A STUDY OF THE REDUCTION OF VARIOUS DIALKYL

AROYLPHOSPHONATES AT THE DROPPING

MERCURY ELECTRODE

By

DAVID STEPHEN RULISON

Bachelor of Science

Southeastern Massachusetts Technological Institute

North Dartmouth, Massachusetts

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Thesis Approved:

K. D. Berlin
Thesis Adviser

Tom E. Moore

Louis P. Varga

Herbert A. Pohl

D. Durham
Dean of the Graduate College

ii

This thesis is dedicated to the memory of

Dr. Paul Arthur   without whom this work

would not have been undertaken

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

Reported electrochemical studies of organic compounds have been performed at the dropping mercury electrode using amounts so small that product analysis after electrolysis cannot be performed. Another method has been to electrolyze the materials at a large electrode, producing sufficient quantities of materials to make product analysis feasible. However, some studies have shown that the products from a microelectrode may differ from those at a large electrode.

Little has been reported in the literature concerning the electrochemical behavior of organophosphorus compounds. In one report, dialkyl acylphosphonates were shown to exhibit polarographic activity. Early experiments in these laboratories showed that dialkyl aroylphosphonates also are electroactive. Knowledge of the electrochemical behavior of various dialkyl aroylphosphonates along with other evidence may eventually provide some insight as to the physiological activity of organophosphorus compounds.

The first goal of the present study was to examine the mechanism of the electrolytic reduction of various dialkyl aroylphosphonates at the dropping mercury electrode both with and without a proton donor present. Special polarographic equipment was developed for this examination, as well as methods of preparing and handling anhydrous organic solutions. The second objective was to determine whether the ease of reduction of the esters is affected by substituents on the aromatic

ring. The final goal was to compare the ease of reduction of the es-

ters with similarly substituted benzils.

CHAPTER I

HISTORICAL

Millicoulometry. The technique known as millicoulometry (or oc-
casionally microcoulometry) has been used for a number of years. A
small amount of an electroactive substance is oxidized or reduced at a
dropping mercury electrode (DME) over a measured time interval during
which the current will gradually decrease. By calculating the number
of coulombs which have passed during the oxidation or reduction and
comparing this to the amount by which the concentration of electro-
active substance has decreased, the number of electrons transferred per
molecule or ion may be computed.

The usual technique involves first placing a small volume of a
solution containing a known concentration of the electroactive solute
in a microcell and deaerating with a very slow stream of an inert gas.
Volumes of solution from a few tenths of a ml. to 0.05 ml. have been
used.[10,22,67] An external reference electrode is essential. If an inter-
nal reference electrode is used, the reduction products from the cathode
may reach the anode, where they may oxidize; the same may occur with the
products of oxidation from the anode. This process of cyclic oxidation
and reduction can only lead to erroneous results.[40]

The limiting current is measured and the DME is allowed to remain
at a potential on the plateau of the wave for perhaps 20 minutes. The
solution is stirred briefly with a slow stream of gas, and the limiting

1

current is measured again together with the time that has elapsed since the electrolysis was begun. This procedure is continued until the current has fallen to perhaps half of its initial value; an hour or two is usually sufficient time for this to occur. Each of the measured currents must be corrected for the separately measured residual current.

The method of calculation of $\underline{n}$ (electrons transferred) is based upon the equation

$$i_d = kC = -nFV\frac{dC}{dt}$$

where i_d = diffusion current (microamperes)

C = concentration of electroactive substance (moles/l.)

V = solution volume (ml.)

After integration and rearrangement, one obtains[10,22,40]

$$\log i_d = \log i_d^o - \frac{4.501 \times 10^{-6}kt}{nV}$$

Plotting i_d vs. t gives a straight line from whose slope $\underline{n}$ may be calculated if k and V are known. The value of k is easily calculated from the ratio of the initial wave height to the initial concentration. Alternatively, $\underline{n}$ may be determined algebraically.

When very small volumes of solution are used, the technique is subject to various sources of error.[65] One of the most important is the "depletion effect."[51] During the intervals between measurements, the concentration falls off more rapidly than it does in the bulk of the solution, because the mixing action by the falling drops is not very efficient. Hence the current is always smaller than it would be if the solution were homogeneous, and this leads to too large a value of $\underline{n}$. Typically the result is 10% too high.[10,22] Hume and Peattie obtained $\underline{n}$-values for cadmium ranging from 1.5 to 3.0.[26] Reilley and co-workers

reported an average n-value of 2.61[50]

Various attempts have been made in an effort to minimize the errors connected with millicoulometry. Explicit integration of the current-time curve has been performed using a current integrator in series with the cell.[10] The reduction of cadmium ion yielded an average value of 2.03 ± 0.02 electrons using this technique.

DeVries and Kroon[15] employed a second polarographic cell (containing a known volume of a standard solution of a substance for which n is known) in series with the one containing the sample of interest. The quantity of electricity flowing through the circuit can be deduced from the decrease in the limiting current in the reference cell. By comparison of this to the decrease of the current in the sample cell, n-values for the sample may be calculated easily using the following equation:

$$\left(\frac{i}{i_o}\right)_A \cdot \frac{C_A V_A}{n_A} = \left(\frac{i}{i_o}\right)_B \cdot \frac{C_B V_B}{n_B}$$

Here, i_o and i are the initial and final currents, respectively; C is the concentration of electroactive material; V is the volume of solution. With this method, the reduction of thallous ion yielded an n-value of 1.02 electrons.

A pilot-ion technique yielded n-values of 1.95 for the reduction of nickel ion, 1.97 for lead, and 5.82 for iodate.[14] In this method, the sample being investigated and a reference substance for which n is known are present in the same solution, the electrolysis being performed at a potential where the sum of their diffusion currents is obtained. After sufficient electrolysis, the decrease in the currents due to the standard and the sample, and the concentration and known n-value for

the standard may be used in the following equation to calculate $\underline{n}$ for the sample:[14]

$$\frac{\log(i_d^o/i_d)_A}{\log(i_d^o/i_d)_B} = \frac{(i_d^o)_A n_B C_B}{(i_d^o)_B n_A C_A}$$

where A and B are the standard and sample, respectively. The reference substance must be chosen with great care, for errors may result if it, its reduction product, or any intermediate formed during its reduction can react with the sample of interest or its reduction product.

Although millicoulometric studies have been performed on the reductions of metal ions, little has been reported concerning organic materials. Weaver and Whitnack examined the reduction of various organic nitrogen compounds.[65] For example, the reduction of $\underline{p}$-nitroaniline at pH 10 yielded an average $\underline{n}$-value of 6.04 electrons, which was in agreement with the theoretical value for the reduction to $\underline{p}$-diamino-benzene. At the same pH, nitroguanidine was found to require an average of 5.05 electrons. This is not in agreement with theory. Since it was known that aminoguanidine was the reduction product of nitroguanidine in acid solution,[37] nitroguanidine was reduced in 6N HCl; the experiments yielded an average $\underline{n}$-value of 6.35 electrons. The authors postulated the following mechanism for the reduction at pH 10:

$$\underset{\text{H}_2\text{N-}\overset{\overset{\text{HN}}{\|}}{\text{C}}\text{-}\overset{\overset{\text{H}}{|}}{\text{N}}\text{-}\text{NO}_2}{}$$ Nitroguanidine

$\downarrow$ +2e

$$\underset{\text{H}_2\text{N-}\overset{\overset{\text{HN}}{\|}}{\text{C}}\text{-}\overset{\overset{\text{H}}{|}}{\text{N}}\text{-}\text{N=O}}{}$$ Nitrosoguanidine

$\downarrow$ +2e + 2H$^+$

$$\underset{\text{H}_2\text{N-}\overset{\overset{\text{HN}}{\|}}{\text{C}}\text{-}\overset{\overset{\text{H}}{|}}{\text{N}}\text{-}\text{NHOH}}{}$$ Hydroxylaminoguanidine

$\downarrow$ +2e

$$\underset{\text{H}_2\text{N-}\overset{\overset{\text{HN}}{\|}}{\text{C}}\text{-}\overset{\overset{\text{H}}{|}}{\text{N}}\text{-}\text{NH}_2}{}$$ Aminoguanidine
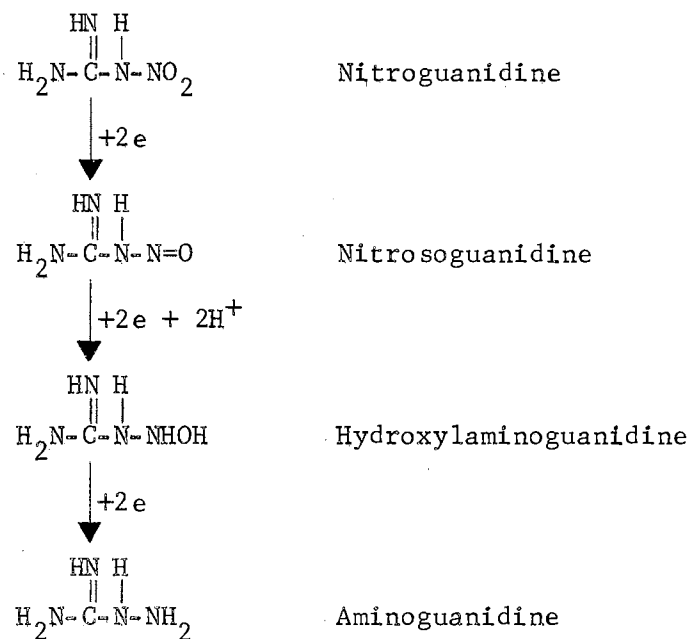
This mechanism was postulated although the reduction of nitroso-guanidine at pH 10 yielded an n-value of 3.07, less than the expected value of 4. (One wonders why the authors did not reduce nitrosoguanidine in acid solution).

DeVries and Kroon,[15] using their dual cell arrangement, reduced fumaric acid in 0.12M HCl and calculated an n-value of 2.00 electrons. This was deemed reasonable for the reduction of fumaric acid, although the authors present no evidence for this; it might be assumed that only the double bond was reduced. When p-nitrobenzoic acid was reduced in potassium hydrogen phthalate buffer (pH 2.65) in 10% aqueous ethanol, an average n-value of 4.07 electrons was calculated. This is within 2% of the expected value of 4 electrons.

Although coulometric data may be obtained using the technique of millicoulometry, the amounts of materials produced during electrolysis are generally so small that product analysis is virtually impossible. This is a disadvantage, since for a particular compound numerous

products may be possible via different mechanisms, each requiring the same number of electrons. Thus coulometric data alone are not sufficient for the determination of mechanisms, although numerous authors have postulated mechanisms on the basis of $\underline{n}$-values only.

Controlled-Potential Coulometry. In order to produce sufficient quantities of the products of reductions or oxidations of various materials, electrolysis may be performed at a large electrode such as a mercury pool. Coulometric data also may be obtained during the run; the technique is then generally termed controlled-potential coulometry. In the almost identical technique of controlled-potential electrolysis, coulometric data are not usually obtained.

The majority of coulometric measurements of $\underline{n}$ have been performed with quantities of the order of 1 meq. of starting material present in 50 to 100 ml. of solution.[40] This corresponds to concentrations well above those likely to be employed in polarography. During electrolysis the potential is maintained on the plateau of the wave just as in milli-coulometry. At this potential, neither the supporting electrolyte nor any other constituent of the solution is reduced or oxidized to any appreciable extent. The current will be due entirely to the reduction or oxidation of the substance responsible for the wave. If the overall reaction is simply $A \pm n \cdot e \longrightarrow B$, the current will decay exponentially toward zero as the concentration of the substance decreases and the number of coulombs consumed will approach the limit described as follows:

$$Q_\infty = \int_0^\infty i \, dt = \underline{n} F V C^O = \underline{n} F N^O$$

where N^O is the number of moles of electroactive substance present at the start of the electrolysis. This is equivalent to Faraday's Law.

Provision must be made for the integration of the electrolysis current and care must be taken to avoid the oxidation or reduction of other substances during the electrolysis, or to correct for the extents of such side reactions if they cannot be eliminated. The above equation may be used to evaluate N^o if $\underline{n}$ is known and to evaluate $\underline{n}$ if N^o is known. The former technique has been the subject of various reports, such as that of Rechnitz,[49] and will not be discussed further here.

The latter technique has served to illuminate the voltammetric characteristics of a host of organic and inorganic substances. Where the $\underline{n}$-value itself does not suffice to identify the product unambiguously, its measurement can be supplemented by physical or chemical identification after the electrolysis is complete. Therefore the mechanism of the oxidation or reduction may be determined correctly.

The integration of current-time curves may be achieved by graphical, mechanical, electrochemical or electronic means.[49] The graphical methods are equivalent to those discussed in connection with millicoulometry. From plots of log i vs. t, Rosie and Cooke[52] determined $\underline{n}$-values for various ions and a few organic compounds. Their results are summarized below.

Material	n, obtained	n, theoretical
Thallium	0.99	1
Cadmium	1.91	2
Copper	2.06	2
Lead	2.02	2
Chromate	2.88	3
Azobenzene	1.94	2
Benzil	1.97	2
Indium	3.01	3
o-Dinitrobenzene	11.75	12

The average error in the $\underline{n}$-values is 2.3%.

Numerous organic compounds have been examined by controlled-potential coulometry. The following studies are given as examples. Lingane[34] employed a hydrogen-oxygen coulometer in a study of the reduction of picric acid. An n-value of 17.07 electrons was found in disagreement with the value of 18 expected if all three nitro groups were reduced to amine groups. Without product analysis, Lingane postulated a coupling reaction to account for the discrepancy.

An early study was performed by Pasternak,[46] who employed the hydrogen-oxygen coulometer of Lingane.[34] Products were characterized by means of mixture melting points with authentic samples. A series of saturated and unsaturated carbonyl compounds was examined. At pH 1.3 and 8.6 benzil was found to reduce quantitatively to benzoin via a two-electron mechanism. At pH 8.6 benzoin was found to reduce further via a two-electron step to hydrobenzoin. At pH 1.3, benzophenone was reduced quantitatively to benzopinacol.

Elving and Bennett[16] examined the reduction of glyoxal and found that 3 electrons were transferred, but the products were a complex mixture including ethylene glycol. The authors proposed the following reaction scheme:
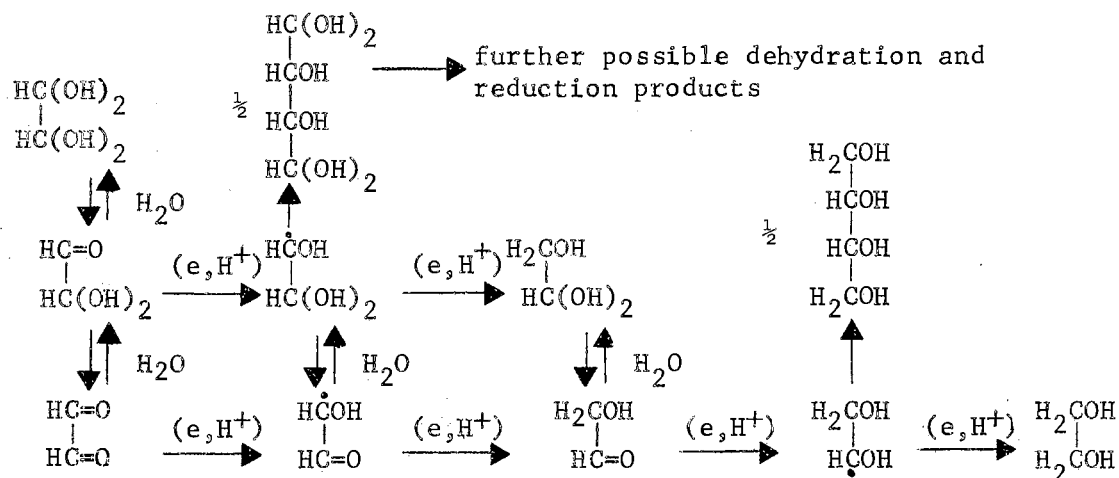
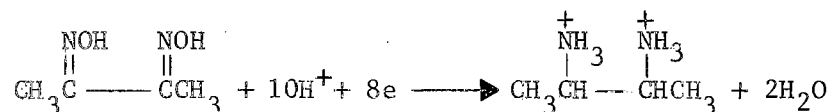One finds that the experimental evidence for this mechanism is rather weak. The authors oxidized the reduction mixture with periodic acid and used as evidence the fact that formaldehyde and formic acid were detected.

In another study Elving and coworkers[17] reduced α,α'-dibromosuccinic acid and found that a 2-electron mechanism yielded maleic and fumaric acids depending upon the experimental conditions.

Electronic and electromechanical current integrators are needed to attain the accuracy, precision, and sensitivity of which controlled-potential coulometry is inherently capable. By means of an electronic current integrator, Spritzer and Meites[60] examined the reduction of dimethylglyoxime. Accurate coulometric data and product analysis indicated a complex mechanism the final product of which was 2,3-diamino-butane:

$$CH_3C(\overset{NOH}{||}) \text{---} C(\overset{NOH}{||})CH_3 + 10H^+ + 8e \longrightarrow CH_3CH(\overset{\overset{+}{N}H_3}{|}) \text{---} CH(\overset{\overset{+}{N}H_3}{|})CH_3 + 2H_2O$$

Coulometric determinations were made difficult owing to simultaneous hydrogen evolution.

These examples illustrate the utility of controlled-potential coulometry. Coulometric data may be obtained during an electrolysis, and sufficient quantities of materials are produced to make product analysis possible. With this information the often complex mechanisms of electrode reactions may be elucidated.

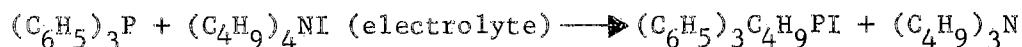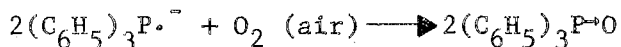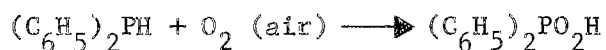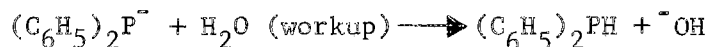Electrochemical Studies of Organophosphorus Compounds

In comparison to the number of reported investigations of the electrochemical behavior of organic compounds containing other elements, the amount of reported research on organophosphorus compounds is very

small.

Reports have been published concerning polarographic studies of hydroxyalkyl phosphines,[28] phosphonium salts,[38] and various nitrophenyl phosphates.[23] A series of papers has been released concerning the polarographic behavior of various metal ions and complex ions in the presence of certain organophosphorus compounds.[56-59] A few electro-chemical studies which describe the development of polarographic methods for analysis of such compounds as Malathion [S-(1,2-dicarbethoxyethyl) O,O-dimethyl dithiophosphate] and Parathion (O,O-diethyl O-p-nitrophenyl thiophosphate) have also been reported.[11,30,44,53]

Wawzonek[64] examined the behavior of triphenylphosphine and related compounds in acetonitrile and dimethylformamide. Triphenylphosphine was found to reduce via a one-electron mechanism to an anion radical which cleaved to yield a phenyl radical and diphenylphosphide ion. The phenyl radical abstracted a hydrogen atom from the solvent to yield benzene. The diphenylphosphide ion reacted with water during workup to yield diphenylphosphine. Numerous other products were formed during workup. Controlled-potential electrolysis was used to prepare quanti-ties of products sufficient for analysis. The results of the study are summarized below:

$$(C_6H_5)_3P: + e \rightleftharpoons (C_6H_5)_3P \cdot^-$$

$$(C_6H_5)_3P \cdot^- \longrightarrow C_6H_5 \cdot + (C_6H_5)_2P^-$$

$$C_6H_5 \cdot + \text{solvent} \longrightarrow C_6H_6$$

$$(C_6H_5)_2P^- + H_2O \ (\text{workup}) \longrightarrow (C_6H_5)_2PH + {}^-OH$$

$$(C_6H_5)_2PH + O_2 \ (\text{air}) \longrightarrow (C_6H_5)_2PO_2H$$

$$2(C_6H_5)_3P \cdot^- + O_2 \ (\text{air}) \longrightarrow 2(C_6H_5)_3P \rightarrow O$$

$$(C_6H_5)_3P + (C_4H_9)_4NI \ (\text{electrolyte}) \longrightarrow (C_6H_5)_3C_4H_9PI + (C_4H_9)_3N$$
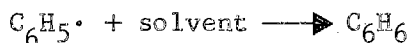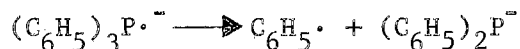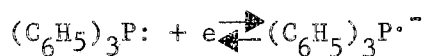
In a more recent report,[54] the same system was examined and a mechanism was found which was in disagreement with the previous study. The results of the later work are as follows:

$$(C_6H_5)_3P: + e \rightleftharpoons (C_6H_5)_3P \cdot^-$$

$$(C_6H_5)_3P \cdot^- + solvent \longrightarrow (C_6H_5)_2PH + C_6H_5 \cdot$$

$$2C_6H_5 \cdot \longrightarrow C_6H_5-C_6H_5$$

$$C_6H_5-C_6H_5 + e \longrightarrow C_6H_5-C_6H_5 \cdot^-$$

$$(C_6H_5)_2PH + O_2 \text{ (air)} \longrightarrow (C_6H_5)_2PO_2H$$
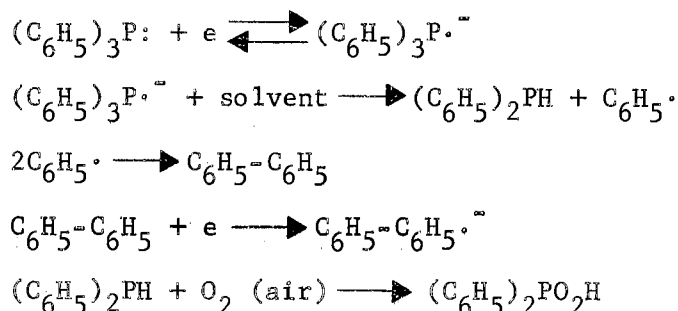
It should be noted that biphenyl was detected as a major product whereas benzene was absent, which was the reverse situation in the previous work.[64] In addition, the later paper[54] did not report the detection of triphenylphosphine oxide or the salt formed by reaction with the supporting electrolyte. These findings are unusual when one considers that both authors reported identical experimental conditions.

The reduction of O,O-dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate $[(CH_3O)_2P(O)CHOHCCl_3]$ has been examined.[31] Polarography and controlled-potential coulometry were employed to determine that the phosphoryl group was not reduced, but reduction proceeded via a two-electron step as illustrated.

$$(CH_3O)_2P(O)CHOHCCl_3 + 2e + H^+ \longrightarrow (CH_3O)_2P(O)CHOHCHCl_2 + Cl^-$$
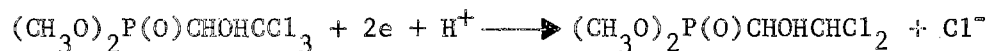
Santhanam and coworkers[55] studied the electroreduction of tris($\underline{p}$-nitrophenyl) phosphate at the DME. The reaction was found to proceed via a four-electron step to yield 4,4'-dinitrobiphenyl and dihydrogen $\underline{p}$-nitrophenyl phosphate:

$$(NO_2C_6H_4O)_3P{\rightarrow}O + 2e \longrightarrow (NO_2C_6H_4O)_3P{\rightarrow}O^{2-}$$

$$(NO_2C_6H_4O)_3P{\rightarrow}O^{2-} + 2HS \text{ (solvent)} \longrightarrow (NO_2C_6H_4O)P(O)(OH)_2 + 2S^- +$$

$$NO_2C_6H_4C_6H_4NO_2$$

$$(NO_2C_6H_4O)P(O)(OH)_2 + e \longrightarrow (NO_2C_6H_4O)P(O)(OH)_2^{..}$$

$$NO_2C_6H_4C_6H_4NO_2 + e \longrightarrow NO_2C_6H_4C_6H_4NO_2^{..}$$
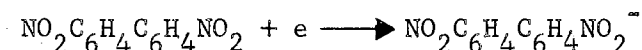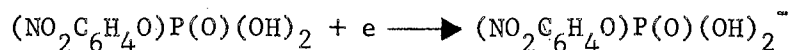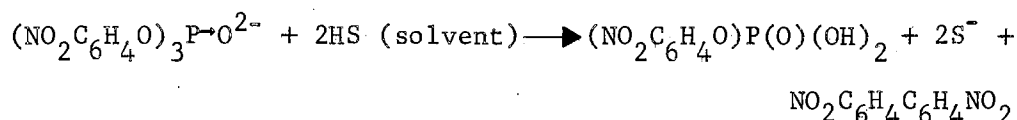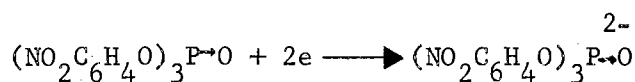
A few diethyl acylphosphonates are recorded[1] to exhibit well-defined polarographic waves with half-wave potentials about 1.4v. vs. the saturated calomel electrode. Diethyl alkylphosphonates are apparently inactive polarographically. Since the isolated carbonyl was not reducible in the applied voltage range of the electrolyte used, the authors concluded that reduction of the diethyl acylphosphonates was effected because of conjugation between the carbonyl and phosphoryl groups. Neither product analysis nor the number of electrons transferred during reduction was determined.

A study of a series of phosphorylated aldehydes in aqueous solution[48] indicated an equilibrium existed between protonated and enol forms, the concentrations of which depend upon the pH, as follows:

At low pH
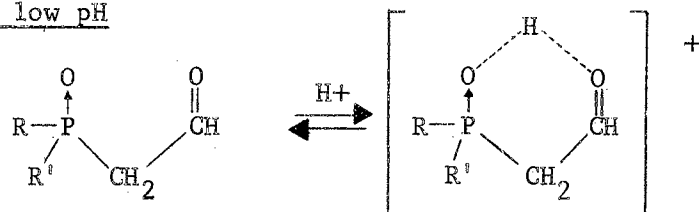
At high pH
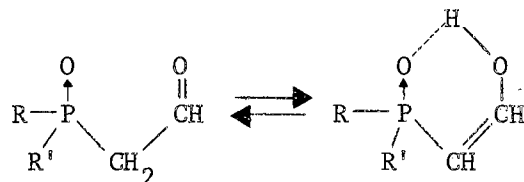
The aldehyde was found to reduce in a two-electron step as determined by millicoulometric methods. In addition, the slope of a plot of observed half-wave potentials versus Hammett σ-values of the various ring substituents yielded satisfactory values of $\rho'(dE_{\frac{1}{2}}/d\sigma)$. For phosphinyl-acetaldehyde, ρ' was found to be +0.52v. and for phosphinylpropionaldehyde, +0.27v. These values indicated that electron-withdrawing substituents on the ring facilitate reduction.

CHAPTER II

DISCUSSION

A new coulometric cell for macro-microelectrolysis has been developed and tested with metal ions and several organic compounds. Each sample was deoxygenated thoroughly before being transferred to the cell and electrolyzed for periods up to 10 days without oxygen interference. During this time, data was taken from the current-time curve for later n-value calculations. After electrolysis, organic samples were retrieved for analysis by GLC.

Determinations of the n-values for the reduction of several metal ions such as Li^+, Mg^{++}, and Cd^{++} gave results of 1.003, 2.012, and 1.995 electrons, respectively. These data are taken as a reliable test of the accuracy of the system for providing coulometric n-values.

A most important discovery in the program was that electrolysis of organic compounds can be performed satisfactorily. An n-value of 2.038 electrons was calculated for the reduction of benzil to benzoin. Since the cell could be hermetically sealed, prolonged electrolysis was possible so that reaction conversion was such as to make product analysis facile and accurate by GLC. Several dialkyl aroylphosphonates were reduced smoothly, and a complete product analysis was performed on each mixture. In addition, reproducible coulometric data for finding n-values were obtained from each experiment. (The mechanism of reduction of the dialkyl aroylphosphonates is outlined).

Design of the Polarographic Cell. The special coulometric cell
described on page 53 was designed to include the following features:
the capability of hermetically sealing samples of electroactive mate-
rials while performing prolonged electrolysis at a DME; the capability
of reclaiming the samples after electrolysis in order to permit an
analysis of the products of the electrode reaction. It was stated
earlier that controlled-potential electrolysis at a mercury pool elec-
trode may be used both to prepare large quantities of products and
simultaneously to obtain coulometric data. However, various papers
have been published which report that the products of electrolysis at a
mercury pool on occasion are different from those at a microelec-
trode.[21,33,35] In this program it was decided to study reductions at
the DME and not to use a mercury pool. However, the process of reduc-
tion at a microelectrode generally occurs so slowly that periods of
days are required before sufficient conversion of reactants occurs in
order that a product analysis can be made. In view of this circumstance,
two alternatives were proposed: to maintain a stream of inert gas over
the surface of the solution during the entire electrolysis, thus elim-
inating oxygen interference; to build a system which could be hermeti-
cally sealed after sufficient purging. Earlier work in this laboratory
indicated that the former technique led to poor coulometric data due to
solvent loss through evaporation. The situation was not greatly im-
proved by pre-saturating the purging gas with solvent.[25]

A great deal of trial-and-error work was required before a suc-
cessful cell was completed (Figure 7). The final cell was of all-glass
construction, employing standard-taper fittings at all points of con-
nection. The deoxygenator (Part C) was essentially identical to that

used by Hilbig,[25] but improvements were necessary before the apparatus
was satisfactory. A Teflon 3-way stopcock 1 was used when it was found
that the solvent would occasionally leak through a similar glass stop-
cock in this position. The Teflon stopcock had the advantage that it
could be conveniently tightened in position, thus eliminating leakage.
The glass frit on the gas dispersion tube was replaced by a bulb con-
taining numerous small holes after it was found that glass frits retain
water after washing unless they are heated for inconveniently long
periods. The new arrangement could be dried rapidly in the oven. The
septum fitting on the top of the deoxygenator was added to permit con-
venient insertion of liquid samples by syringe. The purging gas was
found to carry the sample down into the deoxygenator, leaving none of
the solution inside the purging gas tube.

The cell top was modified several times before a satisfactory
arrangement was found. The design finally adopted avoided the usually
leaky ports on the tops of many common cells. The mercury for the DME
entered via a closed system, and rubber tubing connections were only
necessary immediately above and below the cell top. The platinum loop
was added in order to be able to suspend a small thermometer on a wire
harness. In this way, one could ensure that the temperature of the so-
lution inside the cell was identical to that of the constant tempera-
ture bath (25.0 ± 0.1^{o}).

Numerous efforts were made to reduce diffusion of the solution of
interest through the asbestos fibers and into the bridging tubes. Since
it was found that fibers whose resistance was 20,000 ohms or less (in
0.1M aqueous KCl) permitted a large amount of diffusion, it was decided
to install fibers of such high resistance that diffusion was made

negligible over the period of the electrolyses. After numerous trials, a matched pair of 100,000 ohm fibers was placed at the DME compartment ends of the bridging tubes. These were found to permit very little diffusion over long periods, and the resistance of the cell was found to be well within the range of the iR compensator. It was observed that diffusion would occur through these fibers if gas pressure inside the cell was not relieved before sealing. A matched pair of 40,000 ohm fibers was placed in the reference electrode ends of the bridging tubes.

The lower part of the main cell was modified by placing a stopcock in the mercury levelling tube. When excess amounts of lubricant were present in the cell, it was found that mercury would occasionally trap pockets of solution in the capillary tubing and carry them along into the waste mercury reservoir. The expanded portion of the capillary tubing (E) of Figure 7 was added and prevented this. Experiments showed that even with large amounts of lubricant present, the mercury flowed freely and without trapping any solution in the capillary tubing.

Part D (Figure 7) was a specially-constructed container to reclaim and store solutions after electrolysis. The spherical joint permitted convenient attachment to the cell after removing the waste mercury reservoir. In addition, this joint permitted Part D to rotate 180° so that any mercury could be expelled which was accidentally transferred along with the solution. The septum fitting on Part D was found to permit convenient direct removal of sample by syringe for GLC analysis.

Various types of lubricating grease were used in sealing the cell. Hydrocarbon greases such as KEL-F and Apiezon were tried unsuccessfully. There are evidently some unsaturated compounds in these lubricants which are electroactive. Spurious polarographic waves were observed

whenever such lubricants were used in sealing the apparatus. The DME became very erratic and no meaningful polarographic waves were obtained. Experiments showed that a silicone lubricant was best for the desired application. It was found to contain no electroactive constituents and was insoluble in all solvents employed. The amounts of lubricant used on each joint or stopcock were critical. If too little was used, oxygen interference was evident after a few days. If too much was used, difficulties arose due to plugged stopcocks or capillary tubing. It was found necessary to soak the entire apparatus overnight in alcoholic potassium hydroxide after every four or five runs in order to remove excess silicone lubricant.

Successful experiments with both inorganic and organic materials showed that the final design of the apparatus was satisfactory for this work.

Development of the Dehydration Apparatus. It was deemed important in this program to be able to efficiently dehydrate solvents without introducing contaminants. The final design of an apparatus to perform this task is discussed in the Experimental section.

Anhydrous Techniques. It was necessary to develop methods of handling dehydrated solutions in order to avoid moisture pickup from the atmosphere. Syringe techniques were used throughout. The syringes were fitted with stainless steel Luer-Lok stopcocks. The techniques employed are discussed in the Experimental section.

The Reduction of Dialkyl Aroylphosphonates. This program was initiated in an attempt to elucidate the mechanism of reduction at the DME of a series of dialkyl aroylphosphonates I. A further objective was to examine the effect of ring substituents on the $\overset{\text{O O}}{\underset{}{\text{C-P}}}$ system.

$$\underset{\text{I}}{\text{R}-\!\!\!\!\boxed{}\!\!-\!\!\underset{\parallel}{\overset{O}{C}}-\underset{\underset{OR'}{\big\uparrow}}{P}\!\overset{\nearrow O}{-}\!-OR'}$$
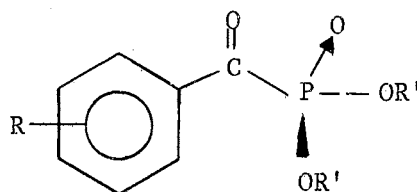
I

	R	R'
a.	H	C_2H_5
b.	p-t-C_4H_9	C_2H_5
c.	o-Cl	C_2H_5
d.	p-Cl	C_2H_5
e.	o-CH_3O	C_2H_5
f.	p-CH_3O	CH_3

Berlin and Taylor[8] postulated that interaction of a filled nonbonding orbital on oxygen of the phosphoryl group could occur with the π orbital of the carbon atom of the carbonyl group. This effect could account for the observed low range (1639-1672 cm.$^{-1}$) frequencies for absorption of the carbonyl group in aroylphosphonates. α-Diketones are known to show absorption in the range 1710-1730 cm.$^{-1}$ for the carbonyl groups while aroyl aldehydes usually show a peak from 1695 to 1715 cm.$^{-1}$.[1] It was thought that perhaps this same interaction could retard election transfer to the carbonyl group and thus make the aroylphosphonates more difficult to reduce than similarly substituted α-diketones.

Polarograms were taken of samples of dialkyl aroylphosphonates in various solvents. 2-Propanol, which could be dried conveniently using the apparatus described on page 48, was tried and eventually discarded. The heights of the polarographic waves of the dialkyl aroylphosphonates in 2-propanol were of such low magnitude that coulometric calculations

using the drop in the polarographic wave height would have not been accurate. 2-Butanone was found to yield better-defined polarograms, but the difficulties involved with dehydration without introducing contaminants were such that the use of that solvent was discontinued. Acetonitrile was finally chosen as the solvent since it could be easily dehydrated to a low water concentration without introducing contaminants. Many organic materials were found to dissolve readily in acetonitrile, including all materials examined in this study. Polarograms of the dialkyl aroylphosphonates were found to be of heights sufficient to give a significant decrease per unit time upon electrolysis. A final advantage was that the resistance of acetonitrile was low enough that approximately 0.1 M solutions of the dialkyl aroylphosphonates could be examined polarographically. Even at these high concentrations, the total cell resistance was within the range of the iR Compensator.

The choice of supporting electrolyte also required study. Lithium chloride was found adequate for the experiments in 2-propanol, but had the decided disadvantage of being hygroscopic. It was found to be practically insoluble in 2-butanone. Lithium perchlorate was found to be soluble in 2-butanone and acetonitrile, but it also was hygroscopic. Various tetra-alkylammonium salts were tried in acetonitrile; tetra-methyl- and tetraethyl-ammonium halides were insoluble. Tetra-n-butylammonium bromide was found to be soluble, but solutions of this salt in acetonitrile were found to have resistances above the range of the iR Compensator. Tetra-n-butylammonium perchlorate was finally chosen as the supporting electrolyte for use in acetonitrile. It was easily prepared and crystallized using methods in the literature.[27,32] It showed no signs of decomposition when heated at 110° and it was

stable to percussion. It was found to be very soluble in acetonitrile and had the added advantage of being only slightly hygroscopic; it combines the advantages inherent in the use of a supporting electrolyte with tetra-alkylammonium as the cation and perchlorate as the anion. Tetra-alkylammonium salts are known to suppress polarographic maxima[32] which is an added advantage.

After electrolysis of the solutions of dialkyl aroylphosphonates, separation of the reduction products was necessary. Samples of the solutions themselves could not be injected into the gas chromatograph, because of the tetra-n-butylammonium perchlorate. Therefore an extraction was necessary with a solvent which was immiscible with acetonitrile but would remove the organic materials from the acetonitrile without dissolving the supporting electrolyte. Attempts to find a suitable solvent are made difficult by the fact that a large number of organic solvents are miscible with acetonitrile. Finally, 2,2,4-trimethyl-pentane was found to be immiscible with acetonitrile and not dissolve the supporting electrolyte. When attempts were made to extract the organic materials from the reduction mixtures, it was observed, however, that 2,2,4-trimethylpentane did not remove sufficient quantities of the products to be easily detectable by GLC. Therefore, the acetonitrile was first removed under reduced pressure, and the residue was extracted with an equal-volume mixture of benzene-2,2,4-trimethylpentane. This procedure was found to dissolve sufficient amounts of the organic compounds in the reduction mixtures for GLC analysis. When removing samples for analysis, care was taken to avoid pulling small particles of the insoluble supporting electrolyte into the syringe. Studies were made to determine whether or not volatile reduction products were

removed under reduced pressure along with the acetonitrile. GLC analysis of the solvent showed only one peak, however.

Polarograms of all the dialkyl aroylphosphonates examined were found to be similar (Figure 1). All polarograms exhibited prewaves, the heights of which were different for the various compounds. These prewaves varied in height directly with the height of the mercury column. This is indicative of an adsorption-controlled process.[40] For the second (main) waves, an examination was made of the variation in half-wave potential with DME drop time. No dependence was found, which indicated a reversible reaction, for it is known that the half-wave potential for a reversible reaction is independent of drop time.[40] Experiments were performed to examine the change in the height of the main waves with height of the mercury column. Since no dependence was found, the results indicated a "kinetic" current; i.e. one whose magnitude is determined by the rate at which the electroactive species is produced by a preceding chemical reaction.[40] The evidence thus far indicated a reversible step (electron takeup) followed by a chemical reaction, followed by a further electron transfer. Mechanisms of this type are known as ECE mechanisms.[62] Polarograms of Ia-Ie (page 19) exhibited also a small wave well after the main wave and very near the rise corresponding to the discharge of the supporting electrolyte.

Experiments showed no correlation between polarographic wave heights and concentrations of the dialkyl aroylphosphonates. For identical concentrations of the same ester, an approximate relationship was found to exist between the main wave height and the time of deoxygenation. In addition, the polarographic wave heights did not remain stationary with time, but rose abruptly over the first few hours and

then slowly decreased over the next few days. The half-wave potentials

moved towards more positive potentials during this same period. Since

it was suspected that these effects were in some way connected with

hydrolytic decomposition of the esters,[8] a comparison was made of a

polarogram of a mixture of benzoic acid and diethyl hydrogenphosphonate

with one of a sample of diethyl benzoylphosphonate to which water had

been added. The polarograms were essentially identical. This suggested

that the lowering of the polarographic wave heights with time was due

to hydrolytic decomposition of the esters.

$$ArC\text{-}P(OC_2H_5)_2 + H_2O \longrightarrow ArC\text{-}OH + HP(OC_2H_5)_2$$

When coulometric studies were performed on the main polarographic

waves of the dialkyl aroylphosphonates in acetonitrile, non-integer

values less than unity for the number of electrons transferred were ob-

tained, as shown in Table I. This was evidently due to the fact that

during electrolysis, the diffusion currents were being decreased by a

process other than reduction, probably hydrolysis.

It was possible by GLC analysis of the mixture from the reduction

of Ia to identify all components. The main products were benzoin and

diethyl hydrogenphosphonate; a minor amount of IIa was found. In a

$$R\text{---}\underset{\text{CH}}{\underset{|}{\bigcirc}}\ \ \underset{\text{OR'}}{\overset{O}{\underset{|}{P}}}\text{---OR'}$$
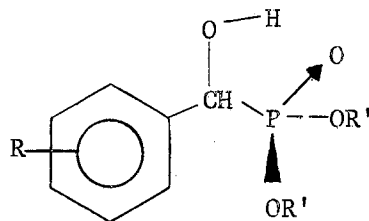
II

R		R'
a. H		C_2H_5
b. p-Cl		C_2H_5

TABLE I

COULOMETRIC DATA FOR REDUCTIONS OF VARIOUS DIETHYL

AROYLPHOSPHONATES, $R-C_6H_4\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2{}^a$

R	Range of concs. studied	Conc. ratio of benzoic acid/ phosphonate	n
H	$1.3-4.3 \times 10^{-2}M$	0	0.3-0.7
		≥ 2	1.95-2.03
p-t-C$_4$H$_9$	$0.9-2.6 \times 10^{-2}M$	0	0.4
		≥ 2	2.02
o-Cl	$1.3-3.6 \times 10^{-2}M$	0	0.3
		0.8	0.75
		≥ 2	2.07
p-Cl	$1.0-3.8 \times 10^{-2}M$	0	0.7
		1.5	1.8
		≥ 2	1.95-2.00
o-CH$_3$O	$1.2-2.8 \times 10^{-2}M$	0	0.4
		1.4	0.4
		2.8	0.66

^{a}All solutions were 0.2 M in $(n-C_4H_9)_4\overset{+}{N} ClO_4^-$.

separate experiment with Id, similar analysis revealed the major prod-
ucts to be 4,4'-dichlorobenzoin (IV) and diethyl hydrogenphosphonate.
The only other component, which was minor, was IIb.

This evidence suggested that the mechanism of the dialkyl aroyl-
phosphonates at the DME under essentially anhydrous conditions could
be expressed as follows:
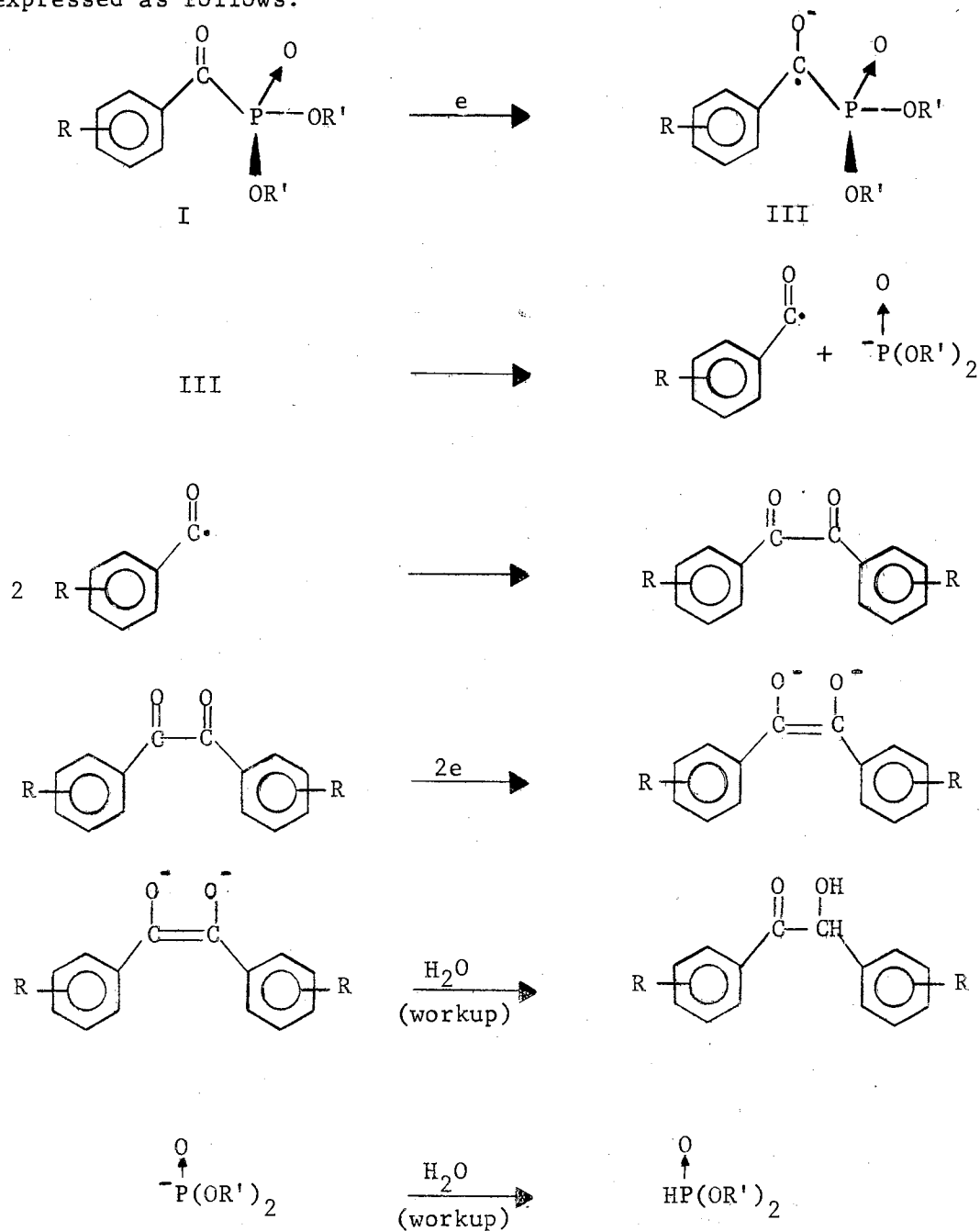
The small amounts of the diethyl α-hydroxyarylphosphonates were evident-
ly a result of slow hydrolysis of the ester (Ia or Id); thus a small
quantity of the corresponding acid acts as a proton source.

$$\text{Ia (or Id)} \xrightarrow{\text{H}_2\text{O}} \text{ArCO}_2\text{H} \;+\; \overset{\text{O}}{\underset{\uparrow}{\text{H}}}\overset{}{\text{P}}(\text{OC}_2\text{H}_5)_2$$
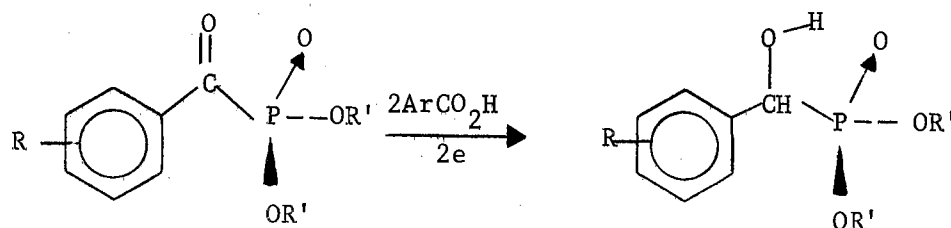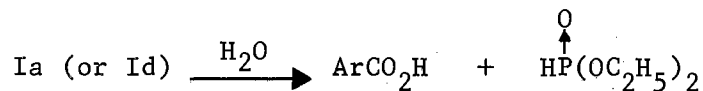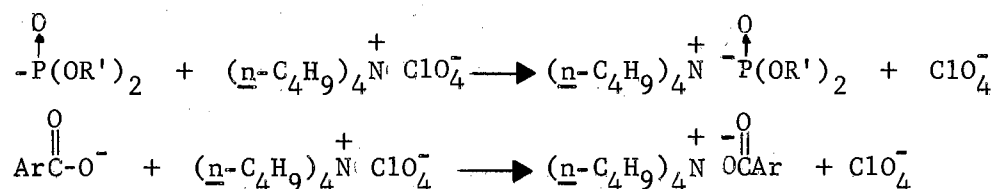

Although the diethyl phosphonate anion and the anion of the car-
boxylic acid are released in the reaction, these probably go through
the following sequence:

$$-\overset{\text{O}}{\underset{\uparrow}{\text{P}}}(\text{OR'})_2 \;+\; (\underline{n}\text{-}C_4H_9)_4\overset{+}{N} \; ClO_4^- \longrightarrow (\underline{n}\text{-}C_4H_9)_4\overset{+}{N} \; {}^-\overset{\text{O}}{\underset{\uparrow}{\text{P}}}(\text{OR'})_2 \;+\; ClO_4^-$$

$$Ar\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-O}^- \;+\; (\underline{n}\text{-}C_4H_9)_4\overset{+}{N} \; ClO_4^- \longrightarrow (\underline{n}\text{-}C_4H_9)_4\overset{+}{N} \; {}^-\overset{\text{O}}{\underset{\parallel}{\text{O}}}\overset{\parallel}{\text{C}}Ar \;+\; ClO_4^-$$

The tetra-n-butylammonium salts would not be extracted from acetoni-
trile. (This reaction would occur at the reference electrode junction).

$$2Cl^- \;+\; 2Hg^o \longrightarrow Hg_2Cl_2 \;+\; 2e$$
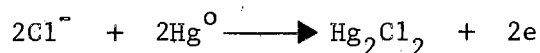
The final reaction is the oxidation of mercury at the acetone calomel
reference electrode.[66]

The potentials at which the dialkyl aroylphosphonates were elec-
trolyzed corresponded to points on the first waves of benzil and substi-
tuted benzils. Coulometric studies on the first wave of benzil yielded
an $\underline{n}$-value of 2.038 electrons. Philp and co-workers reported a 2-
electron mechanism in the reduction of benzil to the dianion of

stilbenediol in dimethylformamide.[47] In addition to actual product

analysis, further evidence for the formation of benzoins was found upon

examination of the DME during electrolysis. A fleeting crimson or red-

violet color was observed upon the surface of each mercury drop. When

strong base was added to a solution of benzoin, a similar color devel-

oped. As determined by Michaelis and Fletcher[41] and later confirmed by

Ihrig and Caldwell,[27] the red-violet color which appears during the

oxidation of benzoin to benzil in alkali is due to the following inter-

mediate:

$$\text{ArC} \overset{\overset{\displaystyle O^-}{|}}{=} \overset{\overset{\displaystyle O\cdot}{|}}{\text{CAr}} \longleftrightarrow \text{ArC} \overset{\overset{\displaystyle O\cdot}{|}}{=} \overset{\overset{\displaystyle O^-}{|}}{\text{CAr}}$$

The red color observed on the mercury drops during electrolysis possibly

could have been due to this same intermediate in the reduction of a

benzil to the corresponding benzoin.

The proposed mechanism agreed well with polarographic evidence

which indicated the first electron transfer to be reversible. The

radical anion formed undergoes C-P bond cleavage to yield benzoyl radi-

cals which subsequently dimerize. This would correspond to the inter-

mediate chemical step in the kinetic polarographic wave observed. The

reaction must occur very rapidly so that the benzil is subsequently

reduced at the electrode surface and does not diffuse into the bulk of

the solution (benzil or 4,4'-dichlorobenzil could not be detected by

GLC analysis in mixtures from Ia or Id, respectively). Because two

polarographic waves could not be resolved under the experimental con-

ditions examined, it was not possible to use methods such as that of

Nicholson[43] to determine the reaction rate constant for the intermed-
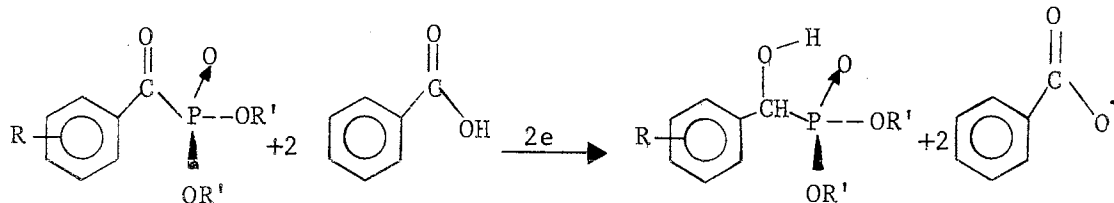
iate chemical step.

In an effort to explain the initial sharp rise of the polaro-graphic waves of the dialkyl aroylphosphonates, the effects of adding a proton source during electrolysis were examined. Benzoic acid was se-lected as the proton source, since it was found to be soluble in the medium and was a weak acid (strong acids lead to slow hydrolysis of the esters.[8]). The waves were raised to much higher current values than previously observed when benzoic acid was not added. The effect on the main waves by added benzoic acid was similar to that found when water was purposely added to the solutions. In addition, no prewaves were visible on polarograms of any of the dialkyl aroylphosphonates, and the half-wave potential was shifted to a more positive value in each case. No small waves were observed after the main waves. Maxima usually ap-peared with dialkyl aroylphosphonate concentrations above 0.015 M. A typical polarogram is shown in Figure 2. Plots of half-wave potentials vs. drop time had slopes of approximately 70 mv., indicating that the electrode reaction was irreversible.[40] The heights of the polarographic waves were found to be proportional to the square root of the height of the mercury column. This was indicative of diffusion-controlled cur-rents. Without electrolytic reduction, the wave heights were found to remain stationary for many days, indicating that no decomposition oc-curred. During electrolysis, no red color was observed on the surface of the mercury drops.

Experiments showed that the polarographic wave heights were direct-ly proportional to concentration of the dialkyl aroylphosphonates when the benzoic acid concentration was at least twice that of the dialkyl aroylphosphonate. Figure 3 contains a plot of $i_{d/C}$ (current per unit concentration) vs. the concentration ratio of benzoic acid/

aroylphosphonate, and shows that i_d/C becomes constant when the concentration ratio ≥ 2. This indicated that two protons were required for the reduction of each molecule of dialkyl aroylphosphonate. Figure 4 shows the variation in half-wave potential with the same ratio.

As illustrated in Table I, coulometric determinations when the above-mentioned ratio ≥ 2 yielded $\underline{n}$-values very near 2 electrons for the reduction processes for all compounds studied with the exception of Ie. Analysis by GLC of a sample of Ia after reduction, with benzoic acid present, showed only one product. This was identified as being IIa. No benzoin was detected in the mixture. A similar study using Id revealed that the single product was IIb and again the corresponding benzoin was observed to be absent.

Thus, the reduction of diethyl aroylphosphonates at the DME in the presence of excess benzoic acid may be expressed as follows:

$$R\text{---}C_6H_4\text{---}C(=O)\text{---}P(=O)(OR')(OR') + 2\ C_6H_5\text{---}C(=O)OH \xrightarrow{2e} R\text{---}C_6H_4\text{---}CH(O\text{---}H)\text{---}P(=O)(OR')(OR') + 2\ C_6H_5\text{---}C(=O)O^-$$

Referring again to Table 1, it should be noticed that regardless of the benzoic acid/aroylphosphonate ratio, an $\underline{n}$-value of 2 electrons was __not__ obtained for the reduction of Ie. The polarographic wave height was found to decrease slowly under nonreducing conditions. Wave lowering may be a function of the slow decomposition of Ie, possibly by increased ease of hydrolysis by an acid-catalyzed process. Polarograms showed that the reduction process is not voltage-independent, as was the case with the other esters. The polarographic wave did not reach a plateau, but had a pronounced slope.

An attempt was made to correlate observed half-wave potentials for the dialkyl aroylphosphonates with Hammett σ-values for the various ring substituents.[47] Figure 5 shows the plot obtained using the half-wave potentials from polarograms of solutions of 0.01 M dialkyl aroylphosphonates and 0.04 M benzoic acid. The results from Ie were not included in the plot, as they were greatly different. This deviation of the $\underline{o}$-CH$_3$O group has been previously reported.[69] The point for Ic was calculated by using a method by Zuman.[69] By use of a method from the literature,[40] calculations were performed based upon the slope of the plot of Figure 5 to obtain an approximate value of ρ ($dE_{\frac{1}{2}}/d\sigma$) of +4.7 indicating that electron-withdrawing substituents facilitate reduction. Behavior of this nature has been attributed to the nucleophilic character of the electrode.[61,68] Zuman[68] has made an extensive study of the application of the Hammett equation to polarographic half-wave potentials. Numerous types of compounds were analyzed, including substituted benzaldehydes, benzophenones, and acetophenones. In 38 of the 40 reactions in the series of the benzenoid type, the sign of the reaction constant was found to be positive (electron-withdrawing substituents facilitate reduction). The reaction constant for the dialkyl aroylphosphonates is +0.67v. as calculated using the method of Zuman. This is larger than the majority of reaction constants reported, indicating the susceptibility of the aroylphosphonate reduction to substituent effects.

Calculation of i_d/C (Figure 3) for Ic indicates that the $\underline{o}$-Cl group does not interfere with the reduction process. However, the low i_d/C value and shape of the polarographic wave of Ie indicate that the bulky $\underline{o}$-CH$_3$O group retards electron transfer at the site of reduction

(the carbonyl group).

It was previously suggested that orbital overlap may occur between the nonbonding electrons on the oxygen atom of the P→O group and the π orbital on the adjacent carbonyl carbon atom.[8,9] It might be assumed that electron transfer to the carbonyl group in electrolysis would be less easy with the dialkyl aroylphosphonates than with α-dicarbonyl compounds. This difference was observed, as shown in Table II which compares the observed half-wave potentials of Ia and Id with the corresponding benzils. A search of the literature did not reveal a comprehensive and similar study of substituted benzils.

Summary

A polarographic cell has been constructed in which prolonged electrolyses of electroactive materials at the DME may be successfully performed. Accurate n-values for the reductions of various inorganic and organic materials indicated the reliability of the apparatus.

From available results, the reduction of the dialkyl aroylphosphonates in the presence of excess benzoic acid proceeds via a two electron-two proton mechanism to yield the appropriate dialkyl α-hydroxyarylphosphonate. In the absence of acid, an ECE (electron transfer-chemical step-electron transfer) mechanism[62] apparently operates to yield the corresponding benzoin. The complete reaction sequence may be summarized as follows:
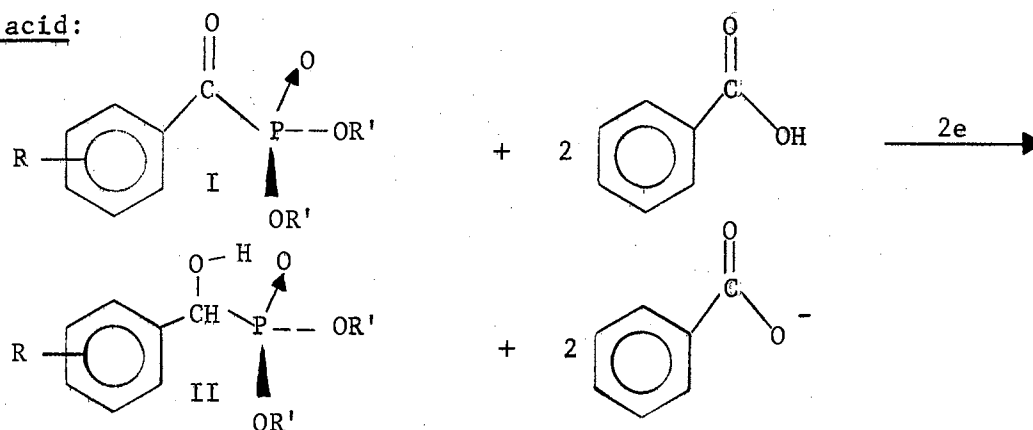
With acid:

Without acid:
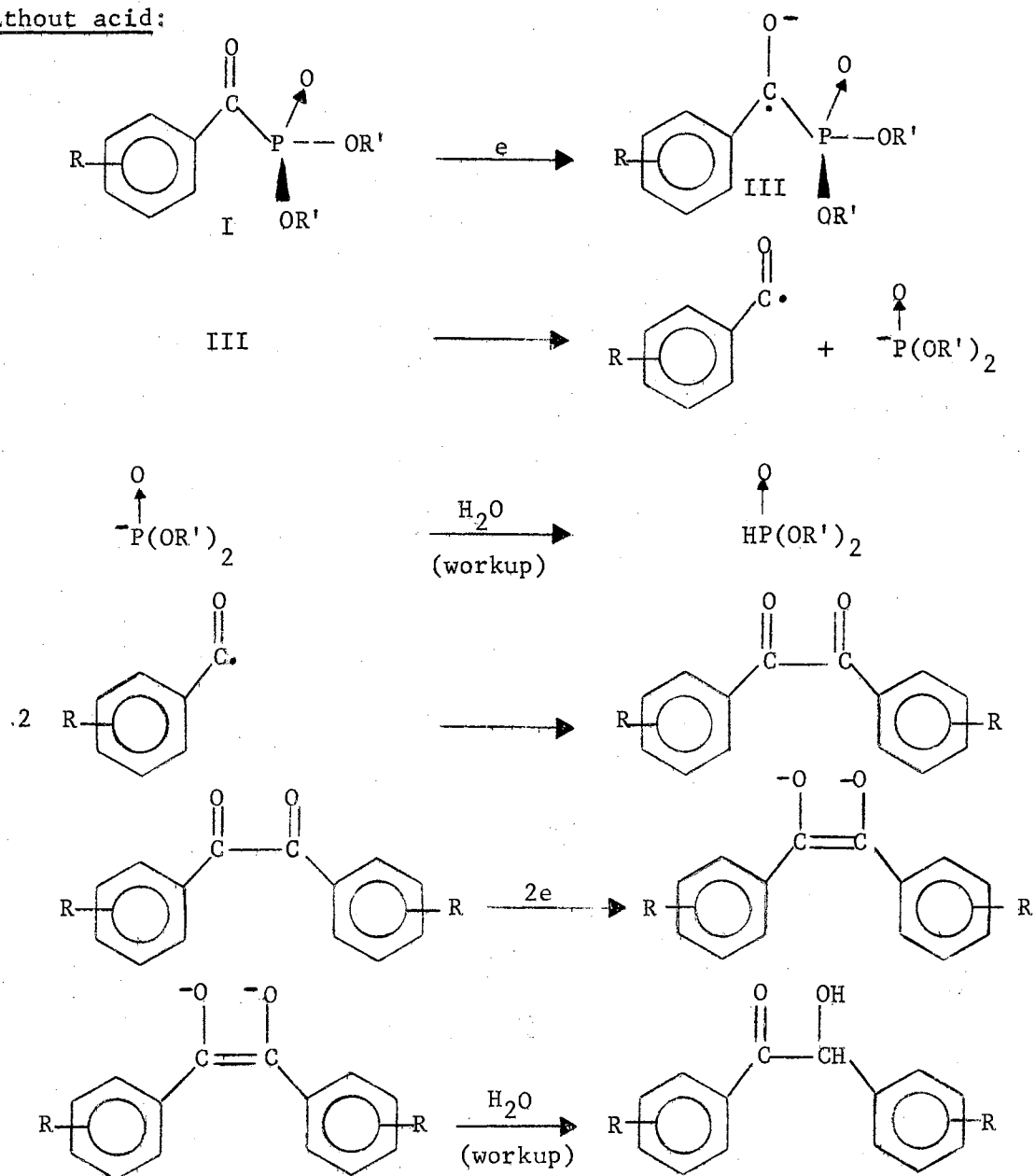
TABLE II

COMPARISON OF OBSERVED HALF-WAVE POTENTIALS OF
DIETHYL AROYLPHOSPHONATES AND BENZILS[a]

Compound	$-E_{\frac{1}{2}}$ vs. ACE (v)	
	(first wave)	(second wave)
Ia	0.967	
benzil	0.772	1.57
Id	0.929	
4,4'-dichlorobenzil	0.558	1.44

[a]All solutions were 0.01 M in the material of interest,

0.04 M in $C_6H_5CO_2H$, and 0.2 M in $(\underline{n}\text{-}C_4H_9)_4\overset{+}{N}$ ClO_4^-.

A satisfactory Hammett plot was obtained which indicated that electron-withdrawing substituents on the aromatic ring increase the ease of reduction of the dialkyl aroylphosphonates. The magnitude of the reaction constant indicated the susceptibility of the reduction to substituent effects.

Evidence was presented for overlap between the nonbonding electrons on the oxygen atom of the P→O group and the π orbital on the adjacent carbonyl carbon atom. The dialkyl aroylphosphonates were reduced less easily than similarly substituted benzils.
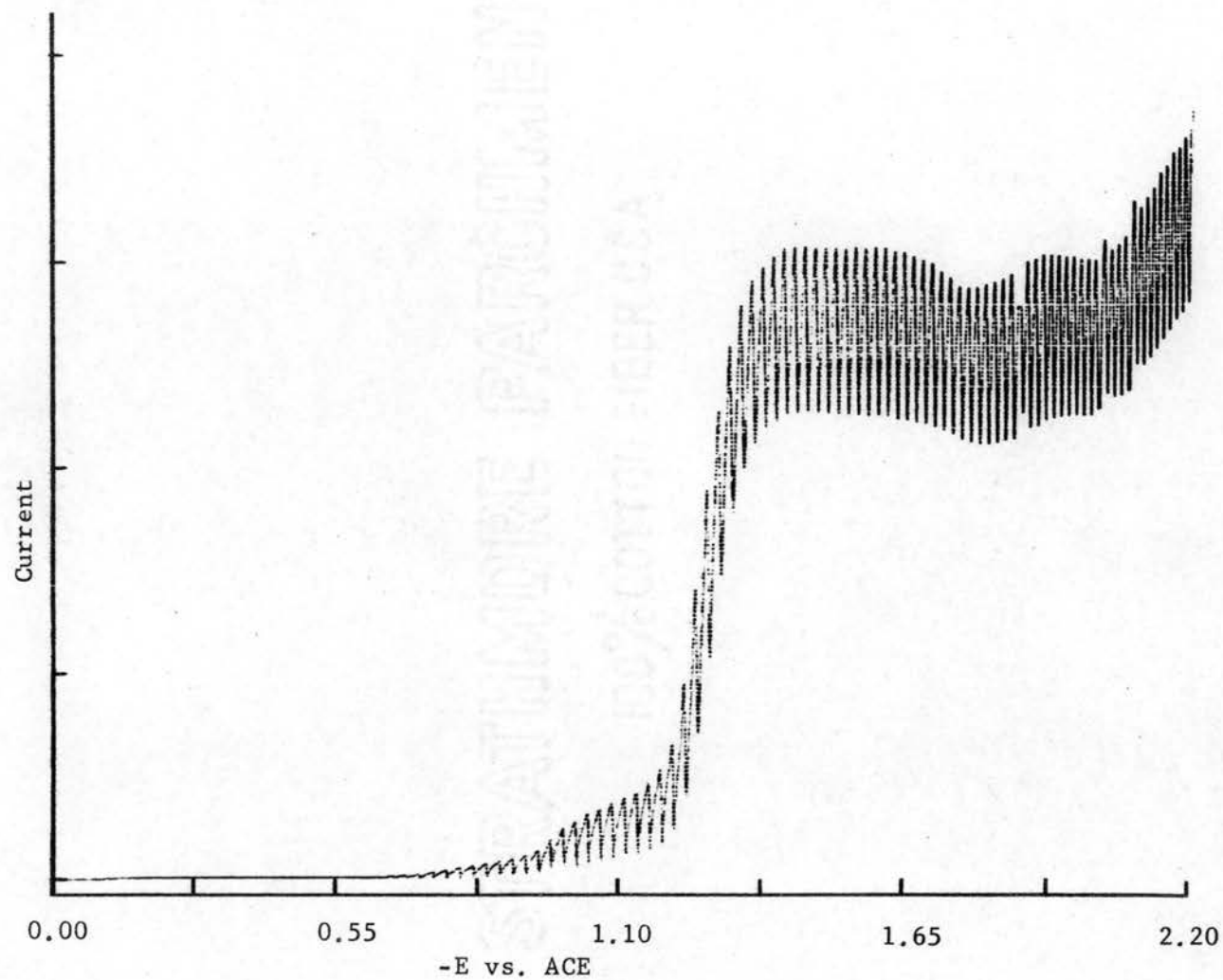
Figure 1.   Polarogram for reduction of Ia, 2.038 x 10^{-2}M.   The solution contained 0.2 M $(\underline{n}\text{-}C_4H_9)_4\overset{+}{N}$ ClO_4^- in acetonitrile; current sensitivity was 0.3 μa/mm.
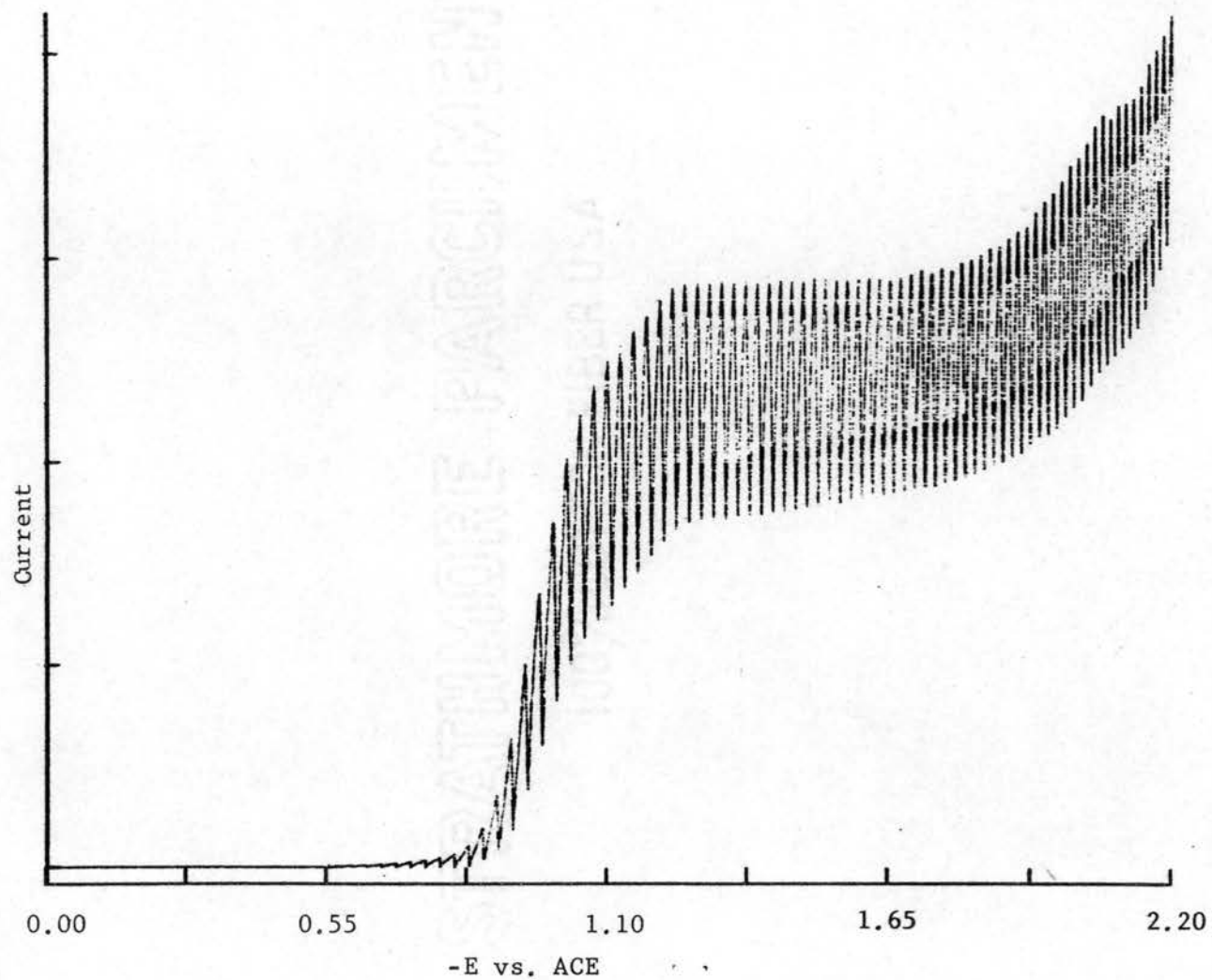
Figure 2. Polarogram for reduction of Ia, 1.306×10^{-2}M. The solution contained 0.2 M $(\underline{n}\text{-}C_4H_9)_4\overset{+}{N}$ ClO_4^- in acetonitrile with 0.04 M benzoic acid. Current sensitivity was 0.6 μa/mm.
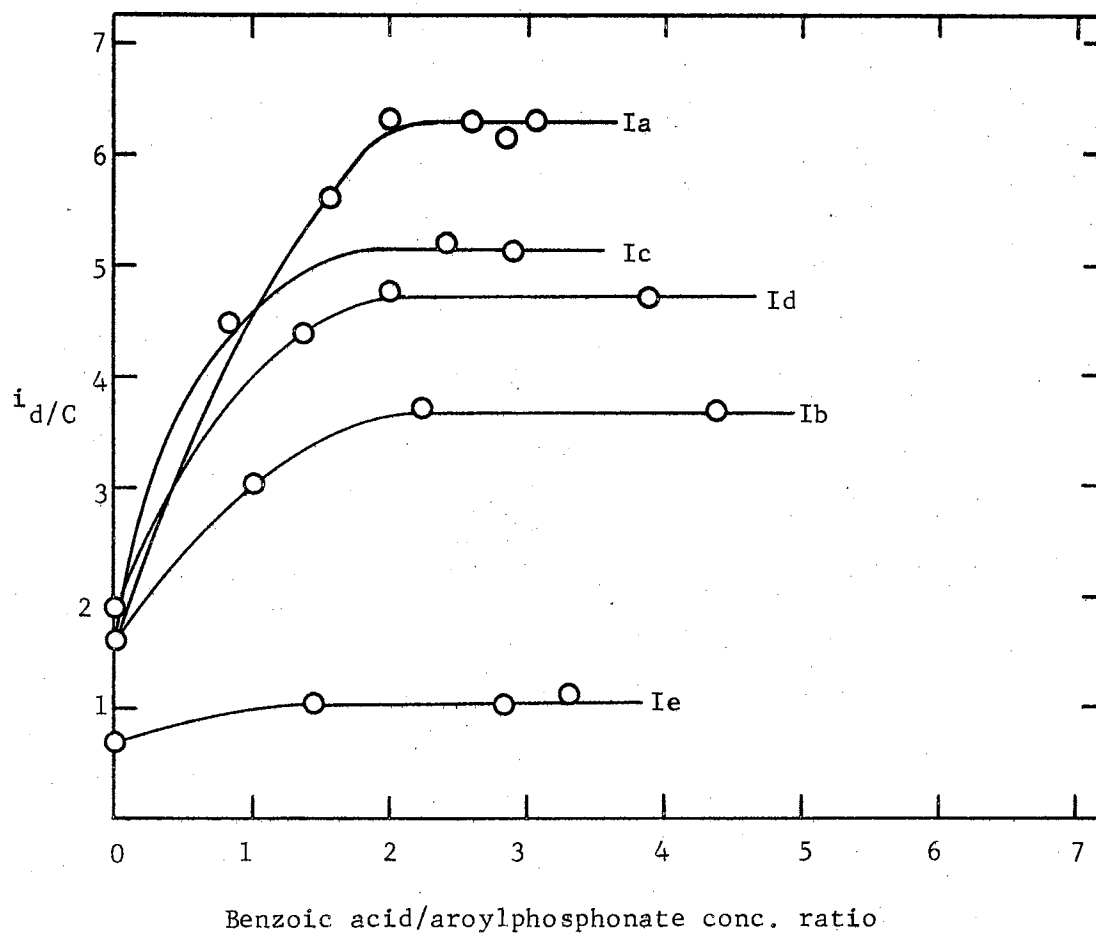
Figure 3. Plot of i_d/C vs. ratio of concentrations of benzoic acid/aroylphosphonate. The concentrations of aroylphosphonate are the same as in Table 1.
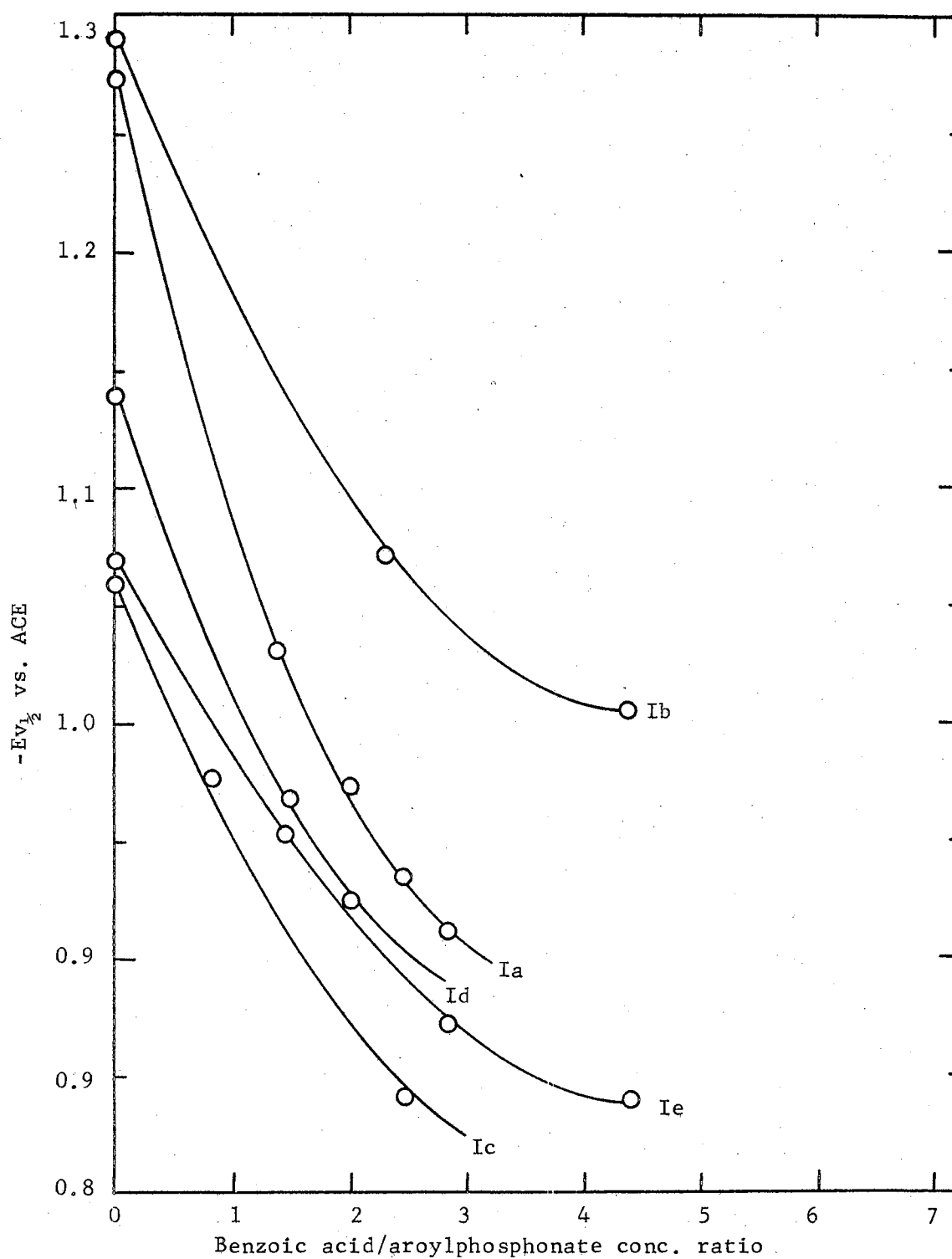
Figure 4. Plot of observed half-wave potentials vs. ratio of con-
centrations of benzoic acid/aroylphosphonate. The
concentrations of aroylphosphonate are the same as
in Table I.
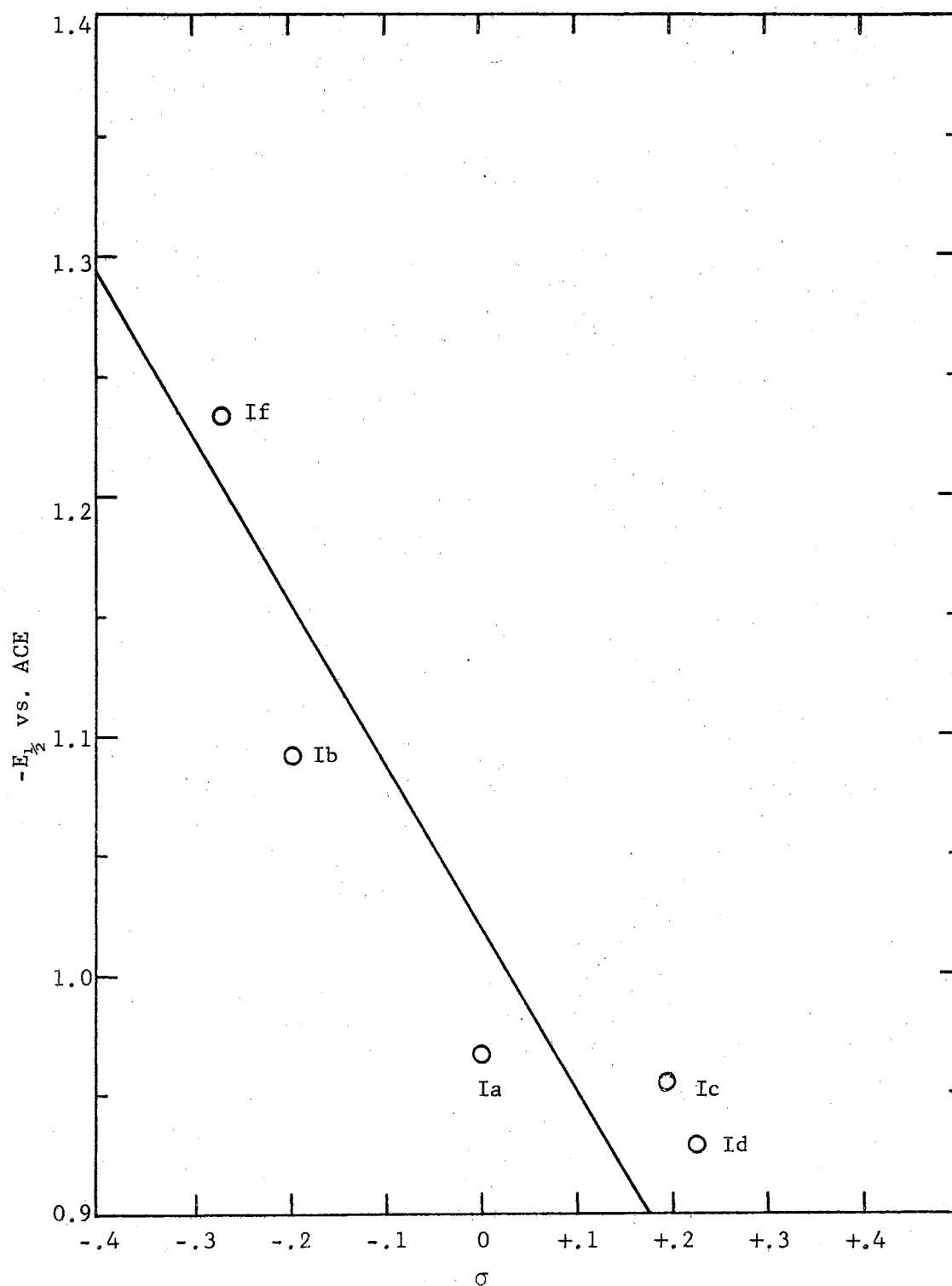
Figure 5. Plot of observed half-wave potentials vs. Hammett σ-values.
Each solution contained 0.01 M aroylphosphonate, 0.04 M ben-
zoic acid, and 0.2 M $(\underline{n}\text{-}C_4H_9)_4\overset{+}{N}$ ClO_4^- in acetonitrile.

Figure 6. Molecular Sieve Dehydration Apparatus

Figure 7. Polarographic Cell and Associated Equipment

CHAPTER III

EXPERIMENTAL[a-f]

Materials. Acetone (Fisher Scientific). Reagent grade was used after a single distillation under nitrogen; b.p. $56.0-56.5°$.

Acetonitrile (J. T. Baker). Reagent grade was used after a single distillation under nitrogen; b.p. $81.5-82.0°$.

Ammonium Chloride (J. T. Baker). Reagent grade was used without further purification.

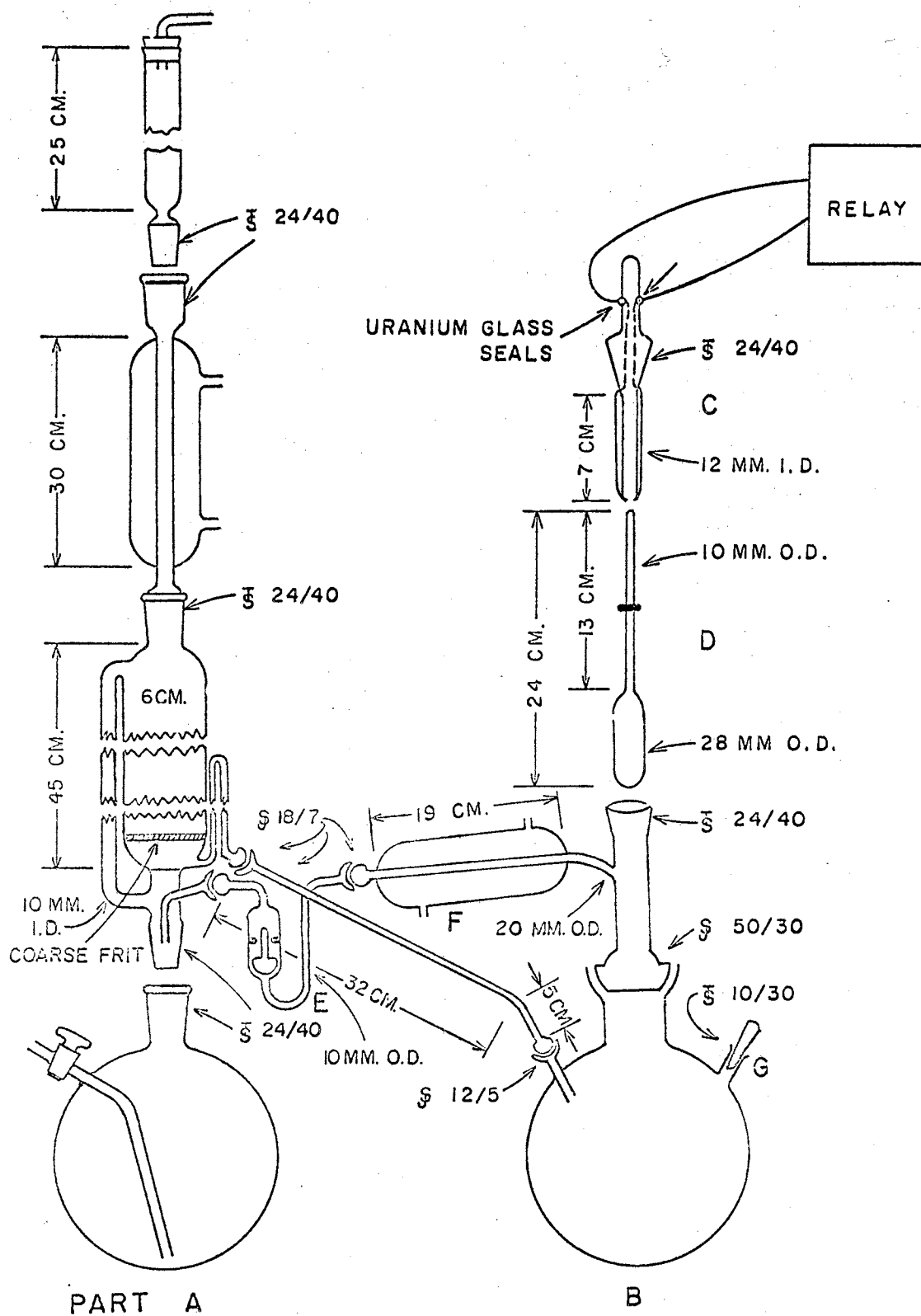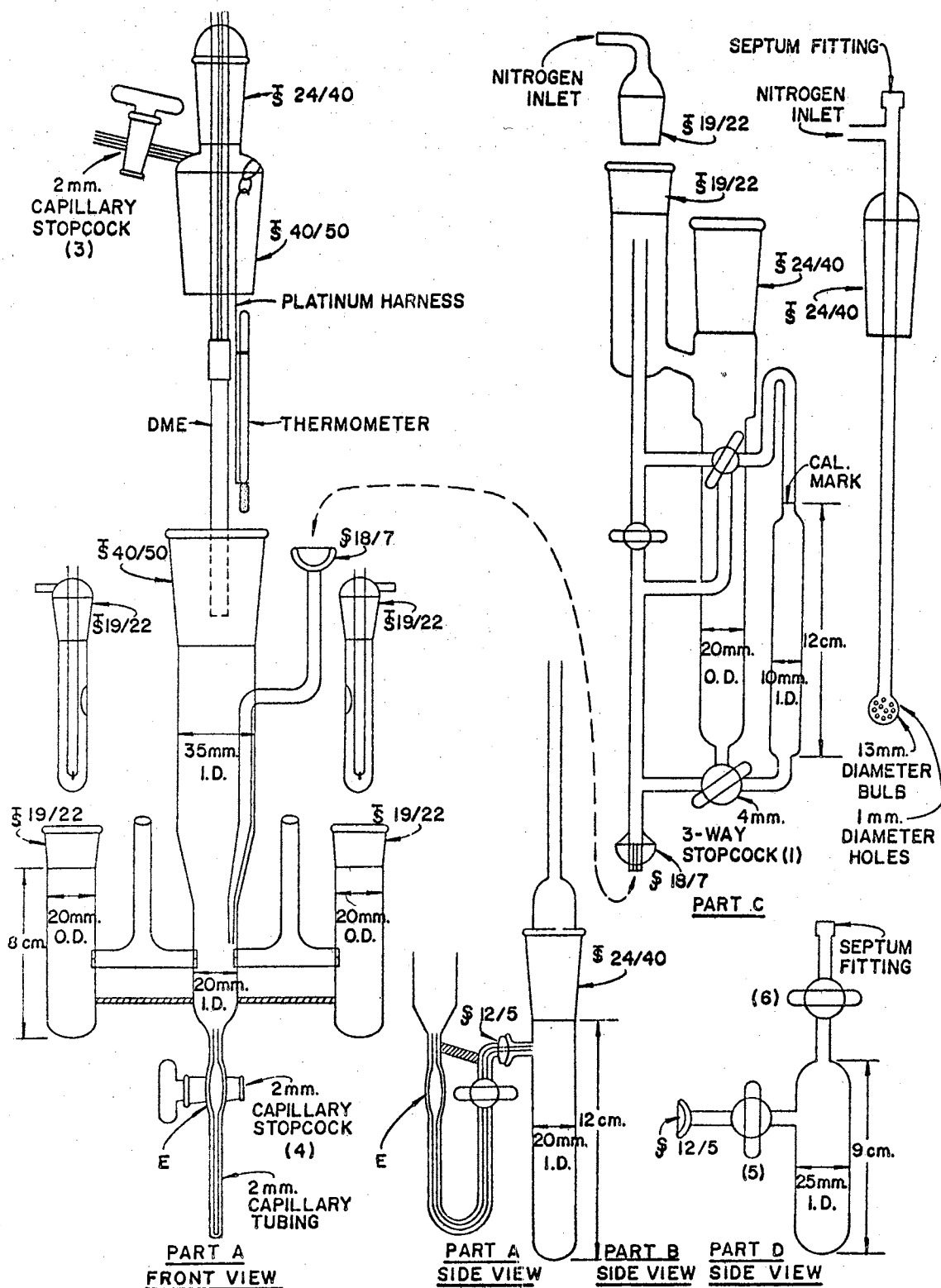[a]The nuclear magnetic resonance (NMR) spectra were determined on a Varian Associates Model A-60 Analytical NMR Spectrometer with a field-sensing stabilizer ("Super Stabilizer"). Tetramethylsilane (TMS) was used as an internal standard.

[b]All melting points were corrected and determined with a Fisher-Johns Melting Point Apparatus.

[c]The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

[d]The infrared (IR) spectra were obtained using a Beckman IR-5A recording spectrometer in potassium bromide pellets.

[e]Current-voltage curves were recorded using a Sargent Model XXI Polarograph with a Model A iR Compensator.[5] During electrolysis, the applied constant potential was obtained from a commonly available stable battery with a simple voltage divider. The value of this potential was periodically checked with a potentiometer. Open-circuit DME characteristics: m = 0.919 mg./sec., t = 7.35 secs.

[f]Gas chromatographic analyses were performed on a Varian-Aerograph Model 1520 instrument equipped with hydrogen flame and thermal conductivity detectors. The column was 10 ft. x ¼ in. diameter and was packed with 12% SE30 on acid-washed, 80/100 mesh Chromosorb G. A flow rate of 75 ml./min. of nitrogen was used; GLC analysis was performed at various temperatures within the range $175-225°$.

Benzaldehyde (J. T. Baker). Reagent grade was used after being dissolved in benzene; the resulting solution was washed with 10% aqueous sodium carbonate solution; b.p. 179.5-180.0°.

Benzene (Fisher Scientific). Reagent grade was used without further purification.

Benzil (Matheson). Reagent grade was used without further purification; m.p. 94.0-95.0°.

Benzoin (Matheson). Reagent grade was used without further purification; m.p. 134.0-135.0°.

Bromoethane (Eastman Organic Chemicals). White label grade was used without further purification.

2-Butanone (Eastman Organic Chemicals). Reagent grade was used after a single distillation under nitrogen; b.p. 79.5-80.0°.

Cadmium chloride (Fisher Scientific). Reagent grade was used after being dried for 24 hours at 130°.

4-Chlorobenzaldehyde (Aldrich). White label grade was used after being washed with 10% aqueous sodium carbonate and recrystallization from benzene; m.p. 46.0-47.0°.

4-Chlorobenzoic acid (Eastman Organic Chemicals). White label grade was used without further purification; m.p. 46.5-47.5°.

Chromium Sulfate (J. T. Baker). Reagent grade was used without further purification.

Diethyl Ether (J. T. Baker). Anhydrous reagent grade was used without further purification.

Diethyl Hydrogenphosphonate (Virginia-Carolina Chemicals). White label grade was used without further purification.

Karl Fischer Reagent (Baker and Adamson). Stabilized solution was

used after dilution with methanol.

Ligroin (Eastman Organic Chemicals). Practical grade was used without further purification; b.p. 100-115°.

Lithium Chloride (J. T. Baker). Reagent grade was used without further purification after being dried at 130° for 24 hours.

Lithium Perchlorate (G. Frederick Smith Chemical Co.). Anhydrous reagent grade was used without further purification after being dried at 130° for 24 hours.

Magnesium (Mallinckrodt). Reagent grade was used.

Magnesium Perchlorate (Fisher Scientific). Anhydrous reagent grade was used after being dried at 130° for 24 hours.

Mercurous chloride (Baker and Adamson). Reagent grade was used without further purification.

Mercury (Bethlehem Instrument Co.). Triple-distilled was used.

Methanol (Fisher Scientific). Reagent grade was used without further purification.

Molecular Sieve (Union Carbide Corporation). Type 4A was used after being activated at 300° under nitrogen purge for 3 hours.

Nitrogen (Linde). Lamp Grade was used for purging equipment and drying solutions. For polarographic analysis the gas was used after being passed in succession through two towers of chromous sulfate-sulfuric acid-amalgamated zinc, a column of glass wool, two scrubbing towers containing concentrated sulfuric acid, another column of glass wool, a large tube containing molecular Sieve 4A, two recirculating presaturator towers filled with the solvent of interest and Molecular Sieve 4A, and a final spray trap.

Perchloric Acid (J. T. Baker). Reagent grade was used without

further purification.

Potassium Cyanide (Fisher Scientific). Reagent grade was used without further purification.

2-Propanol (J. T. Baker). Reagent grade was used after a single distillation under nitrogen; b.p. $82.0\text{-}82.5^{\circ}$.

Silicone Lubricant (Dow Corning). Used for all glassware connections.

Sodium Bisulfite (J. T. Baker). Reagent grade was used without further purification.

Sodium Carbonate (J. T. Baker). Reagent grade was used without further purification.

Sodium Perchlorate (G. Frederick Smith Chemical Co.). Anhydrous reagent grade was used without further purification.

Sulfuric Acid (Fisher Scientific). Reagent grade was used without further purification.

Tetra-n-Butylammonium Bromide (Eastman Organic Chemicals). White label grade was used without further purification.

2,2,4-Trimethylpentane (Matheson, Coleman and Bell). White label grade was used without further purification.

Zinc Metal (J. T. Baker). Reagent grade sticks were used.

Preparation of 4,4'-Dichlorobenzoin (IV). This compound was prepared via a general method reported.[36] A saturated aqueous solution of 0.5 g. of potassium cyanide was added slowly to a boiling solution of 50 g. of freshly washed and recrystallized 4-chlorobenzaldehyde in 30 ml. of methanol. A strongly exothermic reaction ensued. The mixture was boiled for 20 minutes, and the methanol was then evaporated under reduced pressure. The residual, pasty mass was taken up in

benzene. The benzene solution was extracted repeatedly with 20% aqueous sodium bisulfite until the extract liberated no aldehyde when treated with alkali; the solution was then washed with distilled water and evaporated under reduced pressure (20 mm.). The residue crystallized as fine colorless needles from ligroin; yield 40 g. (80%). After several recrystallizations, the product melted at 86.5-87.5° (lit.[36] m.p. 87-88°).

Preparation of 4,4'-Dichlorobenzil (V). This compound was synthesized by air oxidation of 4,4'-dichlorobenzoin by a known route.[36] It was found to melt at 196-197° (lit.[6] m.p. 195-196°).

Preparation of Diethyl Benzoylphosphonate (Ia). This was prepared according to the method of Berlin and Taylor;[8] yield 80%, b.p. 137-138° (1.8-1.9 mm.)--lit.[12] b.p. 136.0-137.0°(1.4-1.5 mm.).

Substituted diethyl benzoylphosphonates (o-Cl, p-Cl, o-CH$_3$O, p-t-C$_4$H$_9$) and a sample of dimethyl p-methoxybenzoylphosphonate were obtained from Dr. Robert T. Claunch.

Preparation of Diethyl α-Hydroxybenzylphosphonate (IIa). This synthesis utilized the method of Gawron and coworkers.[20] A solution of 13.3 g. (0.1 mole) of ethylmagnesium bromide was prepared from 2.4 g. (0.1 g. atom) of metallic magnesium in 10.9 g. (0.1 mole) of bromoethane in 65 ml. of anhydrous ether.

A solution of 13.8 g. (0.1 mole) of diethyl hydrogenphosphonate in 60 ml. of anhydrous ether was placed in a 3-necked flask (200 ml.). The flask was equipped with a condenser and a thermometer. After displacement of air by dry nitrogen, the solution of ethylmagnesium bromide was added dropwise by means of an addition funnel over a period of 20 minutes at room temperature. At the same time the solution was

agitated by means of a magnetic stirrer.

To the above-mentioned solution of the bromomagnesium salt of diethyl hydrogenphosphonate, 10.6 g. (0.1 mole) of benzaldehyde in 25 ml. of anhydrous ether was added. The reaction mixture was boiled for 3 hours, after which time the ether solution was shaken with an equal volume of cold saturated aqueous ammonium chloride in a separatory funnel. The ether layer was separated and dried (Na_2SO_4) overnight. After removal of ether and some unreacted benzaldehyde and diethyl hydrogenphosphonate under vacuum at 20 mm. the residue became solid and was recrystallized from benzene-ligroin to give 14 g. (57.4%) of crude material. After several recrystallizations from benzene, a pure product IIa was obtained; m.p. 83-84°, lit.[20] m.p. 83-84°. IR (Plate 1) and NMR (Plate 2) spectra confirmed the proposed structure of this phosphorus ester.

Preparation of 4-Chloro-α-Hydroxybenzylphosphonate (IIb). This material was prepared in a manner similar to that for the compound (IIa). One-tenth-molar quantities of all reagents were used. A yield of 13.9 g. (50%) of crude (IIb) was obtained. After several recrystallizations from benzene-ligroin the pure ester (IIb) melted at 71-72°. A search of the literature indicated that this compound had not previously been reported.

Anal. Calcd. for $C_{11}H_{16}ClO_4P$: C, 47.40; H, 5.79; P, 11.11.

Found: C, 47.02; H, 5.51; P, 10.98.

IR (Plate 3) and NMR (Plate 4) spectra confirmed the proposed structure.

Preparation of Tetra-n-butylammonium Perchlorate. This was prepared according to the method of Kolthoff and Coetzee.[32] Alternatively,

the method of Cokal and Wise was used.[13] The material was dried in a
heated vacuum dessicator at 20 mm. at 90° and stored in the dessicator.
Several recrystallizations from water were necessary before impurities
were polarographically tolerable.

Preparation of Anhydrous Solvents. As it is known[8] that dialkyl
aroylphosphonates are susceptible to hydrolytic decomposition, anhy-
drous solvents were used for all studies. The apparatus described by
Arthur and coworkers[3] was found to efficiently remove water from sol-
vents such as 2-propanol. However, quantities of 2-propanol prepared
in this manner always contained dust from the Molecular Sieve bed.
This dust would settle out only after the solvent was allowed to stand
undisturbed for a few weeks. If polarographic determinations were run
in solvent with the dust in suspension, the dropping mercury electrode
would occasionally become erratic. When a solution of diethyl benzoyl-
phosphonate[8] in 2-propanol was boiled for 24 hours, polarographic analy-
sis indicated that extensive hydrolytic decomposition had occurred; the
polarographic wave height was much lower than in previous studies using
identical solutions. The hydrolysis was evidently catalyzed on the
basic surface of the molecular sieve dust which had washed down into
the distillation flask. To eliminate the presence of the dust, a modi-
fication of the published apparatus was used.[3] This is shown in Figure
6. The left-hand portion of the diagram is similar to the apparatus
described.[3] However, in the new arrangement the liquid siphons and
empties into Flask B, instead of returning to the original flask. Thus
any Molecular Sieve dust and other impurities do not contaminate the
material in Flask A. Parts C and D constitute a device for regulating
the heating rate of Flask B. A platinum band is mechanically held

around the shaft of Part D, which is a float. The position at which the platinum band is to be placed must be determined experimentally. In Part C, two platinum wires (22 guage) are attached so that their lower ends bend under the edges of the tube which fits around the shaft of Part D. Part E is a one-way glass valve which allows flow only from the Condenser F to Flask A. The upper ends of the platinum wires of Part C are connected to a relay which controls the heating of Flask B. Two types of relays have been used successfully: a Supersensitive Relay No. 4-5300 available from American Instrument Co., Inc., and a Thermocap Industrial Control Relay available from Niagara Electron Laboratories, Andover, N. Y.

The apparatus is normally filled through Port G. Solvent is distilled through Condenser F into Flask A until the latter is about two-thirds full. Flask B is then filled approximately to the same level. The apparatus is now ready for operation. If it is desired to dry a solution, the solute must be added to Flask A before the drying operation is started.

Flask A is heated by means of a heating mantle until the solvent boils. Vapors from the solvent rise and condense so that solvent drops onto the Molecular Sieve bed. After passing through the bed, the solvent siphons into Flask B when a sufficiently high level is attained in the Soxhlet extractor. This process continues until the Float D is elevated to the required level to cause the platinum band to make contact with the two platinum wires of Part C, thus actuating the relay and turning on the heating mantle under Flask B.

The vapors from the boiling solvent in Flask B enter Condenser F, after which the condensed liquid passes through the one-way valve into

Flask A which is heated continuously. This process proceeds until the Float D is lowered to the extent that the relay contact is broken, thus turning off the heating mantle under Flask B. As Flask B cools, a partial vacuum develops. This closes the one-way valve E and pulls more solvent over from the Molecular Sieve bed. This in turn actuates the heating mantle under Flask B, and the process continues.

It is important that the heating mantle under Flask B is operated at a higher voltage than that under Flask A. This differential prevents flooding of Flask B and Condenser F as the rate of transfer of solvent from Flask B to Flask A is greater than the rate of filling of Flask B from the Molecular Sieve tower. Experience has shown that the apparatus performs well with the heating mantle under Flask A operated at about 70 volts from a variable transformer with Flask B at about 75 volts.

The modified apparatus has been found to dehydrate efficiently both pure solvents and solutions. Water levels have been reduced from about 0.1% to 0.001% in reagent grade 2-propanol and a 0.1M solution of lithium chloride in 2-propanol over a 30-hour period of reflux. The water content was determined by means of a modified Karl Fischer titration discussed on page 51.

2-Butanone has been successfully dried with this apparatus but under an inert atmosphere of dry nitrogen. Without the inert atmosphere, the solvent in Flask B acquires a bright yellow color after approximately 12 hours of reflux. In addition, the solvent in Flask A becomes a much lighter, but noticeably yellow color. The water content was found to have dropped from 0.8% to approximately 0.002% as assayed by modified Karl Fischer titration. However, GLC analysis of the solvent detected a large number of peaks probably due to aldol condensation
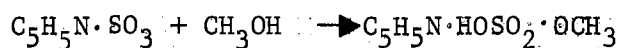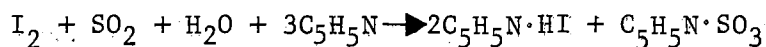
of the ketone on the basic surface of the drying agent. When a new batch of solvent was dried under an inert atmosphere (dry N_2 which was slowly admitted through the filling port G), the solvent in Flask B became only light yellow in color and that in Flask A was colorless. GLC analysis indicated no solvent decomposition. The water content in the solvent was found to be 0.001% after 48 hours.

Assay of the water content of reagent grade acetonitrile, which had been dried for 36 hours at reflux, indicated a drop from 0.09% to less than 0.0005%. No decomposition of the solvent was detected. When a 0.01M solution of diethyl benzoylphosphonate in acetonitrile was de-hydrated using the new apparatus, no hydrolytic decomposition was de-tected. The polarographic wave was of expected height, that is, it was of the same height as observed immediately after mixing of the reagents. Evidently hydrolysis did not occur because the diethyl benzoylphosphon-ate itself did not come in contact with any molecular sieve dust.

Thus it appears that the new apparatus retains the efficiency of the Molecular Sieve as a drying agent, and has the advantage in that both solvents and solutions may be dried without introducing contami-nants.

The Determination of Water. The accurate detection of water in solvents and solutions was a necessary part of this research. Truly anhydrous solution conditions were desired due to the ease with which dialkyl aroylphosphonates decompose through hydrolysis.[8] In addition, mechanisms of reduction may sometimes be different in the presence of varying amounts of a proton source such as water.[18,63] Thus it was de-sirable to be able to determine and control the amount of proton source present.

The method employed was the Karl Fischer technique.[19] In this technique, water is determined through its reaction with a solution containing iodine, sulfur dioxide, pyridine, and a solvent such as methanol. The essential reactions may be illustrated as:

$$I_2 + SO_2 + H_2O + 3C_5H_5N \longrightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot SO_3$$

$$C_5H_5N \cdot SO_3 + CH_3OH \longrightarrow C_5H_5N \cdot HOSO_2 \cdot OCH_3$$

The end point of such a reaction can be determined visually; however, electrochemical methods are more widely employed because they possess high sensitivity.

Although the arrangement of titration cell and burette described by Haynes[24] was found to work well for the solvents and solutions in this research, the circuit with that equipment occasionally gave results which were not reproducible. The method of Haynes[24] and Arthur employed a constant potential in the circuit, and the endpoint in each titration was obtained by noting an increase in current in a galvanometer.

It was anticipated that improved results might be obtained if instead of a constant voltage in the circuit, a low constant current were used, and the end point obtained by monitoring the potential difference between two platinum electrodes.

A 1.5V dry cell battery with 150,000 ohms in series with two platinum electrodes provided a constant current of approximately 10 microamperes. The end point was obtained by monitoring the potential across the platinum electrodes by means of a Heath Model EUW-20A servo recorder and the attached pH Adapter Module.

At the beginning of a titration of water, the potential across the two platinum electrodes is the difference between the emf of the

anode reaction (oxidation of iodide to iodine) and the cathode reaction (reduction of some species in solution, perhaps acid). As the titration proceeds and the reagent reacts with the water, this potential remains constant. With the first excess of Karl Fischer Reagent (iodine), the cathode reaction becomes the reduction of iodine to iodide. Thus the potential essentially drops to zero.

It was found that this method gave sharp endpoints in the determination of samples of water. Successful analyses for water were determined in 2-propanol and acetonitrile. When attempts were made to determine water in 2-butanone, however, an endpoint could not be obtained. A literature search revealed that ketones form ketals[42] with the methanol in the reagent with the subsequent formation of water. Thus an endpoint cannot be reached when large amounts of alcohol are present.

$$R_2C=O + CH_3OH \rightarrow R_2\underset{\underset{OH}{|}}{C}-OCH_3 \xrightarrow{CH_3OH} R_2C(OCH_3)_2 + H_2O$$
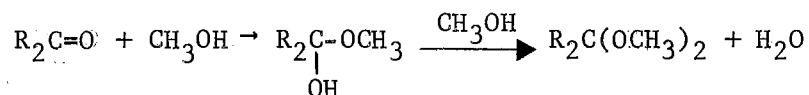
Successful titrations of water in 2-butanone were performed only when a large excess of pyridine was present in the titration vessel; in addition, pyridine must be used to dilute the standard Karl Fischer Reagent.

The Polarographic Cell. It was pointed out previously that the products of electrolysis occurring at a dropping mercury electrode on occasion can be different from those produced at a larger electrode, such as a mercury pool.[21,33,35] In this study it was decided to examine a series of reductions at the dropping mercury electrode, obtaining coulometric data during the electrolysis and producing sufficient quantities of products for analysis by GLC and other methods.

In view of the long periods of time required for sufficient electrolysis at a microelectrode, it was recognized that solvent evaporation must be controlled in order to correlate concentration and wave height. This is essential in order for meaningful coulometric data to be obtained. Previous studies showed that the situation is not greatly improved by presaturating the purging gas with the solvent being used.[25]

A new polarographic cell was constructed which was suitable for work with nonaqueous organic solutions. Because standard-taper ground-glass connections and stopcocks are used throughout, the cell may be hermetically sealed after flushing with a suitable gas. Interference by atmospheric oxygen is eliminated, and there is no need for a continuous stream of gas over the solution during electrolysis. With a DME, successful electrolyses over a period of ten days have been performed with this apparatus. Coulometric data may be obtained during the period of the run, and sufficient amounts of products are formed for analysis by methods such as GLC.

Part A in Figure 7 is a diagram of the main cell of the three-electrode type. The reference cells are the acetone calomel electrodes (ACE) originally reported by Arthur and Lyons.[4] The lower part of the cell is constructed so that mercury from the DME maintains a constant level. Waste mercury drains into the tube labelled Part B as shown in the side view. The expanded portion (E) in the capillary tubing at the bottom of the cell was found to prevent mercury from trapping small pockets of the solution in the capillary tubing and carrying them along into the waste mercury collector. The main cell body has similarities to a cell originally used by Arthur and Vander Kam[5] except that the bridging tubes connecting the DME compartment to the reference

electrodes have high-resistance asbestos fibers at each end and filler tubes so that a variety of electrolytes may be employed. As measured with a conductance bridge using 0.1M aqueous potassium chloride, the resistances of the fibers at the DME compartment ends of the bridging tubes are 100,000 ohms; those of the fibers at the reference cell ends are 40,000 ohms. Solutions (0.1M) of lithium chloride, lithium perchlorate, and tetra-n-butylammonium perchlorate in 2-propanol, 2-butanone, and acetonitrile, respectively, have all been used successfully in the bridging tubes.

The cell top is equipped with a stopcock for use as a gas vent and with a hook of 16 gauge platinum wire so that a small thermometer slung in a harness of similar wire may be suspended inside the cell. The design of the mercury column inlet avoids the usually leaky ports in the tops of many common cells through which rubber tubing containing mercury is passed.

The tube entering the side of the cell and passing down inside is designed to avoid splashing solution onto the walls of the DME compartment. The length of the tube is adjusted so that the end is barely above the top of the solution, the volume of which is approximately 10 ml.

Part C is a deoxygenator in which dry nitrogen bubbles through the solution in order to remove dissolved oxygen. Two gas streams are used, one rapid to flush out the entire system and the other slower to bubble through the solution. A portion of the solution is measured quantitatively in the calibrated side bulb; this solution is then allowed to flow into the main body of the cell. Instead of a glass frit, a bulb with 18 to 20 small holes is used to disperse the gas, for it has been

found that certain glass frits retain traces of water after being washed unless heated for a lengthy period. Part D is a relatively simple device to contain solutions of materials which, after hydrolysis, are susceptible to air oxidation or hydrolysis due to water vapor in the atmosphere. The septum fitting permits convenient removal of electrolyzed sample by means of a hypodermic syringe.

Calibration of the Cell. In order to determine the accuracy and reliability of coulometric data obtained using the polarographic cell, a number of standard materials were reduced. Although errors have occasionally been reported in connection with millicoulometry using very small solution volumes,[67] this apparatus has yielded accurate $\underline{n}$-values for all known materials studied.

Cadmium chloride in various concentrations in anhydrous 2-propanol with 0.1M lithium chloride yielded values of 1.950 to 2.040 electrons, with an average error of 1.8%. The range of concentrations studied was from 5×10^{-4}M to 3×10^{-3}M. The solvent was dried in the apparatus previously described. Lithium perchlorate in a concentration of 5×10^{-3}M in acetonitrile with 0.1M tetra-$\underline{n}$-butylammonium perchlorate as supporting electrolyte yielded a value of 1.003 electrons for the reduction of lithium over a 15-hour period. Magnesium perchlorate under like conditions yielded a value of 2.012 electrons.

Organic materials have been studied in acetonitrile. With 0.2M tetra-$\underline{n}$-butylammonium perchlorate as supporting electrolyte and 0.04M benzoic acid to serve as proton source, benzil yields two well-defined waves of approximately equal height. The half-wave potentials are -0.772 and -1.57v. vs. ACE. Under the same conditions, benzoin yields a wave identical in shape to that of the second benzil wave. Also the

half-wave potential is essentially the same, indicating that benzoin

is the product of reduction for the first wave. When benzil is reduced

at a potential on top of the first wave, concentrations of up to 0.02M

yielded an n-value of 2.036 electrons. A similar reduction in an

aqueous system at low pH values has been reported.[47]

From the results of these determinations, (summarized below), it

appears that with this apparatus, accurate n-values may be obtained

during lengthy electrolyses at the DME.

Reaction	n-value
$Cd^{++} + 2e \rightarrow Cd^{o}$	1.950-2.040
$Li^{+} + e \rightarrow Li^{o}$	1.003
$Mg^{++} + 2e \rightarrow Mg^{o}$	2.012
$\underset{\substack{\parallel \ \parallel \\ O \ O}}{C_6H_5C\text{-}CC_6H_5} + 2H^{+} + 2e \rightarrow \underset{\substack{\mid \ \parallel \\ OH \ O}}{C_6H_5CH\text{-}CC_6H_5}$	2.036

<u>Procedure For a Typical Electrolysis of a Dialkyl Aroylphosphonate.</u>

The glassware was always kept very clean and in the drying oven at 130°

between runs. The polarographic cell and the associated equipment were

removed from the oven and assembled while hot. Dry nitrogen was al-

lowed to purge the glassware while it cooled. It was then reassembled,

using liberal amounts of silicone lubricant, and clamped in place on a

mobile rack which was mounted over a constant-temperature bath. The

bath contained paraffin oil maintained at $25.0 \pm 0.1^{o}C$. By means of a

small squeeze bottle, triple-distilled mercury was forced into the cell

to the desired level by way of the disconnected waste mercury tube.

Part B (Figure 7) was then clamped in place. The mercury supply for

the DME was turned on, and mercury was allowed to flow from the DME.

This served as a check to ensure proper flow of the DME.

Rubber septums were placed over the ends of the bridging tubes on

the main cell. The nitrogen train was activated, and the gas from this source was divided into three streams. One rapid stream entered the left tube of the deoxygenator and passed through this into the main cell body. A slower stream entered the compartment in the deoxygenator which would later contain the solution. Both of these streams vented through Stopcock 3 in the top of the cell (Figure 7.). Ordinarily a simple device such as a gas dispersion tube in a test tube containing a relatively non-volatile solvent was used to monitor the rate of flow of gas. A third stream of nitrogen was admitted through the septums in the bridging tubes by means of 4-inch, 16-gauge hypodermic needles fastened to the ends of pieces of rubber tubing connected to the gas source. Smaller 22-gauge needles were used to vent the nitrogen.

The gas streams were allowed to purge the entire apparatus for approximately 2 hours. During this time, the solution for electrolysis was prepared. A 25-ml. volumetric flask was removed from the oven and a septum cap was placed over the mouth of the flask. Dry nitrogen was admitted through a 6-inch 16-gauge needle and vented through a smaller 22-gauge needle. The gas was allowed to cool the flask for approximately 10 minutes. Then, 1.71 g. (5 x 10^{-3} mole) of tetra-$\underline{n}$-butylammonium perchlorate, which had been stored in a vacuum dessicator, was quickly weighed on paper and transferred to the volumetric flask; this amount was sufficient to make the solution 0.2M in supporting electrolyte. The next step was to weigh 0.1832 g. (1.5 x 10^{-3} mole) of benzoic acid in a weighing "pig" and add it to the flask, also. The solution would thus be 0.06M in benzoic acid. The septum cap was then replaced, and nitrogen was allowed to purge the flask for another 5 minutes. A quantity of diethyl benzoylphosphonate (0.1327 g., 5.479 x 10^{-4} mole) was

weighed in a 0.5 ml. syringe and injected through the septum into the flask. The syringe was then re-weighed. The solution would thus be 2.192×10^{-2} M in diethyl benzoylphosphonate.

Solvent was added to the flask by the following procedure: a septum cap was placed on the removal tube of the apparatus in Figure 6. A hypodermic needle was used to make a hole in the septum cap through which the end of an 8-inch piece of small-diameter polyethylene tubing was placed. The other end of the tubing was pushed through the septum cap on the 25-ml. volumetric flask. A needle was also inserted in this same septum cap. Attached to this needle was a piece of rubber tubing fastened to a one-way squeeze bulb pump. A partial vacuum was created in the flask by means of the squeeze bulb. Solvent was then admitted through the polyethylene tubing until the quantitative mark on the 25-ml. flask was reached. After removal of the tubing and the needle from the septum cap, the flask was shaken thoroughly. The solution was now ready for use.

After 2 hours of purging the apparatus with nitrogen, a 50-ml. syringe equipped with a Luer-Lok stainless steel stopcock was used to remove the solution from the volumetric flask. The syringe was first purged thoroughly with dry nitrogen; 25 ml. of the gas was then injected into the flask and an identical volume of solution was pulled into the syringe.

Three milliliters of a 0.2M solution of tetra-n-butylammonium perchlorate were next injected into each of the bridging tubes on the main cell by means of a 10-ml. syringe. The solution from the large syringe was then injected through a septum cap in the top of the deoxygenator. Nitrogen was bubbled through the solutions in the bridging

tubes and that in the deoxygenator for 30 minutes. The inlet and venting needles were now removed from the septum caps in the bridging tubes. The stopcocks in the deoxygenator were maneuvered in such a manner that some of the deoxygenated solution was transferred into the side bulb. This had been previously calibrated with water and found to contain 9.268 ml. The solution was finally allowed to flow out of the calibrated side bulb and into the DME compartment in the cell. This procedure of deoxygenation was the reverse of that originally recommended by Arthur and Lyons,[4] but the end result was identical.

In succession, Stopcocks 1-3 were closed and the nitrogen supply was shut off. Stopcock 4 was opened to allow excess mercury to drain, and the reference electrodes were placed in the appropriate compartments. The rack holding the entire apparatus was then lowered so that the lower part of the cell was immersed in the constant temperature bath. After allowing 15 minutes for thermal equilibration, the electrodes were connected to the polarograph and an initial polarogram was taken.

The constant potential for electrolysis was chosen to be -1.45v. vs. ACE, which was approximately in the middle of the polarographic wave obtained. Electrolysis was performed at this potential for 47.8 hours. An accurate timer (Precision Scientific Co.) was used to measure the duration of the electrolysis. After 50 per cent of the diethyl benzoylphosphonate had been reduced, the wave height was measured and the timer reading noted. This information was used in the following equation to calculate the number of electrons transferred per molecule in the reduction:

$$n = \frac{16.22\ i_o t}{VCo\ \log\ i_o/i_t}$$

where n =   number of electrons transferred per molecule

    16.22 =   constant containing Faraday's Constant, etc.

     i_o =   initial wave height (amperes)

     V =   solution volume (ml.)

     Co =   initial concentration (moles/1.)

     i_t =   wave height (amperes) at time t

This equation is identical in form to that discussed by Meites.[40]

Using the data from this experiment,

$$n = \frac{(16.22)(208.0\ mm.)(0.8 \times 10^{-6}\ amp./mm.)(45.772\ hrs.)}{(9.268\ ml.)(2.192 \times 10^{-2}\ moles/1.)(0.30313)}$$

n = 2.006 electrons.

The nitrogen supply was now turned on and Stopcock 2 was opened. Nitrogen pressure was applied to the cell to force the mercury out of the constant level tube into the reservoir. When all the mercury had been so removed, Stopcock 4 was closed and the reservoir removed. Part D, which had been thoroughly flushed with dry nitrogen, was clamped in place on the cell. Stopcocks 5 and 6 on Part D were now opened, as was Stopcock 4 on the main cell. Nitrogen pressure then forced the solution out of the cell and into Part D. Stopcock 6 was next closed and Part D was rotated on the spherical joint. Stopcock 6 was then opened very slightly and any mercury was expelled which had been inadvertently transferred along with the solution. By following this procedure, only one or two drops of solution were lost along with the mercury. Both stopcocks on Part D were finally closed, and the sample was stored for future use.

Before analysis by GLC, acetonitrile was removed under aspirator
pressure. Then 0.5 ml. of a 1:1 mixture of benzene and 2,2,4-trimethyl-
pentane was injected to extract the organic materials. No effort was
made to dry the extracting solvent, in which the supporting electrolyte
(tetra-n-butylammonium perchlorate) was found to be insoluble. When
samples were removed by syringe for GLC analysis, care was taken not
to remove small particles of the insoluble supporting electrolyte.

When samples of the mixture from the reduction were injected into
the gas chromatograph, four peaks of similar size were found in addi-
tion to those of the solvent. At 175° and a gas flow rate of 75 ml./
min., the retention times of these peaks were: 3.5, 6.0, 6.7, and 14.0
minutes, respectively. The chromatograph was run for another 30 minutes
to ensure that no other peaks were present. Standard solutions of
known suspected compounds were injected and their retention times com-
pared with the peaks in the mixture from the reduction. If the reten-
tion times of the comparison compounds were very different from those
of the mixture, the compounds were disregarded as being possible pro-
ducts. If the retention times of standards appeared to be the same as
or similar to those of the mixture, a small quantity of standard was
mixed with a similar amount of the solution from the reduction. This
mixed solution was injected, and if the standard enhanced the suspected
common peak, the same procedure was repeated four or five times at dif-
ferent, widely-separated temperatures. If peak enhancement occurred
at every temperature tried, this was taken as confirmatory evidence for
the identity of the compounds.

On the basis of this procedure, the first peak was found to be
diethyl hydrogenphosphonate, the second peak was unreacted diethyl

benzoylphosphonate, the third peak was diethyl α-hydroxybenzylphosphon-ate, and the last peak was benzoic acid (which had been purposely add-ed).

When a metal salt or benzil was electrolyzed, the procedure was essentially the same as that used for a dialkyl aroylphosphonate, with the following exceptions: no benzoic acid was added; the solutions were not saved after electrolysis; no GLC analysis was performed.
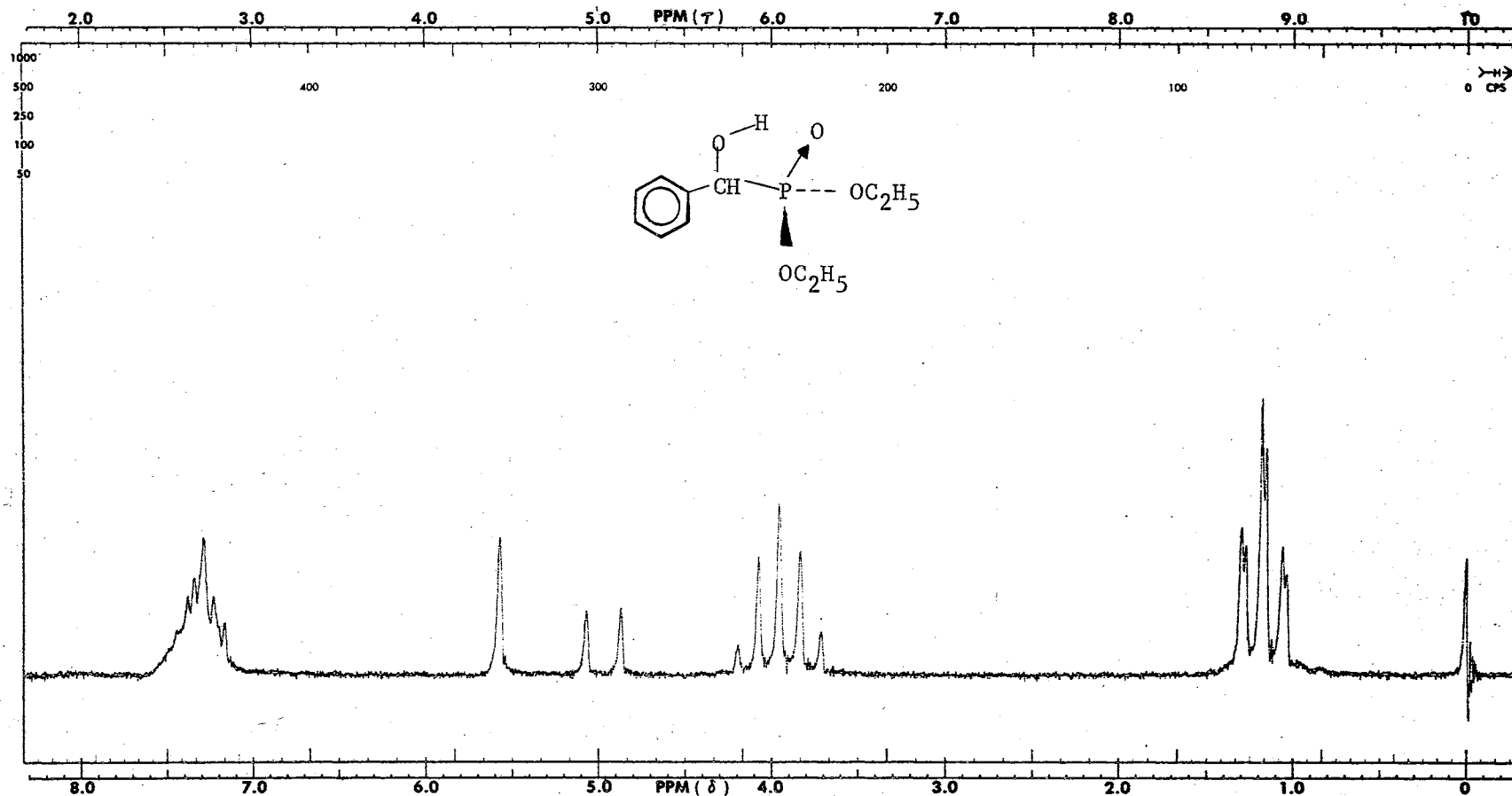
These runs were made for the sole purpose of obtaining coulometric data to check the performance of the apparatus and experimental proce-dure.

Plate 1
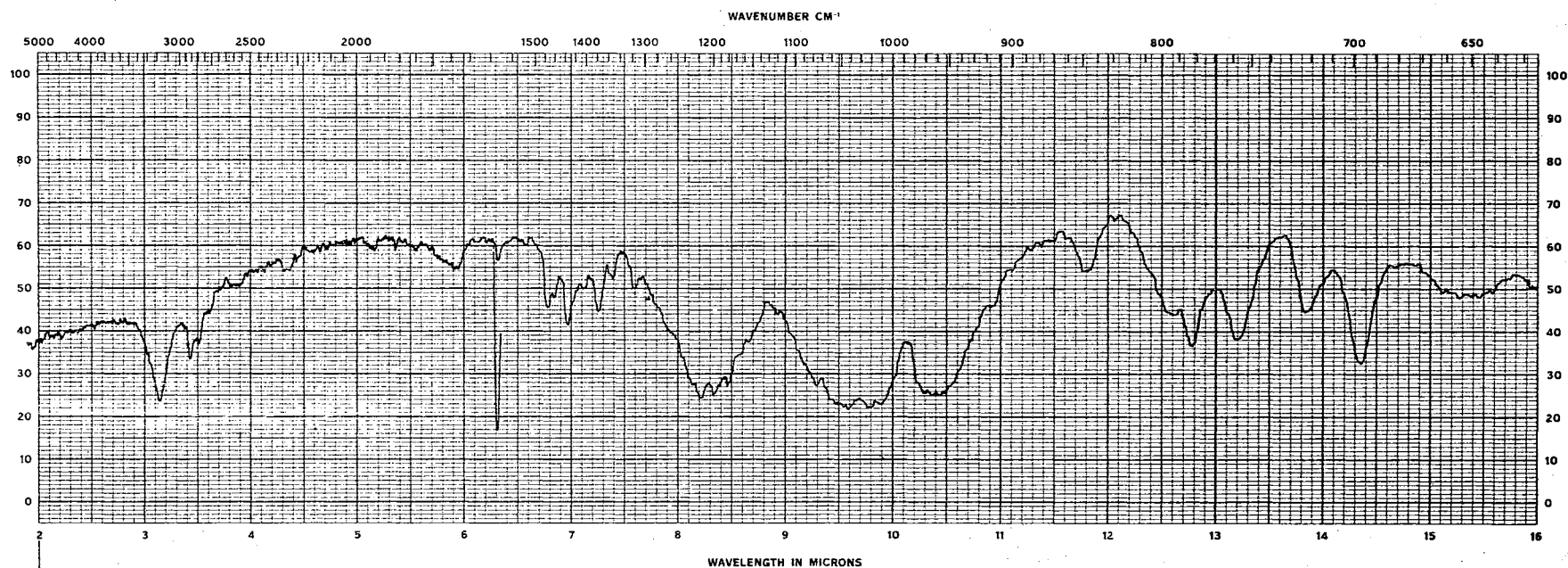
Diethyl α-Hydroxybenzylphosphonate (IIa), KBr Pellet

Plate 2

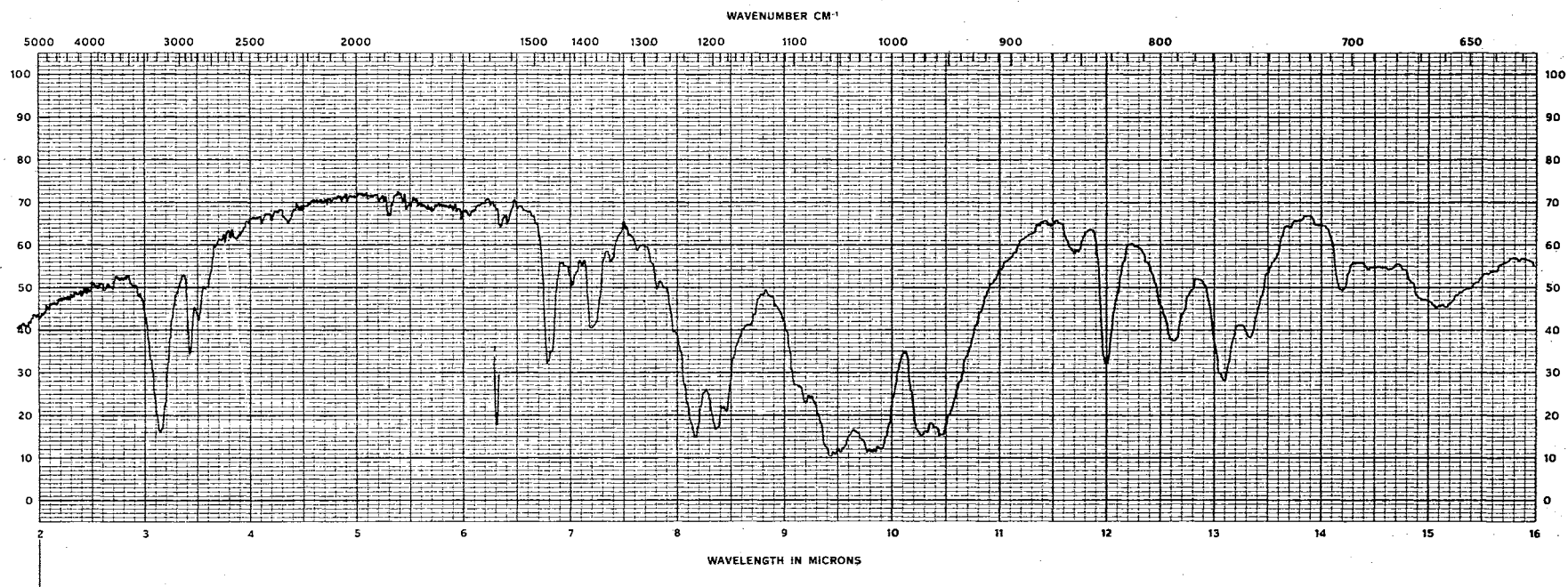Diethyl α-Hydroxybenzylphosphonate (IIa)

Solvent . . . . . CDCl₃   F.B. . . . . 4 cps   S.W. . . . . 500 cps   S.A. 4.0

R.F. Field. . . 0.05 mG   S.T. . . . . 250 sec.   S.O. . . . . 004 cps   I.A. 50

Plate 3

WAVENUMBER CM⁻¹

WAVELENGTH IN MICRONS

Diethyl 4-Chloro-α-Hydroxybenzylphosphonate (IIb), KBr Pellet

Plate 4
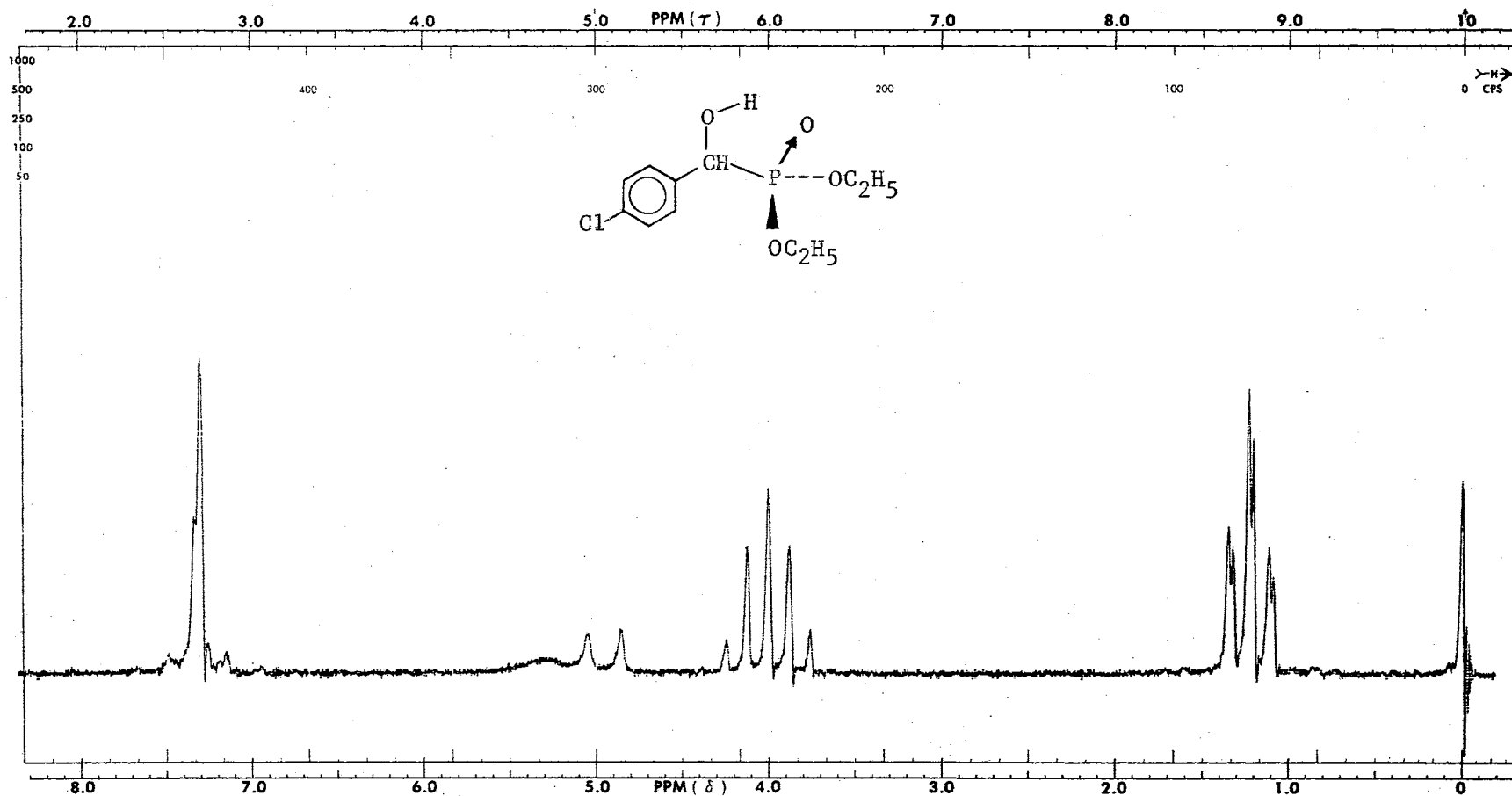
Diethyl-4-Chloro-α hydroxybenzylphosphonate (IIb)

Solvent . . . . .CDCl₃   F.B. . . . . 4 cps   S.W. . . . . 500 cps   S.A. 5.0

R.F. Field. . .0.05 mG   S.T. . . . . 250 sec.   S.O. . . . . 23 cps   I.A. 5.0
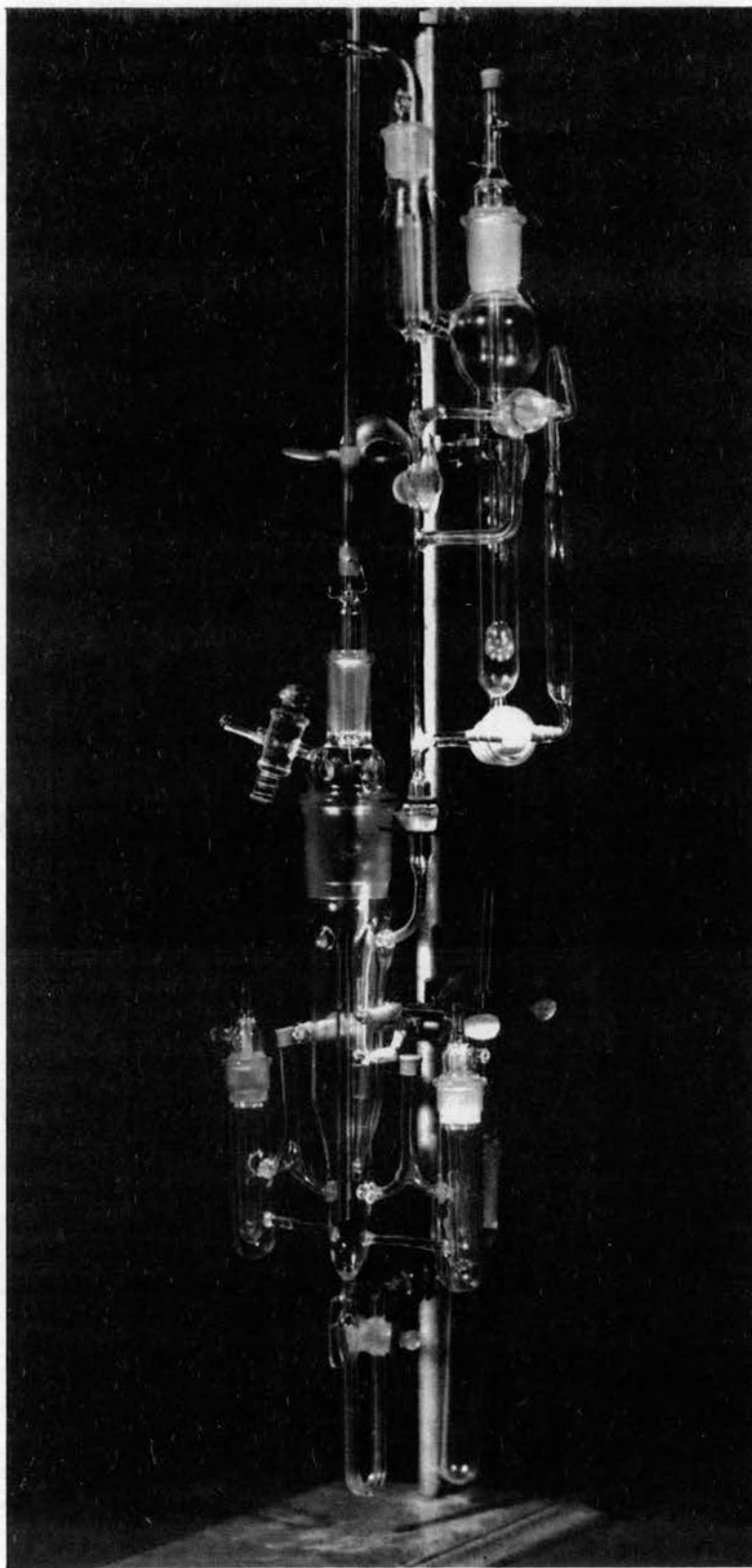
Plate 5. Assembled Polarographic Cell .

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VITA

David Stephen Rulison

Candidate for the Degree of

Doctor of Philosophy

Thesis: A STUDY OF THE REDUCTION OF VARIOUS DIALKYL AROYLPHOSPHONATES
AT THE DROPPING MERCURY ELECTRODE

Major Field: Chemistry

Biographical:

Personal Data: The author was born in New Bedford, Massachusetts,
July 7, 1941, the son of Philip F. and Edith E. Rulison, On
August 3, 1963, he married Judith Louise Mellor.

Education: The author attended public schools in New Bedford,
Massachusetts. He graduated from New Bedford High School in
1959. He received a Bachelor of Science degree in Chemistry
in June, 1963 from what is now the Southeastern Massachusetts
Technological Institute, North Dartmouth, Massachusetts. He
was admitted to the Graduate College of Oklahoma State Univer-
sity, Stillwater, Oklahoma, in September, 1963 and completed
the requirements for the Doctor of Philosophy degree in May,
1968.

Membership in Professional Societies: The author is a member of
the American Chemical Society and Phi Lambda Upsilon, Honor-
ary Chemical Society.