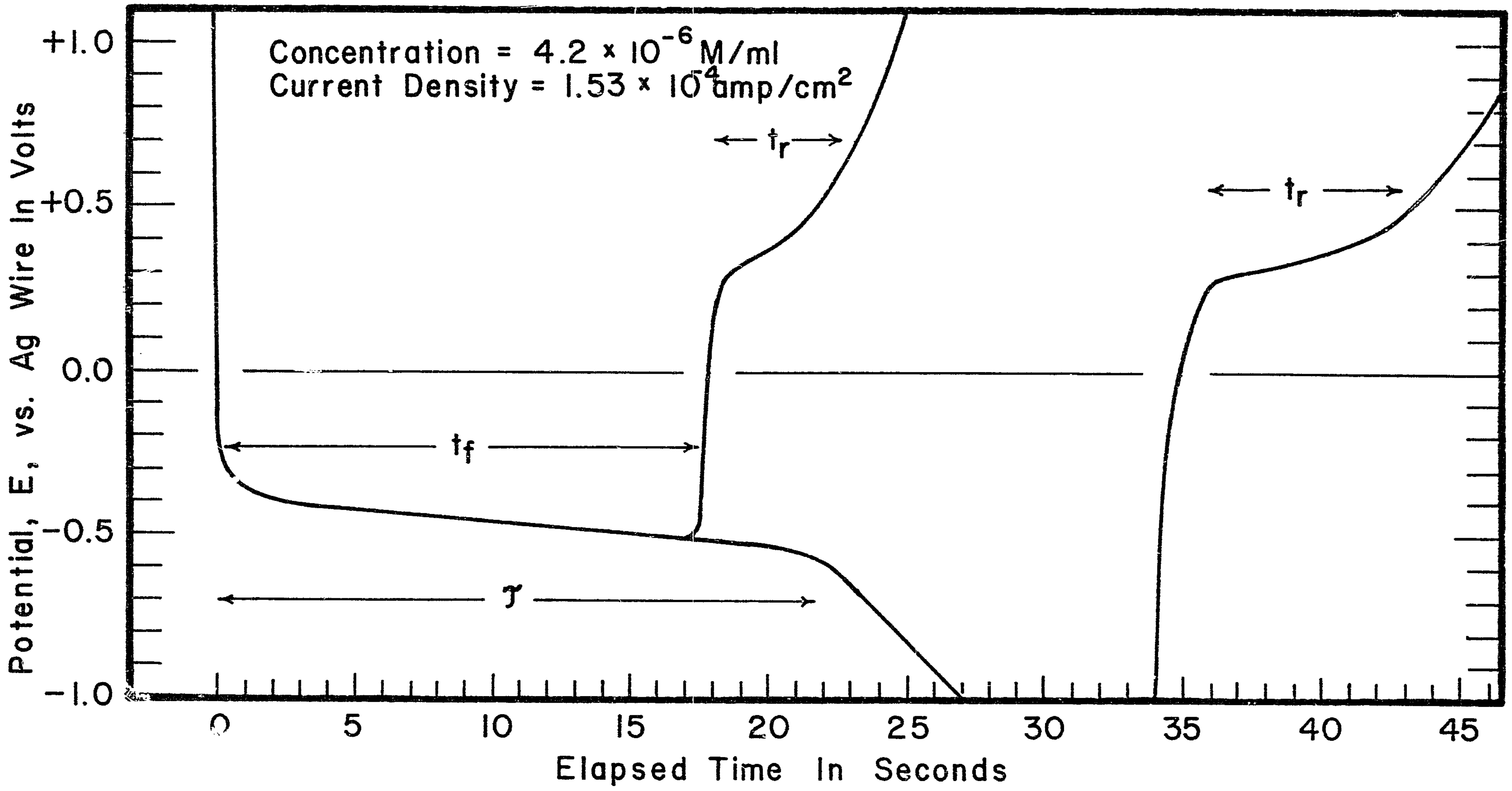


FIGURE 8

A TYPICAL CHRONOPOTENTIOGRAM WITH CURRENT REVERSAL FOR 5,5'-SULFONYL-BIS-BENZOFURAZAN-3,3'-DIOXIDE

TABLE 6

CHRONOPOTENTIOMETRIC DATA FOR THE REDUCTION WITH SUBSEQUENT OXIDATION OF 5,5'-SULFONYL-BIS-BENZOFURAZAN-3,3'-DIOXIDE

Concentration M/ml	Current Amps	τ_{red} Sec	$i\tau_{red}^{1/2}$ Amp·sec$^{1/2}$	$E_{1/4}$ Volts	τ_{ox} Sec	$i\tau_{ox}^{1/2}$ Amp·sec$^{1/2}$	$E_{1/4}$ Volts
2.15×10^{-6}	2.0×10^{-5}	28.3	1.08×10^{-4}	-0.49	7.5	5.4×10^{-5}	+0.31
2.15×10^{-6}	3.0×10^{-5}	18.4	1.29×10^{-4}	-0.49	3.5	5.7×10^{-5}	+0.32
2.15×10^{-6}	3.5×10^{-5}	13.5	1.29×10^{-4}	-0.48	3.1	6.2×10^{-5}	+0.31
2.15×10^{-6}	4.0×10^{-5}	10.2	1.28×10^{-4}	-0.49	2.3	6.1×10^{-5}	+0.32
2.15×10^{-6}	4.5×10^{-5}	7.8	1.26×10^{-4}	-0.50	1.9	6.2×10^{-5}	+0.32
2.15×10^{-6}	5.0×10^{-5}	6.4	1.27×10^{-4}	-0.50	1.7	6.5×10^{-5}	+0.32
4.11×10^{-6}	2.0×10^{-5}	49.8	1.41×10^{-4}	-0.43	15.1	7.8×10^{-5}	+0.24
4.11×10^{-6}	3.0×10^{-5}	26.0	1.53×10^{-4}	-0.43	4.5	6.3×10^{-5}	+0.24
4.11×10^{-6}	3.5×10^{-5}	18.9	1.52×10^{-4}	-0.41	5.7	8.4×10^{-5}	+0.26
4.11×10^{-6}	4.5×10^{-5}	11.6	1.53×10^{-4}	-0.43	3.5	8.4×10^{-5}	+0.26
4.11×10^{-6}	5.0×10^{-5}	9.7	1.51×10^{-4}	-0.44	3.5	9.3×10^{-5}	+0.29
6.86×10^{-6}	3.0×10^{-5}	29.1	1.62×10^{-4}	-0.42	10.4	9.6×10^{-5}	+0.27
6.86×10^{-6}	3.5×10^{-5}	21.7	1.63×10^{-4}	-0.43	6.6	9.1×10^{-5}	+0.27
6.86×10^{-6}	4.0×10^{-5}	16.8	1.64×10^{-4}	-0.43	4.3	8.4×10^{-5}	+0.26
6.86×10^{-6}	4.5×10^{-5}	13.2	1.63×10^{-4}	-0.44	4.5	9.5×10^{-5}	+0.29
6.86×10^{-6}	5.0×10^{-5}	10.6	1.63×10^{-4}	-0.44	2.8	8.4×10^{-5}	+0.29
6.86×10^{-6}	5.5×10^{-5}	8.5	1.61×10^{-4}	-0.45	2.6	8.9×10^{-5}	+0.31
6.86×10^{-6}	6.0×10^{-5}	7.3	1.63×10^{-4}	-0.46	2.8	10.0×10^{-5}	+0.32
1.29×10^{-5}	3.0×10^{-5}	34.7	1.77×10^{-4}	-0.41	12.3	10.5×10^{-5}	+0.29
1.29×10^{-5}	4.0×10^{-5}	19.1	1.75×10^{-4}	-0.42	6.1	10.0×10^{-5}	+0.30
1.29×10^{-5}	5.0×10^{-5}	13.2	1.76×10^{-4}	-0.43	5.9	12.0×10^{-5}	+0.31
1.29×10^{-5}	6.0×10^{-5}	8.7	1.78×10^{-4}	-0.44	3.5	10.8×10^{-5}	+0.31
1.29×10^{-5}	7.5×10^{-5}	6.4	1.75×10^{-4}	-0.45	2.6	12.0×10^{-5}	+0.37
1.29×10^{-5}	10.0×10^{-5}	3.5	1.88×10^{-4}	-0.46	1.7	13.0×10^{-5}	+0.40

the transition time constant of the anodic wave. Whereas, the criteria for diffusion control is met through the constancy $i\tau^{\frac{1}{2}}$ as i is varied at a given concentration, the factor $\frac{i\tau^{\frac{1}{2}}}{C}$ decreases with concentration. This is interpreted on the basis that a chemical equilibrium exists between the electrochemical product and the final product in the reaction sequence. The equilibrium is shifted with change in concentration.

The quarter-wave potential is constant with constant concentration. No discernable pattern is seen in the variation of the quarter-wave potentials of either the cathodic or anodic waves. Both the forward and the reverse waves are apparently controlled by semi-linear diffusion processes. From data collected in an experiment in which the current was reversed prior to the transition time, it is shown in Table 7 that the ratio of time for the oxidation process, t_r, to the reduction process, t_f, was less than 0.33. It is tempting to dismiss the small difference between the observed ratio and the theoretical ratio as an error in the measurements. However, the Karaoglanoff plot as shown in Figure 9 reveals that for the reduction process the reaction has a considerable irreversible character, $\alpha n = 0.56$. For $\alpha = 0.28$ a two electron change may be postulated for the reduction process. From the above observable quantities, it is postulated that the cyclic dinitro compound is reduced to an ion which is in equilibrium with the bis-dihydroxylamine. The insoluble nature of the reduced nitro group in γ-butyrolactone has been amply demonstrated in this work, and it is this property which causes the irreversible character of the reaction. The oxidation process is thought to be the reformation of the cyclic dinitro compound.

TABLE 7

CHRONOPOTENTIOMETRIC DATA FOR 5,5'-SULFONYL-BIS-BENZOFURAZAN-3,3'-DIOXIDE WITH CURRENT REVERSAL

Current Amps	t_f cm	t_r cm	t_r/t_f
2.5×10^{-5}	7.5	1.7	0.23
3.0×10^{-5}	6.1	1.4	0.23
3.5×10^{-5}	5.7	1.5	0.26
4.0×10^{-5}	3.9	1.0	0.26

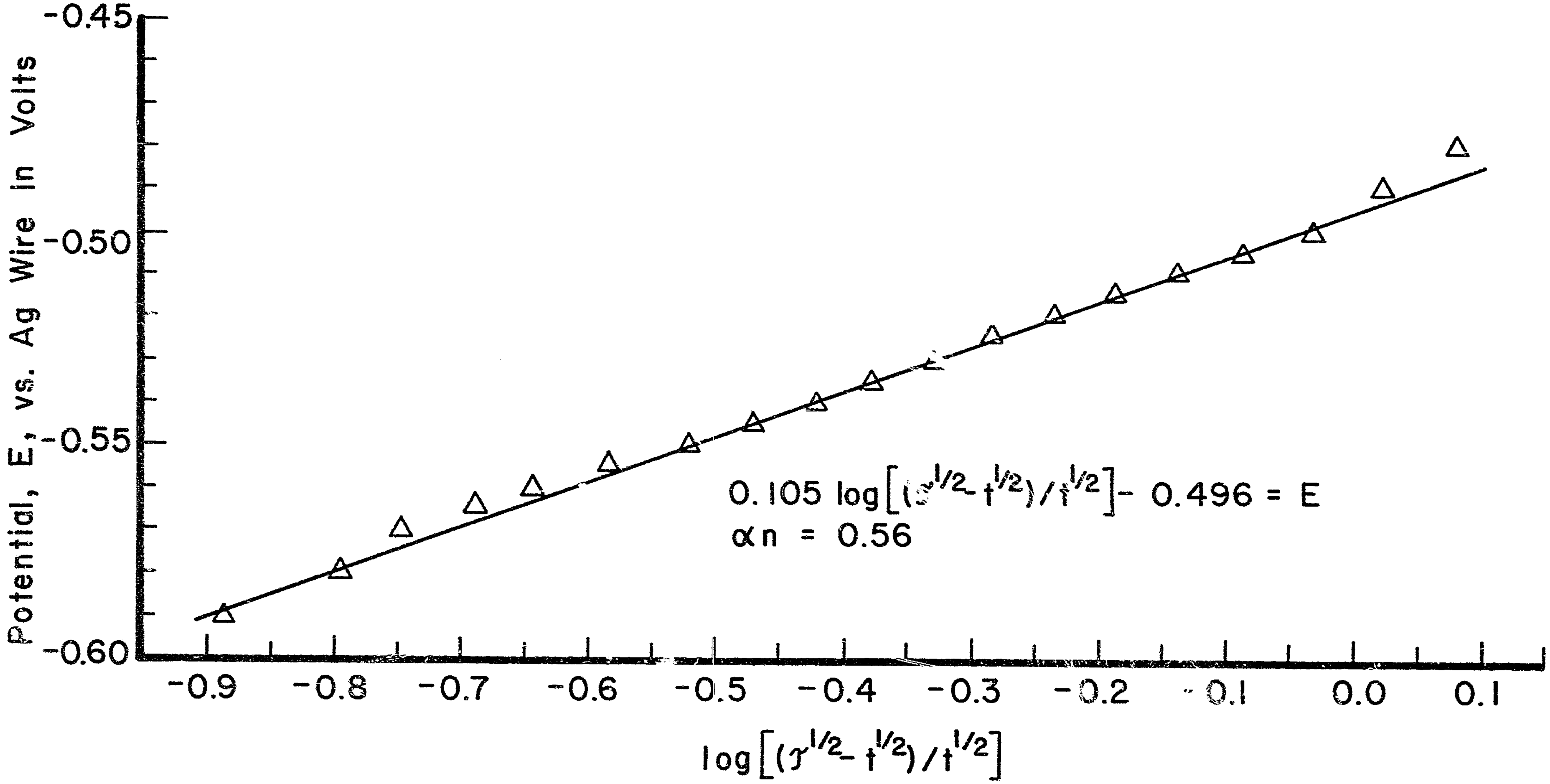


FIGURE 9
KARAOGLANOFF PLOT FOR
5,5'-SULFONYL-BIS-BENZOFURAZAN-3,3'-DIOXIDE

IV. CHEMICAL STABILITY OF POSITIVE CHLORINE COMPOUNDS

The objective of this phase of the project was to assess the degree of reactivity of certain positive chlorine compounds in butyrolactone or electrolytic solutions based on butyrolactone. Four typical chloro-compounds were studied; trichloromelamine, trichloroisocyanuric acid, Dichlor-amine T, and potassium dichloroisocyanurate. The stability of these compounds was studied in three solutions as follows:

1) γ-butyrolactone
2) 1 M $LiClO_4$ in γ-butyrolactone
3) 1 M $LiClO_4$ in γ-butyrolactone with 0.5 cm of Li wire (equivalent to 0.045 g of Li)

To each of these solutions was added 0.200 g. of the positive chlorine compound and the solution or mixture was allowed to stand at room temperature. Tests were run in triplicate. After the predetermined time period the samples were analyzed for positive chlorine by a procedure outlined Driscoll, et al. (13). Time intervals of 0, 2, 4, 24, and 48 hours were usually used dependent on the extent of reaction over the 24-hour period. The residual active chlorine after various time intervals for these compounds is given in Table 8.

Table 8. Residual Chlorine in Positive Chlorine Compounds

Compound	Solution	Time in Hours				
		0	2	4	24	48
Trichloro-melamine	1	88.7			67.4	59.0
	2	88.9			84.2 73.1	72.1
	3				88.6 86.8	85.1
Trichloro-isocyanuric acid	1	85.7			47.9	1.5
	2	89.2			17.9	12.8
	3	85.7			46.1	40.1
Dichlor-amine	1	56.7	41.3	32.4	1.8	0.25
	2	55.5			33.9	17.5
	3	56.2		37.9	12.2	11.6
Potassium dichloroiso-cyanurate	1	58.3			57.3	56.8

The instability of trichloroisocyanuric acid and Dichlor-amine T, in these organic electrolytes is indicated by these experiments. Apparently the presence of Li metal has a stabilizing effect, very conspicuous with respect to trichloromelamine. The potassium salt of dichloroisocyanuric acid is reasonably stable losing only 2% in its positive chlorine content in 48 hours.

V. GENERAL CONCLUSIONS

This investigation, as well as others, has demonstrated the potential usefulness of the cyclic esters as solvents for electrochemical systems. It would appear that the limit to the development of high energy cells resides, not with the solvent or supporting electrolyte, but with the cathode reaction. Or, from a quantitative standpoint, we have the basis for a 5-6 volt galvanic cell but we have no cathode reactions approaching the 2.5 theoretical limit on the cathode side. It should be emphasized that, in the employment of these organic compounds, attention must be paid to chemical reactions with other organic species and inorganic compounds. The bibliography developed on this project should be of value in determining what reactions are possible under the particular experimental conditions existing.

Methods have been developed for analyzing the cyclic esters for trace amounts of impurities, such as water. These methods will make it possible to closely control the purity of materials used to assemble electrochemical systems.

With regard to the cathode reaction, which, right now, is the major problem area in the high energy electrochemical field, certain organic compounds would appear to offer promise for future development. The electrochemical behavior of the positive halogen compounds has not been as encouraging as predicted. Many of these compounds have chemical or electrochemical properties detrimental to their functioning as depolarizers. Several of these compounds react with the solvent itself. The lower reaction rate in the presence of lithium metal is difficult to explain. If the reaction were initiated by the presence of water in trace quantities it might be postulated that lithium metal successfully competes with the chlorine compound for the water and thus lowers the reaction rate. From the electrochemical viewpoint these positive chlorine compounds have quarter-wave potentials which would indicate that they would be reduced at sufficiently cathodic potentials to provide a high energy galvanic couple. However, their relative capacities are low.

On the other hand, the nitroaromatic compounds show exceptional electrochemical properties. Several of these compounds are reduced through 2 or 4 electron processes and in certain instances the process is adsorption controlled. It is felt that steric factors play an important part in the chronopotentiometric reactions described above in a manner that would not necessarily operate in a practical battery. For example, reduction at a planar platinum electrode must be preceded by an orientated adsorption step. This explains why in certain dinitro compounds only two electrons are accepted by the molecule, i.e., only one nitro compound is reduced. In a typical cathode composition containing a carbon mixture of the organic compound it would be expected that greater electron consumption would be achieved because the electron transfer step would be facilitated by exposure in three dimensions to the electron donating material.

To our knowledge the sulfonyl-bis-benzofurazan dioxide compound is the only system which is reduced reversibly without complicating side reactions.

The employment of this compound should make possible rechargeable systems of high energy.

Table 9 summarizes the chronopotentiometric parameters for the compounds investigated in detail. The term $\frac{i\tau^{\frac{1}{2}}}{C}$ may be compared to a capacity, and $E_{\frac{\tau}{4}}$ to an operating potential. Thus the product of the two terms is a comparative measure of the practical available energy of the organic depolarizer. The nitro compounds are of most interest on the basis of this analysis.

TABLE 9

A SUMMARY OF ELECTROCHEMICAL PROPERTIES OF THE COMPOUNDS STUDIED

Compound	$\frac{i\tau^{\frac{1}{2}}}{C}$	$E_{\frac{1}{4}}$(red)	$E_{\frac{1}{4}}$(ox)	Cell Potential*	Energy**
Potassium Dichloroisocyanurate	3	+0.25 v.	-	3.25	9.8
m-Dinitrobenzene	112	-0.69 v.	-	2.31	259
1,3-Dinitro-2,4,5-trichlorobenzene	22	-0.57 v.	-	2.43	53.4
5,5'-Sulfonyl-bis-benzofurazan-3,3'-dioxide	60	-0.50 v.	+0.32 v.	2.50	150

* Potential of galvanic cell with 3.0 v. Li anode

** Comparative "energy," the product of the "capacity," $\frac{i\tau^{\frac{1}{2}}}{C}$ and cell potential

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