

6-1966

The Kolbe electrolysis of benzoic acid

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THE KOLBE ELECTROLYSIS OF BENZIO^{oic}~~ic~~ ACID

by

David Perry Beiter UC 1966
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Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

MAY 1965

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This Thesis

Submitted by

David P Butler

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

William B Martin, Jr.

Acknowledgement

I should like to take this opportunity to thank Professor William B. Martin, Jr., and Mr. Beverly Adams, for their valuable aid in this project.

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Historical Part

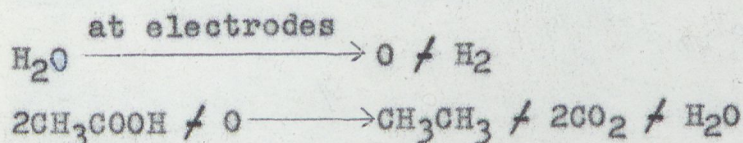
The Kolbe electrolysis is a reaction, taking place on the anode, of an electrolyzed organic salt, RCOOM , yielding, among other things, the organic product RR . The reaction type was studied in the case where R was the phenyl group. The benzoate salt should yield diphenyl, according to the above scheme.

In 1847, Kolbe carried out the first successful electrolysis of an organic salt, potassium acetate. He was attempting to prepare the methyl radical, but instead found ethane, carbon dioxide, hydrogen, ethene, and methyl acetate. Since that time, much work has been done, both on the mechanism and the synthetic usefulness of the Kolbe electrolysis.

Several explanations have been offered for the mechanism of the Kolbe electrolysis, and the mechanism is still open to debate. The discharged ion theory, in one form or another, appears to be the most plausible, but other theories also have backing.

Brockman (1) gave several of the theories proposed up until the time of his book, 1926.

Kolbe* believed that the current decomposed the solvent, water, into nascent oxygen at the anode, which attacked the acid.

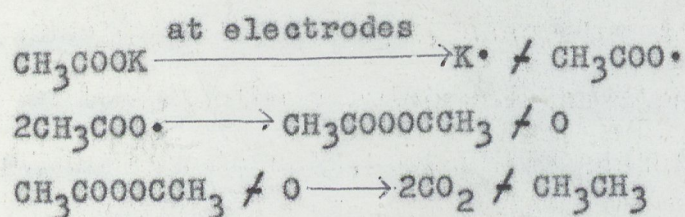


This seems doubtful, since the electrolysis of a solution of the free acid yields only traces of ethane, the major pro-

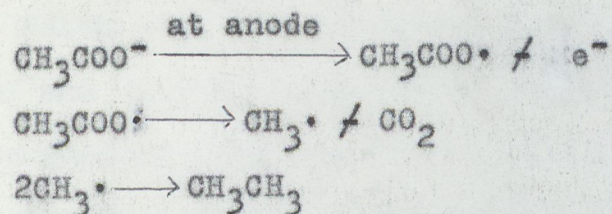
*see Brockman, ref. 1.

ducts being oxygen, carbon dioxide, and carbon monoxide.

Bourgoin* thought that the salt was electrolyzed, giving the metal, and an acid residue. Two of these split out oxygen and formed the anhydride. This anhydride subsequently reacted with the oxygen to give carbon dioxide and ethane.

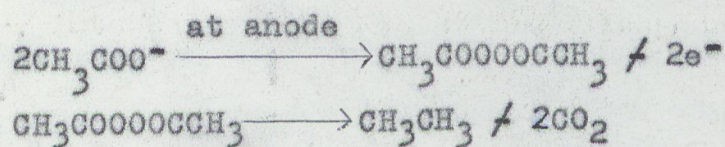


Brown and Walker proposed that the carbonyl anions discharged, and then lost carbon dioxide, and finally two joined to form ethane.



This is the mechanism popularly held today, with some modifications.

Schall*** proposed the formation of a peroxide as an intermediate. This unstable peroxide broke down to form carbon dioxide and ethane.



*see Brockman, ref. 3.

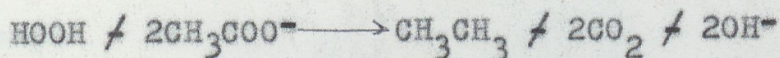
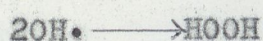
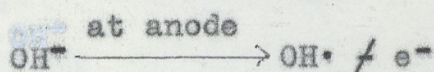
**see Brockman, ref. 4.

***see Brockman, ref. 5.

This was supported by Fichter*, especially by the decomposition of benzyl peroxide. This peroxide decomposed in a solvent mixture of diethylamine and pyridine, and gave results quite similar to that of the electrolysis of the benzoate salt in the same solvent(7).

Since 1926, when Brockman's book was written, other theories have been put forth.

Glasstone and Hickling(11) proposed that hydrogen peroxide was formed, which reacted with acetate ions to give ethane.



Smith and Gilde(2) supported the discharged ion theory of Brown and Walker. They have concluded that the discharged ion decarboxylates and reacts while still attached to the anode.

The free radical polymerization of vinyl acetate was accomplished using radicals formed by electrolyzing potassium acetate(23), lending support to the radical theory. Labeled acetic acid, $\text{C}^{14}\text{H}_3\text{COOH}$, yielded labeled polyvinyl acetate, indicating that the methyl radical initiated the polymerization.

Ebersson(3) concluded that the success of a particular acid is predicted by the ionization potentials. Should the ionization potential, by the electron impact method, be less than 8eV, the radical will be further oxidized to the carbonium ion, in which case the coupled product will not form.

*see Brockman, ref. 10, 11.

Some of the ionization potentials of the radicals are given below. Unfortunately, the phenyl radical was not given by Ebersson.

Radical	Ionization Potential	Formation of Coupled Product in Aqueous Solution
Methyl $\text{CH}_3\cdot$	9.95eV	Yes
Ethyl $\text{CH}_3\text{CH}_2\cdot$	8.78eV	Yes
Propyl $\text{CH}_3(\text{CH}_2)_2\cdot$	8.33eV	No
Isopropyl $(\text{CH}_3)_2\text{CH}\cdot$	7.90eV	No
Butyl $\text{CH}_3(\text{CH}_2)_3\cdot$	8.64eV	Yes
Isobutyl $(\text{CH}_3)_2\text{CHCH}_2\cdot$	8.35eV	Yes
Tertbutyl $(\text{CH}_3)_3\text{C}\cdot$	7.42eV	No
Benzyl $\text{C}_6\text{H}_5\text{CH}_2\cdot$	7.76eV	No
Benzhydryl $(\text{C}_6\text{H}_5)_2\text{CH}\cdot$	7.32eV	No
Cyclohexyl $\text{C}_6\text{H}_{11}\cdot$	7.60eV	No
Cyclopentyl $\text{C}_5\text{H}_9\cdot$	7.80eV	No

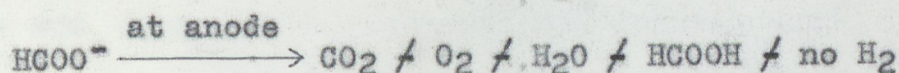
The discharged ion mechanism, with the subsequent decarboxylation and formation of the free radical, has the greatest support. However, the peroxide mechanism maintains a considerable following.

Many different kinds of acids have been electrolyzed by the Kolbe electrolysis, to yield information on both the theoretical and synthetic aspects of this reaction.

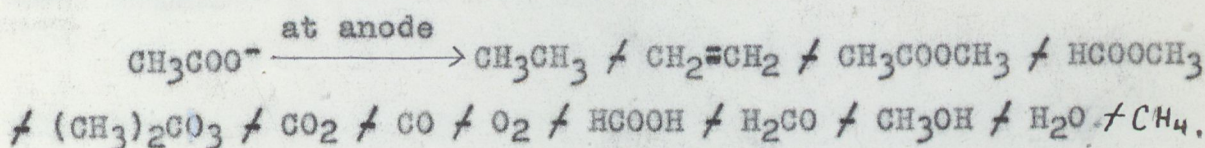
Brockman(2) has a very good collection of the work done

with various acids prior to 1925. These reactions are presented below, and are supplemented with information gained since 1925.

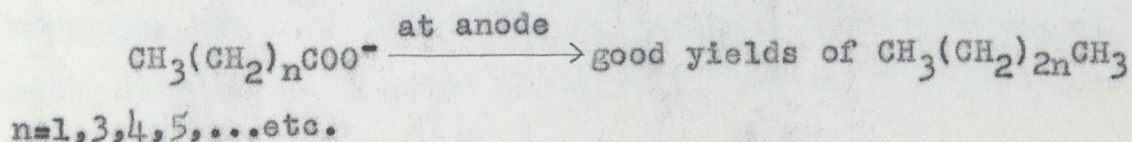
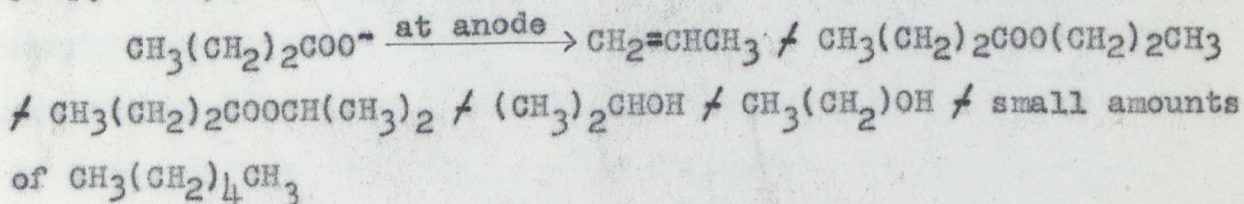
Formic acid did not yield the hydrogen expected if it were to react as a normal acid. Carbon dioxide and oxygen were evolved at the anode, but no hydrogen.



Acetic acid is the most commonly used acid in studies of the Kolbe electrolysis. The reaction can conveniently be studied by an analysis of the gases evolved. Among the products from the acetate were: ethane, methane, ethene, methyl acetate, methyl formate, methyl carbonate, carbon dioxide, carbon monoxide, oxygen, formic acid, formaldehyde, water, and methanol.



The higher straight chain acids yielded the expected coupled products, with the exception of butyric acid. Here only small amounts of hexane were formed, along with propene, propyl butyrate, isopropyl butyrate, propanol, and isopropanol.



An alkene was formed with one carbon less than the acid ion

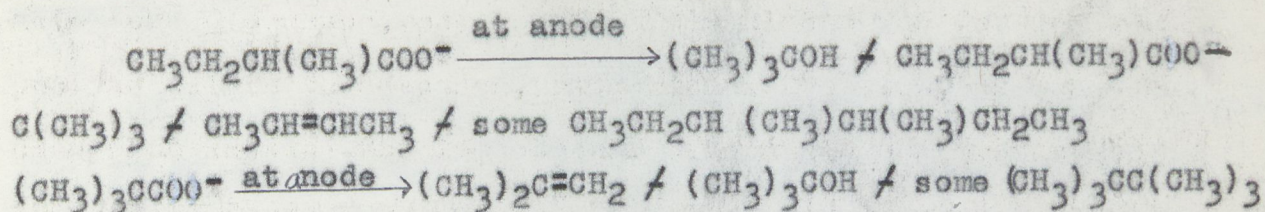
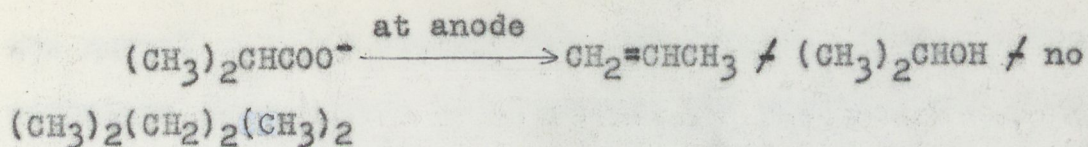
of the longer chain acids, which was not possible with formic and acetic acids. Thus propionic acid formed ethene, butyric acid formed propene, and so on. This alkene was formed from one radical in these cases, rather than from two, as was the case with acetate forming ethene. The analogous product to the ethene formed from acetate, in the longer acids is an alkene with two carbons less than twice the anion. That is, butene and hexene from propionic and butyric acids, respectively.

As the acids increased in length, the solubility of the salt in water became low, and much foaming occurred from the resulting soap solution. To alleviate these problems, an alcohol, usually methanol, was added.

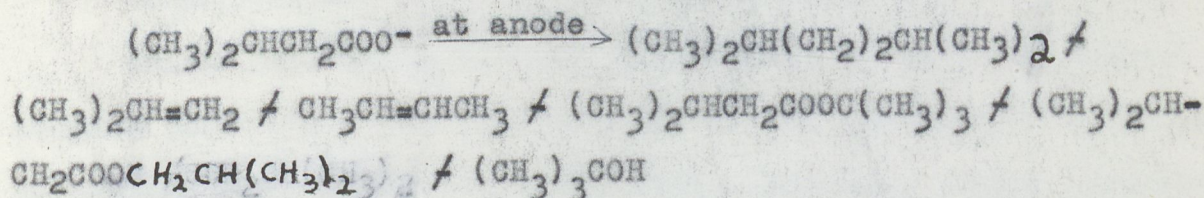
A recent trend has been to run all electrolyses in solutions partly of methanol, whether or not it is needed for the above reasons. Mixtures of Methanol and water, and methanol and pyridine are quite common.

The use of branched chain acids gave varying results. If the alpha carbon had the branch, little of the expected hydrocarbon was found. But if the branching occurred further down the chain, it had less effect, and the normal product was recovered in good yields.

Thus isobutyric acid yielded a little diisopropyl, but mostly propene and isopropyl alcohol. Trimethyl-acetic acid yielded isobutylene, trimethylcarbinol, and only a small amount of hexamethylethane. Alpha-methylbutyric acid yields trimethylcarbinol, the ester of trimethylcarbinol and alpha-methylbutyric acid, 2-butene, and some 3,4-dimethylhexane, the coupled product.

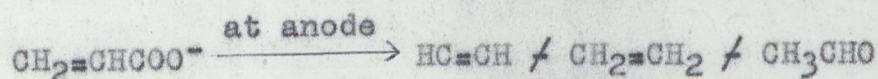


But isovaleric acid yielded a good proportion of diisobutyl, with isobutyl isovalerate, trimethylcarbinol isovalerate, trimethylcarbinol, isobutene, and 2-butene as side products.



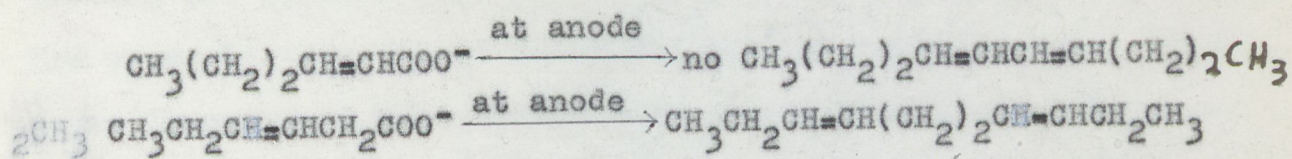
The salts of cyclic aliphatic acids failed to give a normal coupled product. Those cases mentioned by Brockman contained potassium carbonate, which tends to cause the alcohol by the Hoffer-Moest reaction. However, other attempts to couple the cyclo acids have ended in failure.

The electrolysis of the salts of unsaturated acids depended on the distance between the double bond and the carboxyl. When the double bond was adjacent to the carboxyl, little or none of the coupled hydrocarbon was formed. When potassium acrylate was electrolyzed, acetylene, ethene, and acetaldehyde were the organic products formed. No butadiene was found.

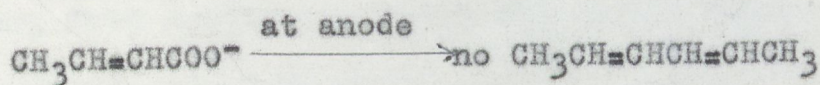


Fichter and Holbro(5) investigated the action of potassium hexeneoate isomers, varying the position of the double bond. With one methylene separating the double bond and the carboxyl,

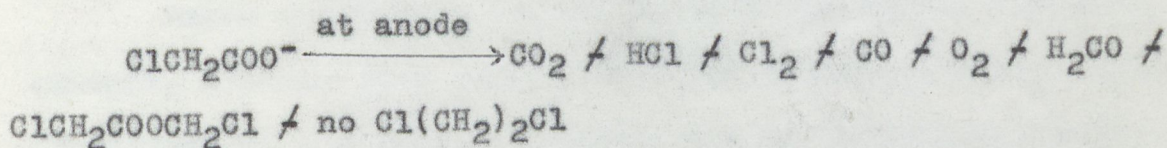
the normal coupled product was not formed. However, when two methylene groups were interspaced, the electrolysis proceeded normally.



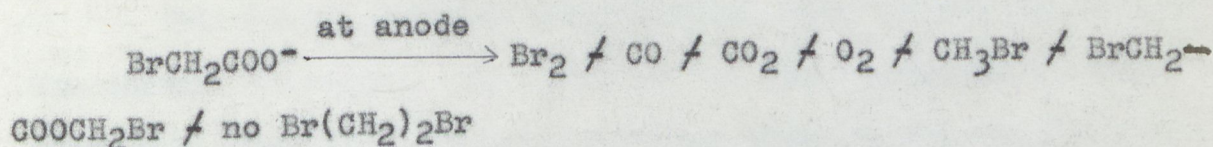
Fichter(6) also tried the electrolysis of potassium crotonate, and found none of the expected hexadiene.



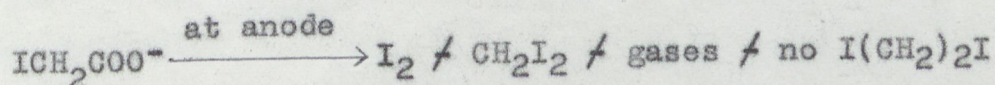
Acids containing halogen also failed to give the normal coupled products. The electrolysis of the chloroacetate yielded carbon dioxide, hydrochloric acid, chlorine, carbon monoxide, oxygen, formaldehyde, and chloromethyl chloroacetate, but no ethylene dichloride.



Bromoacetate yielded bromine, carbon monoxide, carbon dioxide, oxygen, methyl bromide, and bromomethyl bromoacetate, but no ethylene dibromide.

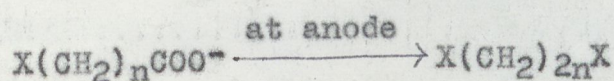


Iodoacetate yielded iodine and methylene diiodide as the only non-gaseous products.



Dichloroacetate, trichloroacetate, alpha dichloropropionate, and 2,2, 3-trichlorobutyrate also failed to yield the coupled products.

Pattison, Stothers, and Woodford(21) performed a series of experiments on the salts of omega-monochlorocarboxylic acids. Writing the general formula in the form $X(CH_2)_nCOOH$, normal coupled products were formed under the following conditions. When X was fluorine, n was greater than three; when X was chlorine, n was two, or greater than three; when X was bromine, n was greater than nine. With iodine, no success could be had, but rather, free iodine was split out in all cases.



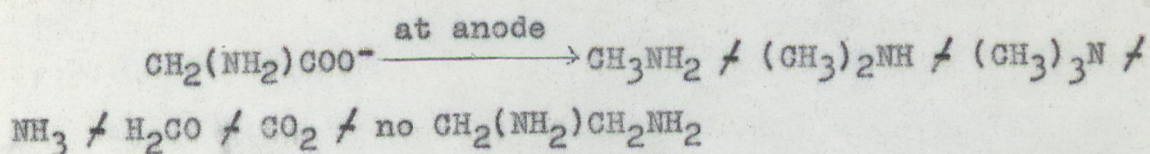
$X=F$ n greater than 3

$X=Cl$ $n=2$, or greater than 3

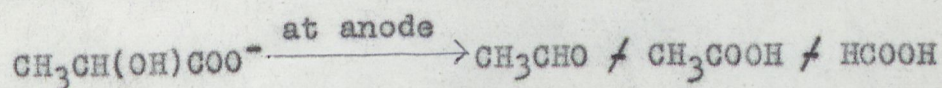
$X=Br$ n greater than 9

$X=I$ no successful coupling

Amino acids also failed to give the normal products. For example, glycine gave mono-, di-, and trimethylamine, ammonia, formaldehyde, and carbon dioxide, but no 1,2-diaminoethane.

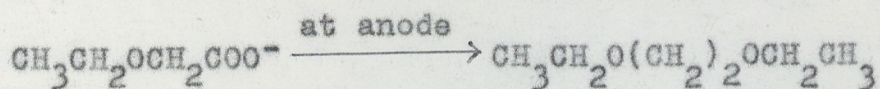


The salts of alpha hydroxyacids also failed to undergo the normal reaction. The products of the electrolysis were aldehydes and acids of fewer carbons than of the original acid, carbon dioxide, carbon monoxide, and water. Thus lactic acid yielded acetaldehyde, acetic acid, and formic acid as the organic products.

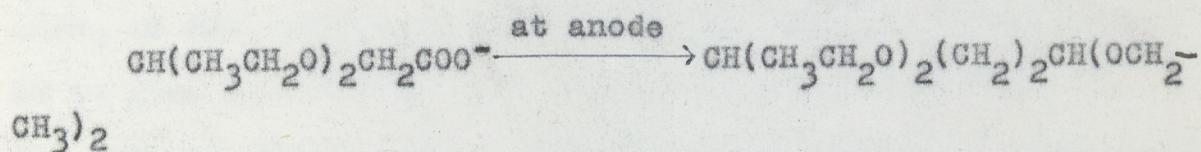


However, this failure did not extend to the alkoxyacids.

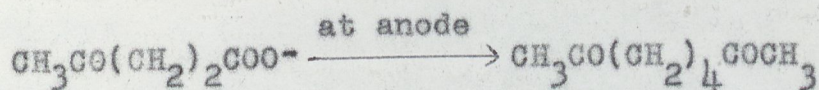
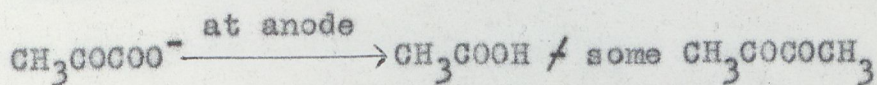
The electrolysis of potassium ethoxyacetate gave 1,2-diethoxyethane.



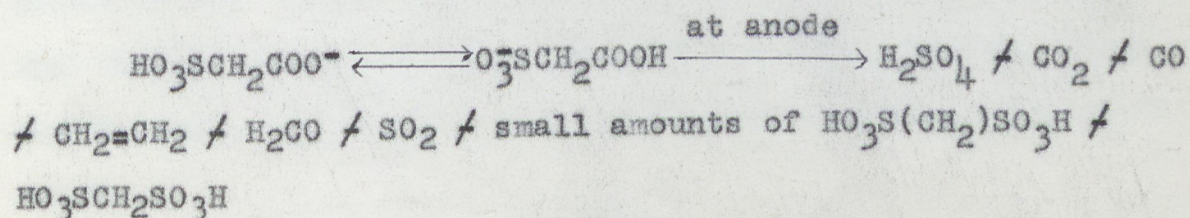
Dialkoxy acids also underwent the normal coupling. Electrolysis of potassium 3,3-diethoxypropionic acid gave a good yield of 1,1,4,4-tetraethoxybutane. The homologous hexane compound can be had from the homologous butyric acid.



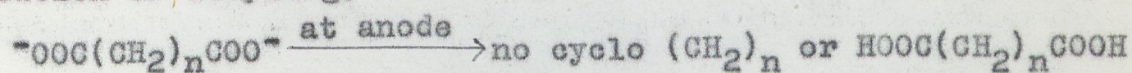
Ketoacids reacted properly, but gave small yields when the oxygen was on the alpha carbon. Thus potassium pyruvate gave a small yield of 2,3-butanedione, but was mostly converted into acetic acid. Potassium 4-oxopentanoic acid gave good yields of the coupled product, 2,7-octadione.



Sulfonic acids of the type with both sulfonic and carboxy groups, failed to give the normal products. Potassium sulfoacetate should have yielded ethane disulfonic acid. However, only small quantities of this could be found, and most of the acid was completely oxidized to sulfuric acid, carbon dioxide, and water. Sulfopropionic acid yielded ethene, sulfuric acid, carbon dioxide, and water, but no 1,4-butanedisulfonic acid.

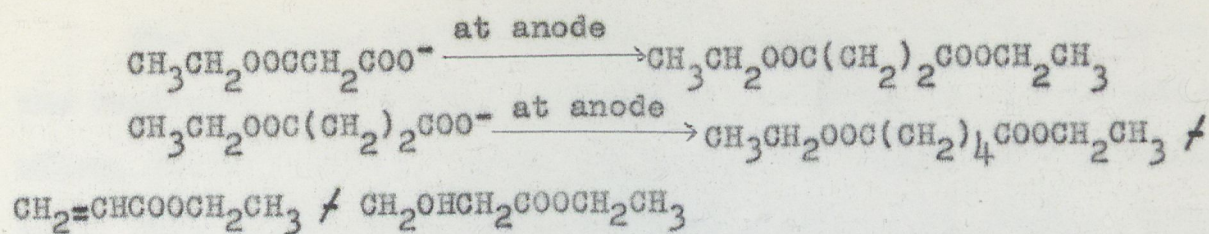


Dicarboxylic acids failed to yield either a longer chain dicarboxylic acid or a cyclic hydrocarbon. Potassium glutarate yielded only propene, carbon dioxide and oxygen. No cyclopropane or octanedioic acid was formed. Potassium 3,3-dimethyl glutarate gave as the hydrocarbon 2-methyl-1-butene, but no dimethyl cyclopropane or 3,3,6,6-tetramethyloctanedioic acid. Potassium adipate gave butenes as products, but neither cyclobutane nor decanedioic acid. Potassium octanedioic acid failed also, as did heptanedioic acid. These last two would be expected to give cyclohexane and cyclopentane, respectively, due to the ease of ring closure. However, only alcohols, acids, both saturated and unsaturated, aldehydes, aldoacids, ketoacids, and a lactone were produced. No indication was found for either cyclization or coupling.



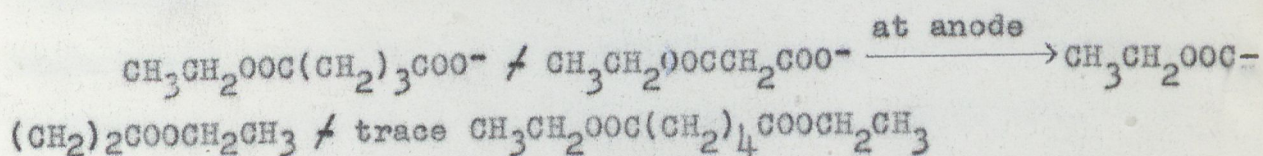
However, if the half salt half ester of a dicarboxylic acid was used, the expected diester was produced. While this did not work for oxalic acid, the higher acids worked very well. Potassium ethyl malonate yielded diethylsuccinate; potassium ethyl succinate yielded diethyladipate. The yields were increased considerable when a diaphragm was used to prevent the esters from hydrolyzing in the potassium hydroxide formed at the cathode.

There was some unsaturated monocarboxylic acid formed, analogous to the formation of the alkene from normal acids. Also, as the degree of substitution on the acid increased, so did the production of the unsaturated ester. Esters of hydroxy acids were also formed, analogous to the alcohols from normal acids.

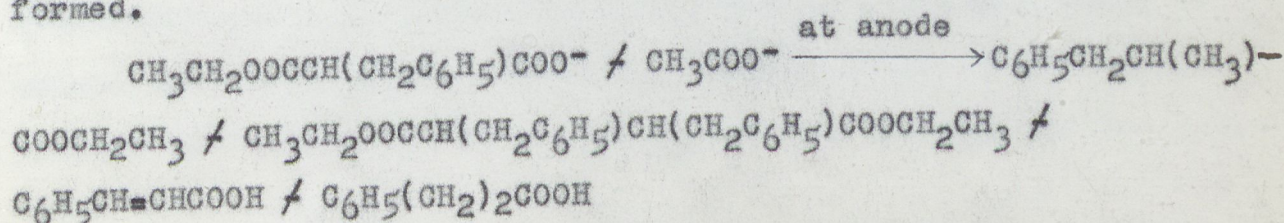


When two different acids were used, a cross coupling occurred. When one was a half salt half ester of one diacid, and the other was from a diacid of one less methylene, the odd numbered diesters were being formed. Other unsymmetric products can be formed in a similar manner. By the use of various substituents and chain lengths, a wide variety of products can be synthesized by the Kolbe electrolysis.

Gilbert(10) in the only other work to be done with the Kolbe electrolysis at Union College reacted the mixed half salts half esters of glutaric and malonic acids. The only product definitely found was diethyl succinate, formed by the union of two malonate radicals. The desired cross coupled product, diethyl adipate, was probably present, but only in small amounts.



Sometimes the presence of one salt seemed to catalyze the coupling of another. Potassium ethyl benzomalonate yielded only oxidation products when electrolyzed. However, when potassium acetate was added, ethyl 2-methyl-3-phenylpropionate acid was formed as might be expected. But in addition, diethyl 2,3-dibenzylsuccinate, cinnamic acid, and 3-phenylpropionic acid were formed.



The presence of the benzene ring caused what is known as the benzenoid inhibition. Potassium benzoate, in aqueous solution, yielded benzoic acid, hydrogen, and oxygen on electrolysis. This effect extended to the cases where the phenyl group was moved down the chain from the carboxyl. Thus phenylacetate and phenylpropionate also yielded none of the coupled product.

$C_6H_5(CH_2)_nCOO^-$ at anode $\rightarrow C_6H_5(CH_2)_nCOOH$ / no other organics $n=0,1,2$, aqueous solution

Other salts containing the phenyl group also failed to give the coupled product, but again regenerated the original acid. Among these were potassium N,N-dimethylaminobenzoate, potassium ethyl phthalate, and potassium 2-nitrobenzoate.

$p-(CH_3)_2NC_6H_4COO^-$, $O-CH_3CH_2OOC C_6H_4COO^-$, or $o-NO_2C_6H_4COO^-$ at anode \rightarrow original acid as only organic product.

However, the copper salts of some of the aromatic acids did yield the coupled product in aqueous solution. Copper 4-aminobenzoate yielded benzidine in good yields. Copper 4-nitrobenzoate also gave good yields of 4,4'-dinitrodiphenyl. Unfortunately, the low solubility of the copper salts makes the technique difficult.

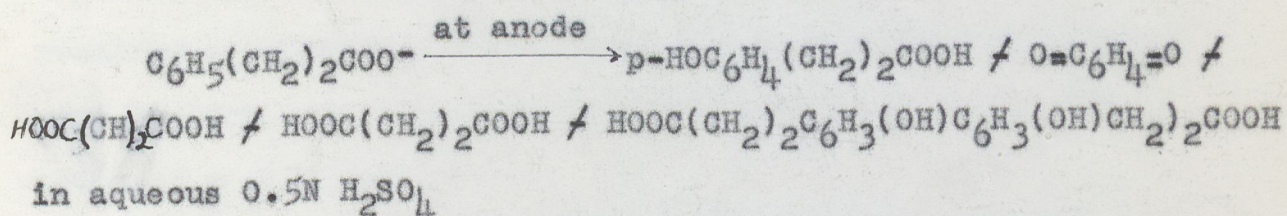
$p-NH_2C_6H_4COO^-$ $\xrightarrow{Cu^{++}}$ at anode $\rightarrow p-NH_2(C_6H_4)_2p'-NH_2$ aqueous solution

$p-NO_2C_6H_4COO^-$ $\xrightarrow{Cu^{++}}$ at anode $\rightarrow p-NO_2(C_6H_4)_2p'-NO_2$

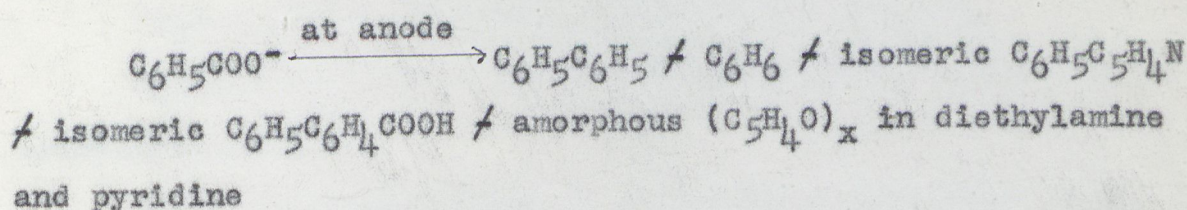
The use of fused salts yielded small amounts of coupled products. A solution of sodium benzoate in molten benzoic acid yielded a small amount of diphenyl upon electrolysis. Potassium 2-nitrobenzoate in molten 2-nitrobenzoic acid yielded small amounts of nitrobenzene. However, the production of the coupled product was halted by the separation of the anolyte and the catholyte by a diaphragm.

It was thought by some that the products were not caused by the electricity passed, but rather were formed by the action of the potassium produced at the cathode, or by the heat.

In 1927, Fichter(8) tried to produce the coupled product from 3-phenylpropionic acid. He electrolyzed potassium 3-phenylpropionate in a solvent of half normal sulfuric acid, and got as organic products, p-hydroxy-3-phenylpropionic acid, quinone, succinic acid, fumaric acid, and a compound of probable structure $(\text{HOOC}(\text{CH}_2)_2\text{C}_6\text{H}_3(\text{OH}))_2$.

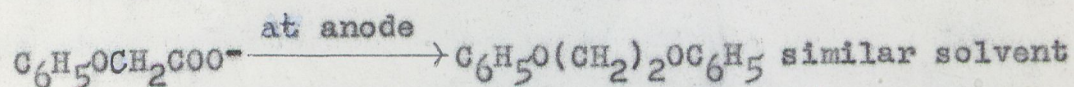
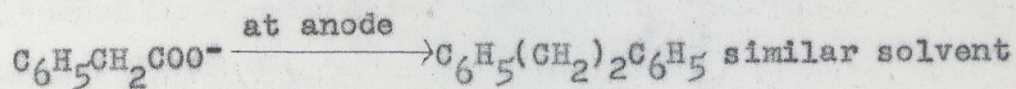
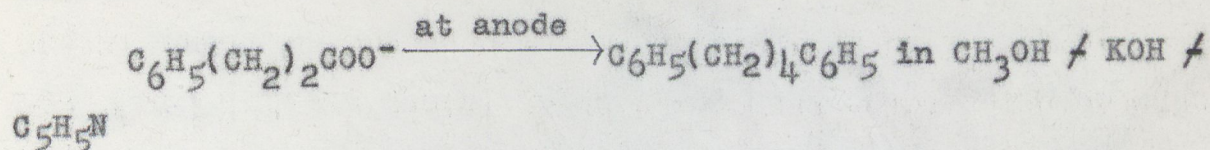


Later, as he changed his solvent to the non-aqueous mixture of diethylamine and pyridine, he successfully electrolyzed aromatic acids(7). Benzoic acid, pyridine, and diethylamine, upon electrolysis gave a poor but definite yield of diphenyl. Other products were benzene, isomeric phenylpyridines, isomeric phenylbenzoic acids, and an unidentified amorphous material of empirical formula about $\text{C}_5\text{H}_4\text{O}$.

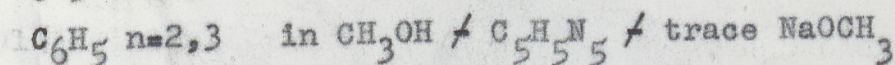
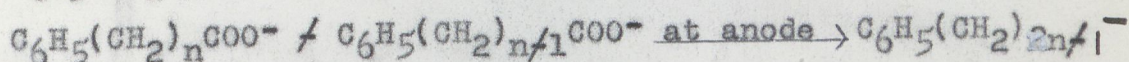
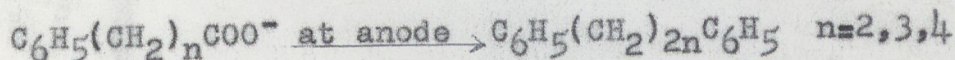


A mixture of 3-phenylpropionic acid, methanol, potassium hydroxide, and pyridine gave a 37% yield of 1,4-diphenylbutane. A 50% yield of dibenzyl was obtained from phenylacetic acid,

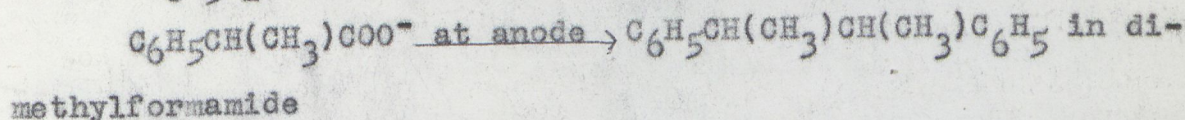
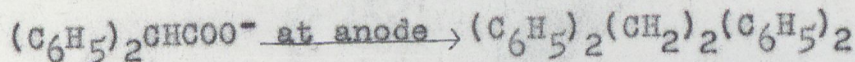
and a 45% yield of diphenoxyethane from phenoxyacetic acid, under similar conditions.



Evans and Whalley(11) produced alpha, omega-diphenylbutane, -hexane, and -octane from the respective acids. The crossed reaction succeeded in producing alpha, omega-diphenylpentane and -heptane. A methanol-pyridine solvent was used, with a trace of sodium methoxide.



Finklestein and Peterson(9) synthesized good yields of the coupled product from diphenylacetic acid and 3-phenyl-2-methylpropionic acid, using dimethylformamide as a solvent. A high potential, 100-200 volts, was used.



Should the production of substituted diphenyls by the Kolbe electrolysis become practical, it will be of considerable importance. Presently, the synthesis of substituted diphenyls is quite difficult, as can be shown by the prices of the compounds. These prices are taken from the current catalog of a commercial

chemical distributor and manufacturer. These are 95-99% pure compounds.

Compound	Price	
4,4'-dimethyldiphenyl	\$6.50 per tenth gram	(18)
3,3'-dimethyldiphenyl	\$28.00 per ten grams	(18)
2,2'-dimethyldiphenyl	\$6.00 per tenth gram	(18)
4,4'-dinitrodiphenyl	\$14.00 per gram	(19)
4,4'-diphenyldiphenyl	\$8.00 per tenth gram	(20)

Needless to say, a better method of preparation would be most welcome.

Experimental Part

The reproduction of the work of Fichter and Stenzl(7) in the electrolysis of benzoic acid was attempted. Should the synthesis of diphenyl have proven successful, it was proposed to attempt the synthesis of various substituted diphenyls, such as 4,4'-dimethyldiphenyl.

An electrolysis cell was prepared as shown in Figure I. The upper half of the cell was a dome-shaped piece of glass, which had an interior ground glass joint at the bottom, which was superfluous. However, the top and the electrodes were removed intact from another apparatus. Leading from the top of the apparatus was a glass tube with a stopcock. Attached to the glass tube was a rubber hose, leading the vapors to the sink.

The bottom half of the cell was a small jelly tumbler, which fitted nicely against the bottom of the upper portion of the cell. The two halves were held together by plastic tape and support from a ringstand and clamps. The electrodes were both of shiny platinum. Each was supported by a piece of platinum wire, sealed through the upper portion of the cell. This also allowed electrical connections to be made to the electrodes. The cathode was a cylindrical platinum gauze, such as used in the quantitative determination of copper by electrolysis. The anode was a strip of platinum foil, approximately one and a half centimeters wide and ten centimeters long. This sheet anode was folded down the side of the cathode, across the bottom, and up the other side. The electrodes were prevented from touching by a piece of glass cloth.

The desired potential was produced by an ordinary lead storage battery. It was regulated by choosing the number of cells to be used, and then adding resistance by means of a rheostat. A voltmeter and an ammeter in the circuit completed the electrical apparatus.

Mallinckrodt reagent grade benzoic acid was used, and not further purified.

Fisher reagent grade pyridine was placed over solid reagent grade potassium hydroxide. This served to remove any water present, and to break up any salts. The pyridine was then distilled, and the central half, boiling at 115° (uncorr.) was taken.

Eastman white label diethylamine was similarly treated. Since this chemical had been in the stockroom for several years, it was quite impure with water and oxidation products. Potassium hydroxide was added until the diethylamine had no effect on it. The still-brown diethylamine was then distilled, and the central portion, boiling at 54.5° (uncorr.) was taken. This boiling point is somewhat lower than the 55.5° given in the handbook(16).

A solution was prepared of 25 grams of benzoic acid dissolved in 30 grams of pyridine and 10 grams of diethylamine. This was a 20% excess of pyridine and 33% excess of diethylamine, over what was used by Fichter. This additional solvent was needed to effect complete solution of the benzoic acid. This solution was placed in the previously described cell and electrolyzed at room temperature, about 20° .

Initially, a potential of 1.95 volts was applied, since high voltages tend to produce more side products. This produced an initial current of 0.013 amps. The current fell to 0.0091 amps after 20 hours, and then remained near 0.0085 amps.

After about 175 hours, it was discovered that most of the current measured had been flowing through the voltmeter, rather than through the cell. This reduced the above 8.5 milliamps to 1.1 milliamps.

In order to produce enough product to analyze, the voltage was increased to 3.11 volts. The meters were now connected only when needed, rather than continuously left in the circuit. A current of 0.0035 amps passed through the cell at this potential.

The solution was electrolyzed for another 250 hours at this potential, and then the electrolysis terminated.

No gases were seen to evolve from the electrodes during the electrolysis, but the colors changed considerably. Initially, the solution was a very pale yellow, which increased in intensity, and slowly changed to a deepening red. The solution continued to darken, and at the termination of the electrolysis was a dark brownish-red. Throughout these changes, the solution remained clear, and no precipitate was formed.

A partial analysis of the reaction mixture was effected by means of the vapor phase chromatograph. While complete analysis was not possible, the most interesting products, diphenyl and benzene were found.

Substances which might harm the instrument were first removed. This was done by extraction with acid and base. While

benzene would evaporate during the processing, this method would remove benzoic acid and the oxidation products of the amines, as well as the amines themselves. A different treatment would be used to preserve the benzene.

An approximately 15 milliliter portion of the electrolyte was placed in a 250 milliliter glass stoppered erlenmeyer flask, and approximately 50 milliliters of purified anhydrous ether was added, and an equal amount of approximately one normal potassium hydroxide. After a thorough shaking, the layers were allowed to separate. A small amount of scum formed on the interface, and was kept in the aqueous portion.

The ethereal portion was removed, and treated with more base, and the aqueous portion with more ether. The freshly added ether and aqueous portions were then combined. Fresh ether was added to the aqueous solution and fresh base to the ether. This was continued, counter-current fashion, until a total of four sets of extractions had been made. More fresh ether was added with the fresh base as needed to keep the volume of ether about 50 milliliters.

The original ether, which now had been thoroughly extracted with base, was then extracted with acid. The other ethereal portions were combined and saved, as were the aqueous portions. Some of the brown color was removed by the base, but much remained with the ether.

The acid extraction proceeded in the same manner as the base extraction. An aqueous solution of approximately one normal hydrochloric acid was used as the extractant. A consider-

able amount of scum formed on the interface, and the last of the color was removed.

A drop of the ether solution was evaporated on a clean watch glass. Only the smallest trace of residue could be noted. Repeated evaporation of drops on a cover slip failed to yield enough for a melting point determination.

Traces of water were removed from the ether with solid potassium hydroxide, and the ethereal extract run on a Perkin Elmer Model 154 vapor phase chromatograph. An "R" column was used at 240°, 10 pounds pressure, and 8 volts at the detector.

Only ether was detected, the peaks from other substances being negligible bumps. It was later found that the high temperature had caused a leak, and the vapors were not reaching the detector.

The sample was then run at a lower temperature, 135°. Again, nothing of consequence, other than the ether, could be found. Finally a solution was made of diphenyl in ethanol, and this run. No peak was found for the diphenyl, after 50 minutes of waiting. The search for diphenyl was suspended.

The portion in which benzene was to be found was treated in a different manner. An approximately 15 milliliter sample was placed in a flask, equipped with a thermometer and a water condenser, and slowly distilled. The distillate up to 130° was collected. This clear distillate was then analyzed for benzene. The residue, a thick dark brown liquid, froze upon cooling.

This distillate was run on the Perkin Elmer Model 154 vapor

phase chromatograph with an "R" column at 122°, 10 pounds pressure, and 8 volts at the detector. Samples of 5 microliters were used, both for the mixtures and the pure samples. Measurements for spiking were made with the microsyringe.

The chromatogram of the electrolyte mixture and reaction products boiling below 130°, is reproduced in Figure II. Peaks are present for pyridine, P; benzene, B; Air; and water or diethylamine, W. An area of several peaks is present, U, from unknown substances. Also, an unknown high boiler, H, appeared after pyridine.

The peak locations for benzene, pyridine, water, and diethylamine were determined by running a pure sample of the substance and then a sample of the mixture spiked with a small amount of the substance in question.

A spiked sample of the Kolbe mixture boiling below 130°, containing 2.44% additional benzene was run under the same conditions as the unspiked sample, and the resulting chromatogram is reproduced in Figure III. This spiked sample allowed a quantitative determination of the benzene produced in the electrolysis.

A formula can be derived (see Appendix I) giving the percentage substance in a sample, X, when a known percentage of spike is added, P.

$$X = NP / (S - N)$$

The area under the peak from the original sample, N, and under the spiked sample, S, are used from the chromatogram.

In this case, 2.44% of benzene was added in the spike. The areas under the peaks were found by considering them to be triangles.

Thus, $X = (15.6 \times 2.44) / (465 - 15.6) = 0.09$ volume %

Since only about half of the 65 grams of the crude reaction mixture boiled below 130° , $65 \times 0.5 \times 0.0009$, or 0.03 grams of benzene were produced. The error in conversion from volume to weight percent is negligible, in context with the other errors of estimation.

The percentage yield, based upon the electrons used, can be calculated (see Appendix III), since the current and time are known.

Thus only 1% of the current was used in the production of benzene.

The diethylamine peak was much smaller than expected, being nearly absent, although it composed a quarter of the solvent.

Since the diphenyl could not be detected with the instrument available, it was decided to send out a sample for the detection of diphenyl. Mr. Beverly Adams of Schenectady Chemicals Inc., ran a vapor phase chromatograph of the sample.

An F&M Model 720 thermal conductivity detector instrument was used, with a two foot column of 20% Se 30 Silicone gum rubber on Chromosorb W. The helium flow was 60cc per minute. The detector temperature was 240° , and that of the injection port 280° . The bridge current was 150 milliamps. Samples of 50 microliters were used.

The temperature conditions were as follows. First, the temperature was kept at room temperature for three minutes. Then it was kept at 60° for a minute. The instrument was then programmed to rise at a rate of 10° per minute until 250° ,

and then hold steady at 250° until the end of the chromatogram.

First, the crude reaction mixture was run. Its chromatogram is reproduced in Figure IV. A multitude of peaks were found. Mr. Adams tentatively identified two of these as diphenyl, D, and benzoic acid, C.

Some of the higher boiling products that might be expected are as follows.

Product	Boiling Point
2-phenylpyridine	270° (17)
3-phenylpyridine	270.4° (17)
4-phenylpyridine	275° (17)
2-phenylbenzoic acid	343-4 (13)
4-phenylbenzoic acid	sublimes (13)
Benzoic acid	249° (12)
Diphenyl	254-5° (14)
4,4'-dipyridyl	304.8° (15)

These, most likely the phenylbenzoic acids, could account for the peaks after the benzoic acid, since they were removed by extraction with base. However, none of these substances can be proposed for those peaks between the pyridine and the diphenyl.

The reaction mixture, extracted with base, but not with acid was also run, and the chromatogram is reproduced in Figure V. A peak, D, was tentatively identified as diphenyl by Mr. Adams. Other peaks were most likely due to ether, E, and pyridine, P.

Also present were unknown peaks, V, before diphenyl.

In order to test the peak supposed to be diphenyl, a spiked sample was prepared. This sample, whose chromatogram is reproduced in Figure VI, was not run under identical conditions. Due to an interruption, the programmed temperature rise was delayed for a few minutes.

Therefore, the distances between the unknown peaks, V , were used as a measuring standard. On the normal sample, the distance between the V_2 and V_5 peaks of this group was 2.3, and the distance between the V_2 and the proposed diphenyl 5.7". The distance between the V_2 and V_5 peaks of the spiked sample was 1.3", and between the V_2 and the diphenyl was 3.1. A proportion was set up, and the diphenyl predicted at $2.3 \times 3.1 / 1.3$ ", or 5.5" from the V_2 peak of the normal sample. Thus, the peak in the sample was in all probability, diphenyl.

A quantitative estimate of amount cannot be made, as for the benzene, since all of the necessary information is not present. However, it can be said that the diphenyl was produced, but in a very small amount.

The unknown peaks used in the above calculations were from neutral or basic substances, since the mixture was extracted with base. However, the phenylpyridines would not be expected to come off before the diphenyl, since their boiling points are considerably higher. Thus, no set of substances can be proposed to fit these peaks.

Conclusion

The benzenoid inhibition has been overcome to the extent that some diphenyl was produced from benzoic acid. While the yield obtained by Fichter and Stenzl was not mentioned, other than being low, the present yield was very low. As a synthetic method, it is still a failure.

Various improvements for the more efficient production and analysis of diphenyl present themselves.

First, the rate of synthesis was very slow. A period of three days was needed to produce a theoretical gram of product. The current should be increased to the point where the synthesis takes place at a more rapid rate.

This could be accomplished by an increase in the conductivity of the electrolyte. A supporting electrolyte, such as tetrabutylammonium sulfate would accomplish this. Potassium diethylamide might be used, as could sodamide. However, aminopyridine might be formed by the Tschitchibabin reaction.

Stirring, in order to prevent the diffusion from limiting the ion flow, could be easily accomplished by using both platinum gauze electrodes from the copper electrodeposition apparatus. In fact, the entire apparatus might be used. While the necessity of the stirring is not great at the low currents used, at higher currents it would be quite important.

The voltage could also be increased. While this leads to the greater production of side products, it would also increase the rate for the production of the desired coupled product. Voltages as high as 200 volts have been used for the

Kolbe electrolysis.

The analyses of Mr. Adams at Schenectady Chemicals, Inc. were most helpful. It was not possible to accomplish an extensive analysis because of mechanical problems and temperature limitations of the Union College vapor phase chromatograph. A V. P. C. capable of working at temperatures in the order of 300° would be most helpful. Other products, such as the phenylpyridines and the phenylbenzoic acids could thus be detected. The finding of samples of the substances could pose a problem, however.

Should higher yields be obtained, conventional methods of analysis could also be used, such as derivatives. Spectrophotometry, both infrared and ultraviolet, could also be used.

The solvent diethylamine, boiling point 55.5° , could not be found in the fraction of products boiling below 130° . This can be explained by evaporation during the electrolysis, and reaction with benzoic acid, forming an amide.

However, when a sample of the low boiling fraction was spiked with diethylamine, no peak appeared for it. The amine was not being held on the column, as a pure sample came through nicely.

No explanation is without objections. Apparently it is reacting with something in the sample. This could be an acid, except that none would be expected that would boil below 130° . Reaction with an ester is eliminated for the same reason. The only substance present in sufficient quantities to react in a 1:1 ratio is the pyridine. However, no reaction can be postulated between diethylamine and pyridine under the conditions present.

Evaporation from the sample is a possibility, but the nearly as volatile benzene remained in the sample. The fate of the diethylamine remains a mystery.

Summary

The synthesis of diphenyl from benzoic acid was accomplished by the Kolbe electrolysis. The complete inhibition, as found in aqueous solvents, was thus overcome by using the non-aqueous mixture of pyridine and diethylamine. However, the yield was not sufficient to warrant consideration of the Kolbe electrolysis as a synthetic method, until improvements are made.

Suggestions were offered for the possible increase in the yield of diphenyl. Should reasonably high yields be achieved, the method could be applied to the synthesis of substituted diphenyls.

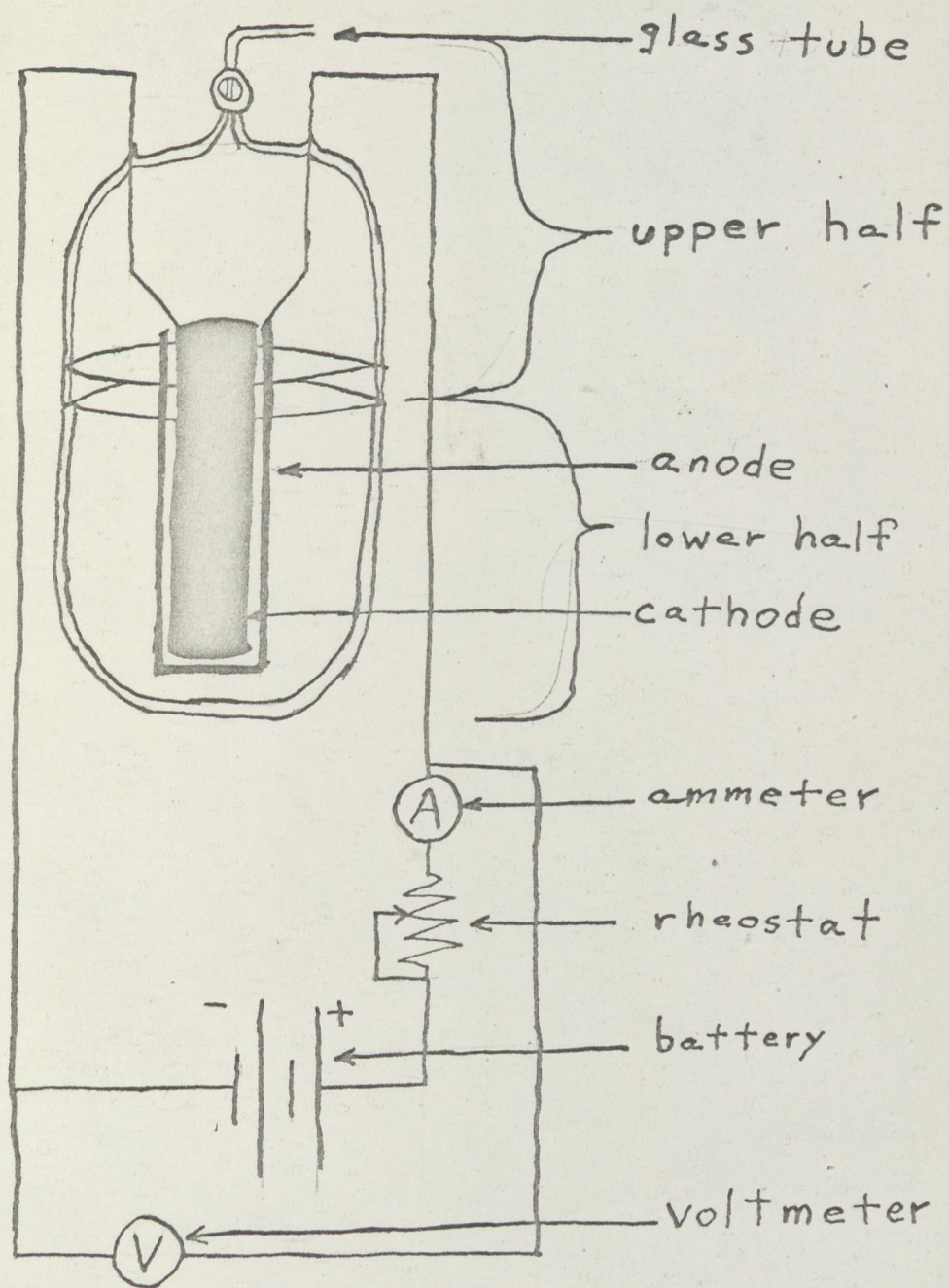
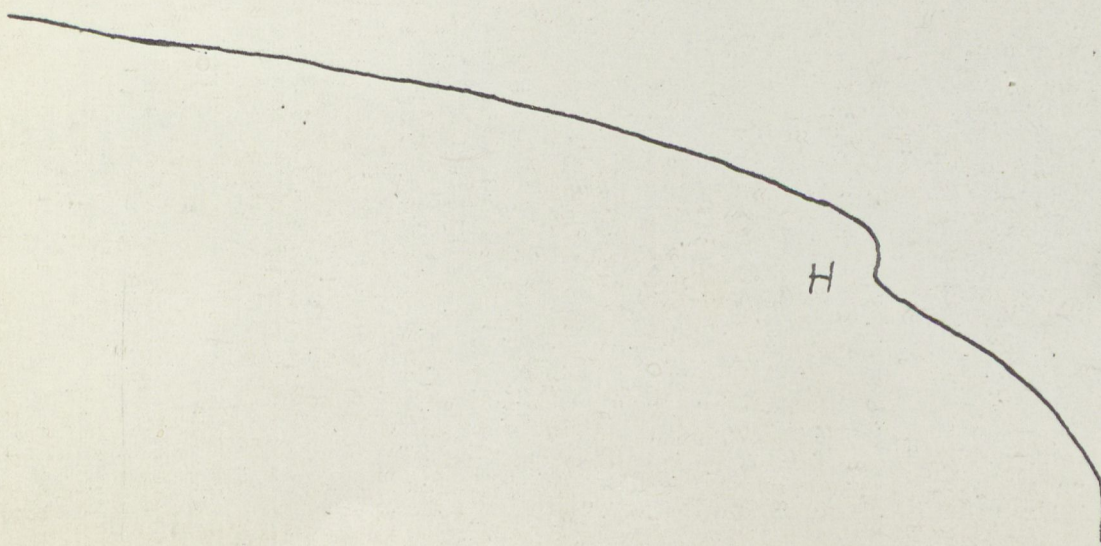
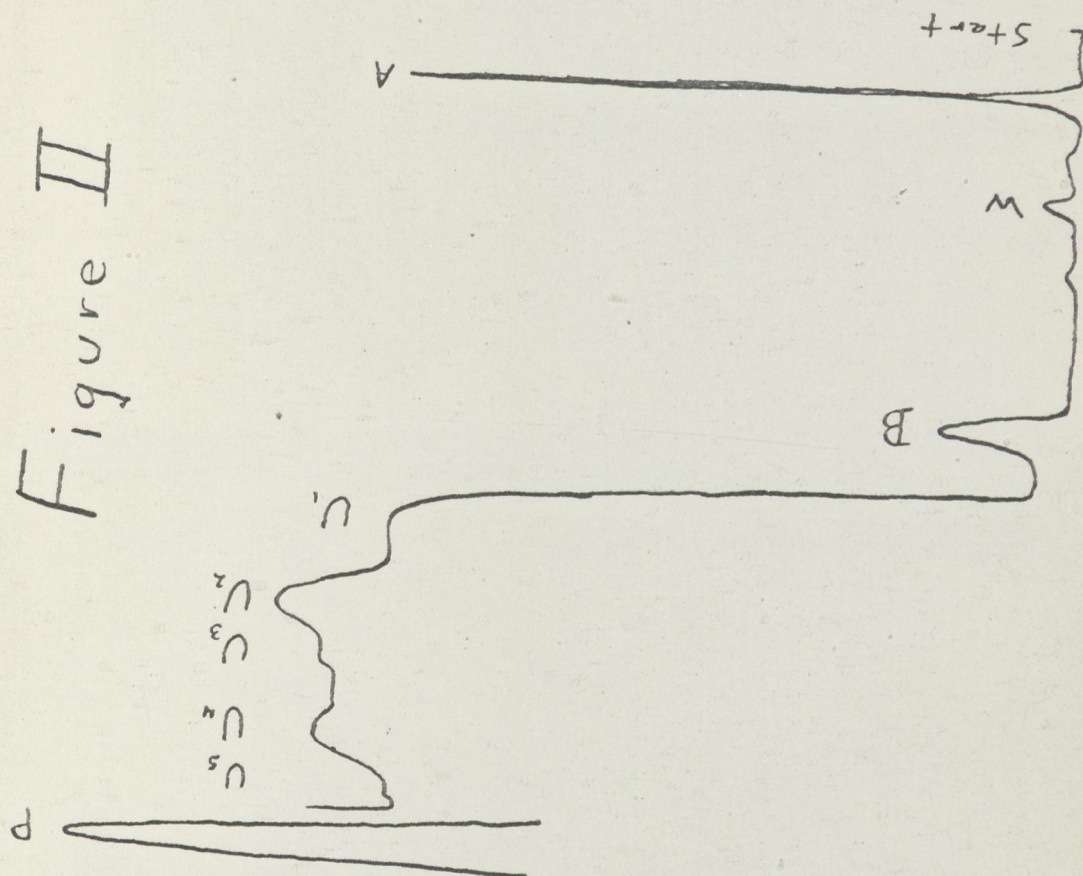


Figure I

Figure II



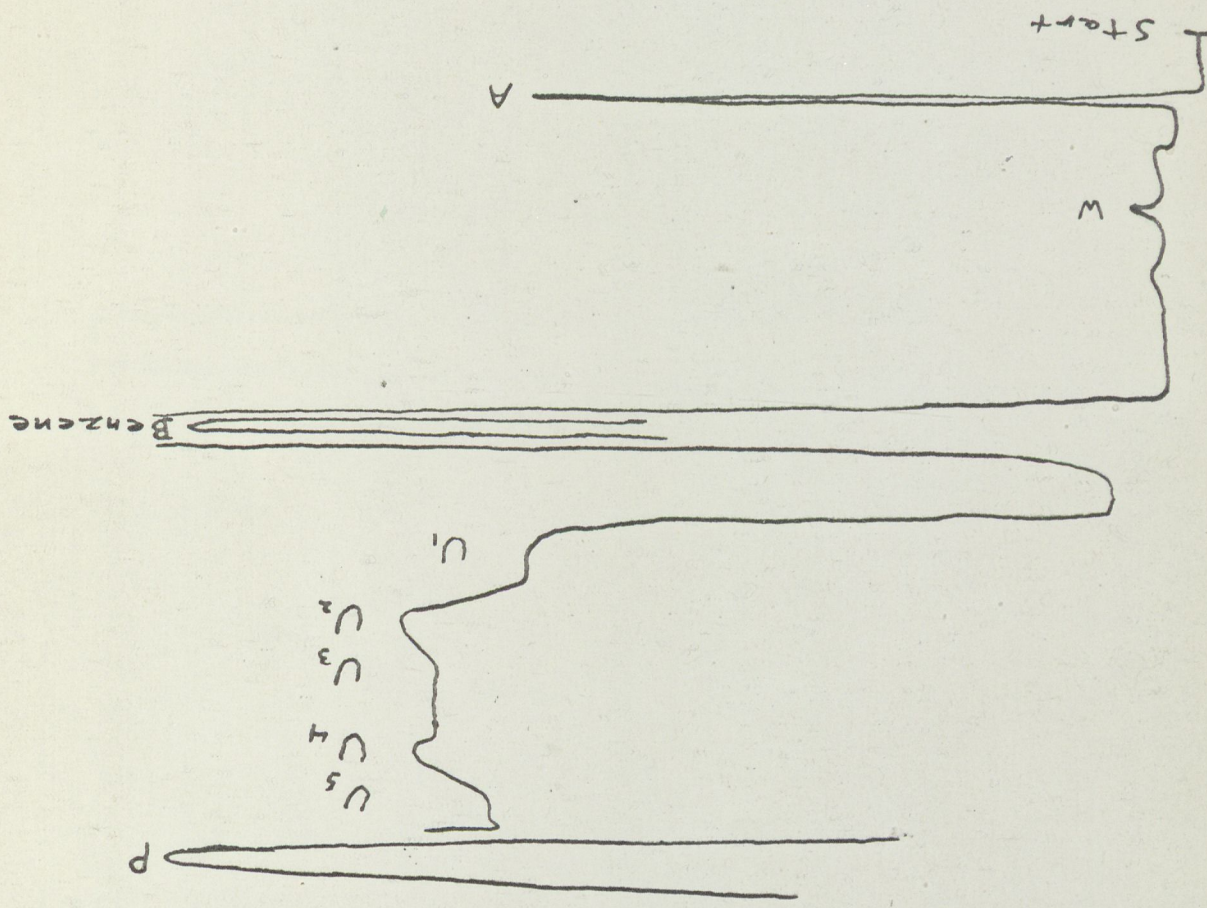


Figure III

Figure IV

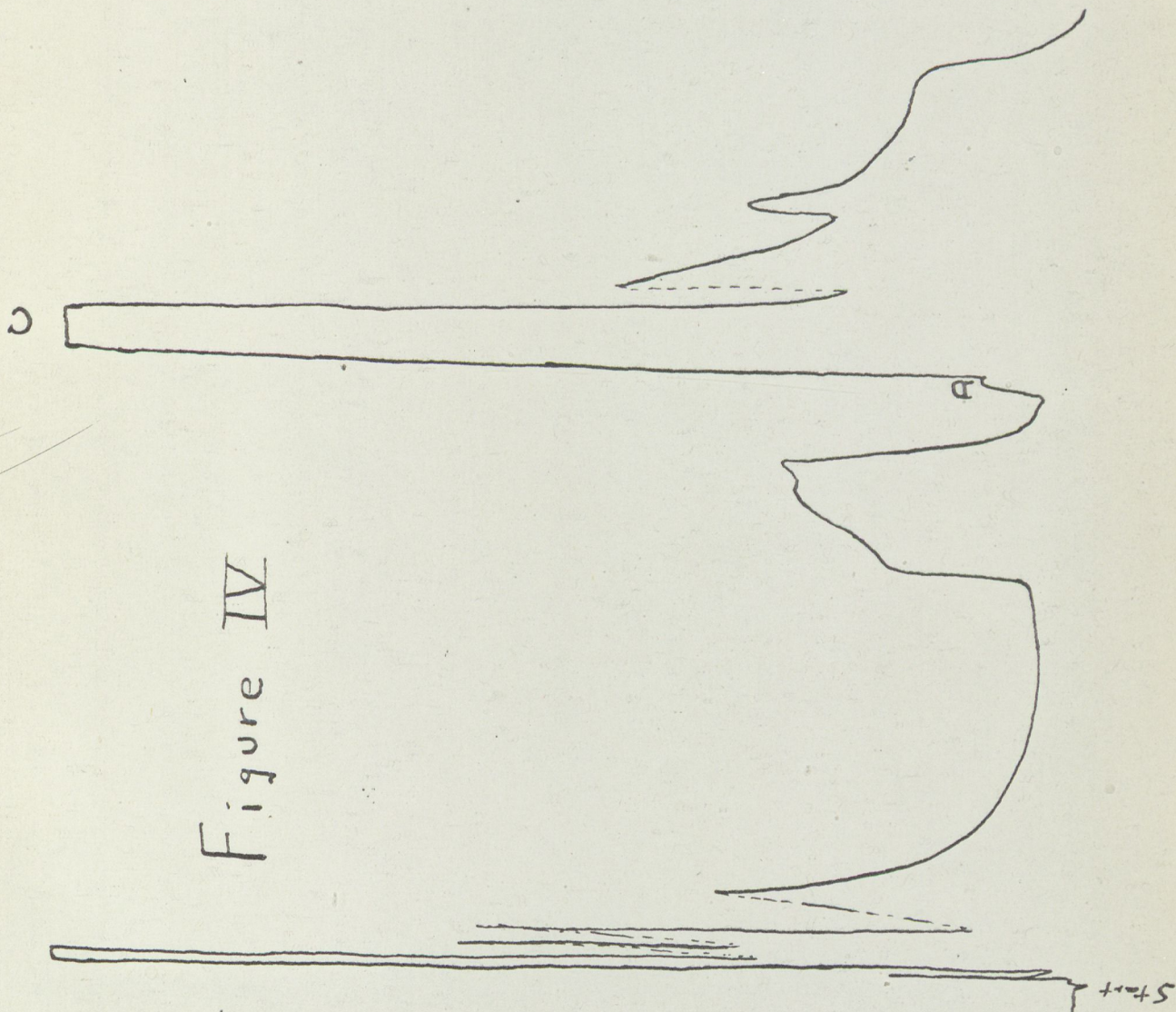
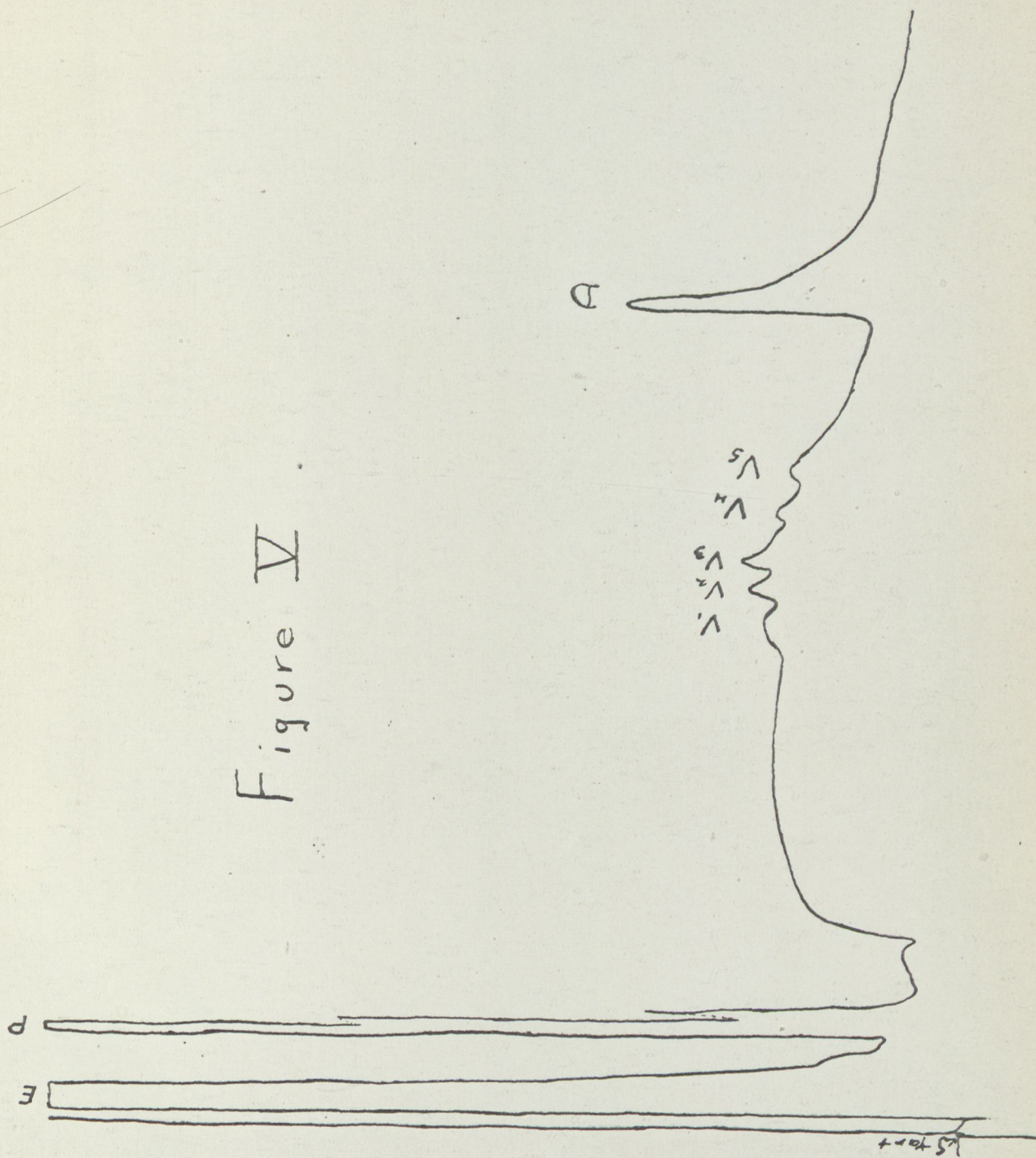


Figure V



Diphenyl

V₅
V₄
V₃
V₂

Start

Figure VI

Appendix I

Derivation of Spiking Formula

N = area under the peak of the normal sample

S = area under the peak of the spiked sample

X = percentage of substance in the normal sample

P = percentage of substance added in the spike

The area under the peak is proportional to the amount of substance causing that peak.

$$N:X::S:(P/X)$$

This proportion can be solved explicitly for X in the following manner.

$$N/X = S/(P/X)$$

$$N(P/X) = SX$$

$$NP/X = SX$$

$$NX = SX = NP$$

$$X = NP/(N-S)$$

Appendix II

Calculation of the Percentage Yield

A current of 0.0011 amps passed for 175 hours, and a current of 0.0035 amps for 250 hours. This is $0.0011 \times 175 + 0.0035 \times 250$, or 1.1 amp-hours. This multiplied by 3600 seconds per hour, gave 3.8×10^3 amp-seconds or coulombs.

This multiplied by 1.036×10^{-5} coulombs per Faraday, gave 4×10^{-2} Faradays passed. Since one Faraday theoretically produced one mole of phenyl radicals, and each radical could produce a molecule of benzene, 4×10^{-2} moles could have been produced.

Each mole of benzene weighs 78.1 grams, so $4 \times 10^{-2} \times 78.1$, or 3 grams of benzene could have been produced. Only 0.03 grams were produced, giving a yield of $3/0.03$, or 1%.

Should all of the current have gone into the production of diphenyl, the same weight would have been produced, 3 grams.

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