

gressed to a very considerable degree, giving the high results obtained for volatile acids and specific gravity obtained from the samples which showed no mold. The germs of the *Coniothecium* fungus having gained access to the fat, or, more probably, having been contained in it originally, and their growth being started by the favorable conditions resulting from the splitting up of the glycerides, attacked the liberated fatty acids and glycerides, and consumed them in proportion to the growth. The growth of the fungus produced further decomposition and a further consumption of fatty acids, with a preferment for those of lower molecular weight, until the remaining mixture of fat and free acids gave the diminished values for volatile acids and specific gravity obtained from the molded samples.

Experiments are now in progress in this laboratory having the object of a more exact investigation of the changes brought about in fats by the growth of mold. This I hope to accomplish by growing pure cultures upon a large quantity of fat of known composition. As these experiments will necessarily require a long time for completion, I report the results set forth above as a preliminary paper.

My thanks are due to Mr. F. E. Simon and Mr. A. B. Adams of this laboratory, by whom the principal part of the analytical work was performed.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 65.]

### AN ELECTROLYTIC STUDY OF PYRORACEMIC ACID.<sup>1</sup>

BY GEORGE W. ROCKWELL.

Received March 12, 1902.

WISHING to study the effect both of the oxidizing and reducing power of the electric current upon an organic body, aiming at the same time to fix the conditions so that other persons upon repeating the experiments might well expect to get similar results, I selected pure pyrорacemic acid for my investigation.

The apparatus employed in the experiments consisted of a beaker glass, a porous cup, which served as a septum for the separation of the anode and cathode liquids, and two platinum

<sup>1</sup> From author's thesis for Ph.D. degree, 1900.

electrodes of 100 sq. cm. surface each. When hydrochloric acid was used as an electrolyte, an anode of carbon was substituted for that of platinum. In several instances lead electrodes were used; these were of the same surface as that of the platinum electrodes.

The solvent generally employed was ordinary alcohol (about 95 per cent.). The concentration of the solution electrolyzed depended upon the conditions assumed for each experiment.

When a temperature sufficient to volatilize alcohol was used, a return condenser was inserted into the neck of the porous cup, by means of a large rubber stopper.

The current employed in most of the experiments was from an ordinary 110-volt incandescent light circuit, which was adjusted by means of lamps and wire resistance frames, so that a current ranging from 0.1 to 10 amperes could be used. Sometimes the current from five chloride accumulators, and in one instance only, that of eight gravity cells of the ordinary type was applied.

The temperature was taken with an ordinary thermometer. The readings were made with the thermometer inserted in the cathode liquid.

Attempts were made to estimate the various products of the electrolysis quantitatively, but I am convinced that they have fallen short in every case.

#### EXPERIMENTAL PART I.

The experiments considered in this part are those in which the oxidizing action of the current was studied.

##### *A. Oxidation in Sodium Hydroxide Solution.*

*Experiment 1.*—This was conducted with the following conditions:

Pyroracemic acid.....	5.56 grams.
Sodium hydroxide .....	10 grams.
Alcohol .....	100 cc.
Temperature .....	Ordinary.
Time .....	22 hrs.
Normal density, N. D. <sub>100</sub> .....	1.3 amperes.
Voltage .....	3 <sup>2</sup> / <sub>3</sub> volts.

Water sufficient to dissolve the sodium hydroxide was also added.

A Bunsen voltameter containing alkali was inserted in the cir-

cuit, in order to compare the volumes of the electrolytic and experimental gases given off in the same period of time.

One comparison was made and the experimental gas analyzed. The results of the analysis are as follows:

Volumes of the gases disengaged in the same time:

Electrolytic .....	79.1 cc.
Experimental .....	12.4 cc.
The experimental gases were.....	$\left\{ \begin{array}{l} 0.4 \text{ cc. CO}_2 \\ 2.8 \text{ cc. O} \\ 9.2 \text{ cc. N} \end{array} \right.$

This analysis shows the presence of air and as the experimental gases evidently did not escape fast enough to prevent the air from entering in at the joints of the apparatus during the time of their collection, no more comparisons were made.

Toward the close of the experiment it was noticed that the brilliancy of the incandescent lamps, through which the current was conducted, was greatly diminished, until finally the filaments became dull red in color. This indicated that the solution in the porous cup had become greatly deficient in its power of conductivity, but the real cause of this behavior was not noticed at the moment.

The contents of the porous cup were poured into a beaker glass, where they were discovered to have changed color, passing from a straw-yellow to a cherry-red. The solution was allowed to stand over night and then was filtered through a coarse filter-paper to remove silica, after which it was distilled over a free flame. The distillate possessed an ethereal odor.

*Experiment 2.*—The oxidation was made with:

Pyroracemic acid.....	4.33 grams.
Sodium hydroxide.....	5 grams.
Alcohol.....	50 cc.
Time.....	5½ hours.
Temperature.....	Ordinary.
N. D <sub>100</sub> .....	1.3 amperes.
Voltage.....	3⅛ volts.

Water sufficient to dissolve the sodium hydroxide was also added. In this experiment the experimental gas was collected after the current had been allowed to act for some time. It was analyzed with the following results, 100 cc. of gas being taken as sample each time.

*Analysis I.*

100 cc. of gas taken during first and second hours :

	cc.
Carbon dioxide .....	24.6
Oxygen .....	9.6
Carbon monoxide .....	14.6
Nitrogen .....	51.2

*Analysis II.*

100 cc. of gas taken during third and fourth hours :

	cc.
Carbon dioxide .....	73.2

*Analysis III.*

100 cc. of gas taken during fourth and fifth hours :

	cc.
Carbon dioxide .....	59.6
Oxygen .....	9.4
Carbon monoxide .....	13.6
Nitrogen .....	17.4

These gas analyses show that the action of the current had taken effect, either in oxidizing some of the carbon of the pyroracemic acid to carbonic acid, or that it had caused a rupture in the molecule  $\text{CH}_3\text{CO COOH}$ , splitting off carbon dioxide.

The contents of the porous cup were treated as above, and it was noticed at this juncture, that the distillate possessed the odor of acetic ether.

*Experiment 3.*—About 29 grams of pyroracemic acid were used ; all the other conditions were not noted, the object being to get a better insight into the gases by a more rapid evolution of the same from the experimental cell. They were collected in samples of 100 cc. after the current had acted for several hours.

*Analysis I.*

	cc.
Carbon dioxide .....	92.8
Oxygen .....	3.0
Carbon monoxide .....	1.0
Nitrogen .....	3.2

*Analysis II.*

	cc.
Carbon dioxide .....	85.0
Oxygen .....	7.8
Carbon monoxide .....	2.8
Nitrogen .....	4.4

The samples for these analyses were collected several hours apart and show conclusively that the action of the current had either caused an oxidation or a breaking-down in the molecule of the pyroracemic acid.

The electrolyte in this experiment possessed the color and odor previously observed.

*Experiment 4.*—Here the conditions were:

Pyroracemic acid.....	19.87 grams.
Sodium hydroxide.....	40 grams.
Alcohol.....	150 cc.
Water.....	100 cc.
Temperature.....	Ordinary.
Time.....	90 hours.
N. D. <sub>100</sub> .....	1.3 amperes.
Voltage.....	3-4 volts.

Thus far I had collected the gases escaping from the experimental cell over the same water, and I observed that the latter possessed an odor characteristic of aldehyde. The electrolyte, also, if noticed carefully, was found to bear an aldehydic odor, besides that of acetic ether and alcohol.

As a consequence of these observations, an Erlenmeyer flask containing ether was inserted into the exit tube leading to the vessel in which the water was contained, and allowed to remain for several hours, after which the flask was removed and dry ammonia gas passed through the ether. A white precipitate of aldehyde ammonia was the result.

*Experiment 5.*—The amounts of material varied but little from those in the preceding experiments.

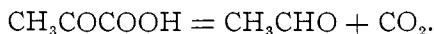
Pyroracemic acid.....	10 grams.
Sodium hydroxide.....	10 grams.
Alcohol.....	100 cc.
Water.....	85 cc.
Temperature.....	30°-80° C.
Time.....	8 hours.
N. D. <sub>100</sub> .....	2.5 amperes.
Voltage.....	6-20 volts.

With the anode liquid made up as above indicated, the experiment was started and allowed to continue until it became almost a non-conductor, as observed in some of the preceding experiments. The temperature and voltage increased while the amperage naturally decreased.

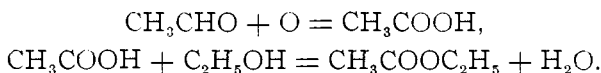
The gases were passed through ether, as before, and the aldehyde precipitated by ammonia. The yield in this experiment was equal to 0.9656 gram aldehyde, or 19 per cent. of the theoretical.

Here it might be the proper place to offer some theoretical explanation of the reactions so far observed.

First, it seems that aldehyde is the first product of the oxidation, and it appears to be formed by the breaking-down of the acid molecule in this manner :

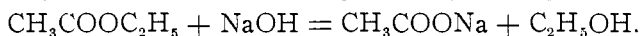


Secondly, from the very characteristic odor of acetic ether, which is, without a doubt, present, I conclude that it must be formed from the acetic acid, which would naturally be the next product of the oxidation, and the alcohol present in the solution thus :



The singular fact about this is that these reactions took place in a solution that was strongly alkaline to begin with. But as we know that such ethers are generally formed in acid solutions, the presence of acetic ether here gives very reliable evidence of the formation of acetic acid as a second product.

Thirdly, another reaction, in all probability, takes place thus :



By this reaction sodium acetate would be formed, regenerating the alcohol.

All these reactions, of course, are only of theoretical interest.

*Experiment 6.*—The material used was :

Pyroracemic acid.....	10 grams.
Sodium hydroxide.....	10 grams.
Alcohol.....	100 cc.
Water.....	110 cc.
Temperature.....	60°-80° C.
Time.....	5 hours.
N. D. <sub>100</sub> .....	2.5 amperes.
Voltage.....	6-56 volts.

The cell containing this solution was placed upon a water-bath and was attached to a return condenser, which served to condense any vaporized alcohol. A low flame was applied to keep the temperature within the limits given. A long glass tube connected the

top of the condenser with two Erlenmeyer flasks, which contained anhydrous ether. This tube served to conduct the exuding gases through the ether.

The experiment was interrupted when the bubbles passed slowly through the ether and in place of the return condenser an ordinary Liebig condenser was attached to the anode chamber and the experiment continued. A liquid very like acetic ether in odor began to distil over at  $76^{\circ}$ - $77^{\circ}$  C., but almost immediately the temperature rose to  $78^{\circ}$  C., when alcohol came over. The distillate was collected for several minutes and it had all the appearance and odor of those residual liquids obtained from the ether extractions in the previous experiments.

The change in color of the anode liquid was undoubtedly due to the usual effect of an alkali on aldehyde.

The precipitated aldehyde ammonia in this case equaled 0.7980 gram, equivalent to 0.5755 gram of aldehyde, or one-tenth of the theoretical yield.

The anode liquid was evaporated on the water-bath after filtration, when it gave a tarry residue, from which nothing could be sublimed.

*Experiment 7.*—The same conditions were observed as given above for Experiment 6, with the exception of the time, which was cut down to four hours and twenty minutes. In this experiment the ether was chilled by ice-water and a copious precipitate of aldehyde ammonia was obtained. It was not weighed.

*Experiment 8.*—This was performed according to the conditions under Experiment 6. A better yield of aldehyde was obtained. The aldehyde ammonia equaled 4.88 grams, equivalent to 3.41 grams of aldehyde, or about three-fifths of the theoretical.

*Experiment 9.*—This experiment was performed with the following conditions:

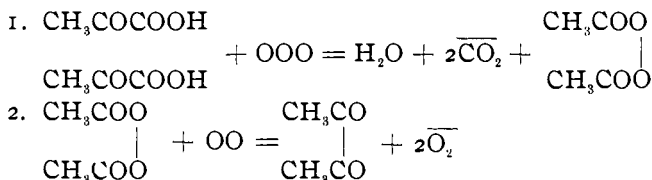
Pyroracemic acid.....	10 grams.
Sodium hydroxide.....	10 grams.
Water .....	110 cc.
Alcohol.....	100 cc.
Time .....	$7\frac{1}{2}$ hours.
Temperature .....	$50^{\circ}$ C.
N. D. <sub>100</sub> .....	1.35-0.85 amperes.
Voltage.....	5-40 volts.

Lead electrodes were used. It is seen, from the above data re-

garding amperage and voltage, that the action proceeded along the same line as it does with the platinum electrodes. The aldehyde was precipitated as aldehyde ammonia, as before; it equaled 1.5522 grams. It was thought that the lead peroxide being formed at the anode might aid in the oxidation, but it seems to have no action.

*Experiment 10.*—The conditions observed here were similar to those of Experiment 9, with the exception of the temperature, which was raised to 70° C. For the platinum electrodes, two carbon electrodes of 45 sq. cm. were substituted. This experiment yielded aldehyde upon the usual treatment. It was not weighed.

It was thought that possibly the carbon would produce milder oxidation, by uniting with the oxygen to form an atmosphere of carbon dioxide, and thus retard the oxidation. In this manner it was hoped to form acetyl superoxide, and then have this break down into diacetyl, thus:



As Schall in 1871 claimed to have obtained a persulphide of an analogous formula to that given to acetyl superoxide, it seems, reasoning by analogy, that if diacetyl exists at all it should be obtained from pyrrocemic acid, if any acid is to yield it, according to the above indicated reactions.

### B. Oxidation in Sulphuric Acid Solution.

*Experiment 1.*—The following material was employed:

Pyrrocemic acid.....	10 grams.
Sulphuric acid (conc.).....	20 cc.
Alcohol.....	100 cc.
Temperature.....	60°-80° C.
Time.....	4½ hours.
N. D. <sub>100</sub> .....	2.5 amperes.
Voltage.....	3 volts.

This experiment was conducted in an apparatus similar to that employed in the sodium hydroxide solutions. Aldehyde ammonia



was precipitated in the usual manner. The anode liquid had the odor of acetic ether.

*Experiment 2.*—In this experiment conditions similar to those in Experiment 1 were observed. The anode liquid was shaken out with ether and distilled as usual; the resulting distillate was of the same nature as those produced by the experiments made in sodium hydroxide solution. This is a further proof of the production of acetic acid, as here we have the production of acetic ether in acid solution.

*Experiment 3.*—The following conditions were observed:

Pyroracemic acid.....	10 grams.
Alcohol.....	100 cc.
Sulphuric acid (conc.).....	25 cc.
Temperature.....	50° C.
Time.....	27 hours.
N. D. <sub>100</sub> .....	0.45 ampere.
Voltage.....	2 <sup>2</sup> / <sub>3</sub> volts.

The thought entertained here was that with low pressure and density there was a possibility of obtaining diacetyl in sulphuric acid solution. No attempt was made to collect the gases. An inverted condenser was used to return any alcohol. The anode liquor was extracted with ether several times, but nothing new was found.

*Experiment 4.*—The conditions in this experiment were:

Pyroracemic acid.....	10 grams.
Sulphuric acid (conc.).....	20 cc.
Alcohol.....	100 cc.
Time.....	7 <sup>1</sup> / <sub>2</sub> hours.
Temperature.....	60° C.
N. D. <sub>100</sub> .....	1.4 amperes.
Voltage.....	4 <sup>1</sup> / <sub>3</sub> volts.

Lead electrodes were employed. Aldehyde was precipitated by ammonia, but was not weighed for the reasons already noted. The anode liquid yielded nothing new.

*Experiment 5.*—The conditions observed here are similar to those under Experiment 4, with the exception of time and density. The time was three hours and N. D.<sub>100</sub> = 0.9 ampere. Carbon electrodes were used. Aldehyde and the other products were obtained. This experiment was interrupted at the point when it

was supposed that the aldehyde would begin to come off, but such a point was not found.

*C. Oxidation in Hydrochloric Acid Solution.*

*Experiment 1.*—The following conditions were observed:

Pyroracemic acid.....	10 grams.
Hydrochloric acid (conc.) .....	30 cc.
Alcohol.....	100 cc.
Time .....	5 hours.
Temperature.....	60°–70° C.
N. D. <sub>100</sub> .....	2.5 amperes.
Voltage .....	5 volts.

A carbon plate was substituted for the platinum anode in these experiments, otherwise they were conducted as those which preceded them. Upon the passage of ammonia gas into the chilled ether a white coloration was produced, but it disappeared after a short time. This was probably due to a little volatilized hydrochloric acid gas in the ether, or perhaps there was sufficient water in the ether to dissolve it. The anode liquid was treated as above, but gave nothing other than what had been noted previously.

*Experiment 2.*—Here I used:

Pyroracemic acid.....	20 grams.
Hydrochloric acid (conc.)....	60 cc.
Alcohol .....	150 cc.
Time.....	24 hours.
Temperature.....	50° C.
N. D. <sub>100</sub> .....	0.4 ampere.
Voltage .....	18 volts.

The anode in this experiment was a common graphite pencil with the wood removed at both ends. My hope was that I might obtain diacetyl, but without avail.

*Experiment 3.*—Material slightly varied again:

Pyroracemic acid.....	20 grams.
Alcohol.....	100 cc.
Hydrochloric acid (conc.) .....	30 cc.
Temperature.....	40° C.
Time.....	10 hours.
N. D. <sub>100</sub> .....	1.35 amperes.
Voltage.....	5 volts

A carbon plate was used. The anode liquid, analyzed as before, revealed nothing new.

*D. Oxidation of Certain Salts of Pyrорacemic Acid.*

The magnesium, sodium and iron salts were made with care and their solutions electrolyzed with the hope of obtaining diacetyl, but it was not found.

*E. Oxidation in Sodium Carbonate Solution.*

*Experiment 1.*—Here I used the following:

Pyrорacemic acid.....	10 grams.
Time .....	6 hours.
Temperature .....	30° C.
N. D. <sub>100</sub> .....	1.35 amperes.
Voltage .....	6 volts.

The pyrорacemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. The cathode liquid was also a solution of sodium carbonate.

It was found that after a time the anode liquid became acid. The escaping gases were tested for carbon dioxide and found to contain 93 per cent. This indicates action similar to that produced in a sodium hydroxide solution.

*Experiment 2.*—Observing that no diacetyl had as yet been obtained, it was suggested to keep the anode liquid perfectly alkaline by means of sodium carbonate added from time to time; also to keep the cathode liquid as nearly neutral as possible by running a stream of carbon dioxide into the same. With these precautions all of the following experiments were directed to the formation of diacetyl.

Pyrорacemic acid.....	20 grams.
Time .....	9½ hours.
Temperature .....	30° C.
N. D. <sub>100</sub> .....	1.35 amperes.
Voltage.....	6 volts.

The pyrорacemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. A small addition of the same was made every half hour. The anode liquid was taken out and distilled over a free flame. The distillate was salted out with common salt and redistilled. This procedure gave a greenish yellow distillate, with a color very like that of diacetyl. This was dehydrated over calcium chloride and distilled again. It retained the same color, but the odor was like that of a weak solution of the pyrорacemic acid itself, after being boiled.

The boiling-point of diacetyl ( $87^{\circ}$ - $88^{\circ}$  C.) was never approached in the distillation of this substance.

*Experiment 3.*—Again I employed the following:

Pyroracemic acid.....	20 grams.
Water .....	100 cc.
Time .....	10 hours.
Temperature .....	$30^{\circ}$ C.
N. D. <sub>100</sub> .....	1.8 amperes.
Voltage.....	10 volts.

The anode liquor was acidulated with dilute sulphuric acid and then distilled; the distillate was salted out as before and redistilled. It gave a greenish yellow distillate, which was treated according to the method of Pechmann.<sup>1</sup> In accordance with this, normal potassium hydroxide was added to the solution to alkaline reaction, but it did not become colorless or a faint brown as Pechmann asserts. It, however, became a light yellow in color. It was then acidulated with dilute sulphuric acid and extracted several times with ether. The ether was distilled off and a yellowish green substance was left instead of a colorless oil as directed.

The object of this treatment was to form if possible the aldol of diacetyl.

From what I obtained from the ether extractions, I attempted to produce *p*-xyloquinone, by treatment with potassium hydroxide, which would constitute a conclusive test for diacetyl. This, however, was not obtained. The *p*-xyloquinone is described as a golden yellow crystalline compound, crystallizing from alcohol in needles and subliming undecomposed. No product of such characteristics appeared in the attempted transformations.

Still laboring under the impression that possibly that greenish yellow material might be the sought-for substance, several experiments were tried, some with the same conditions as those given above and others with conditions slightly different. The anode liquids were all treated as has been described, but no test for diacetyl revealed its presence.

#### EXPERIMENTAL PART II.

In the reduction of pyroracemic acid the porous cup was made the cathode chamber.

<sup>1</sup> *Ber. d. chem. Ges.*, **28**, 1846.

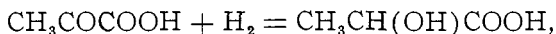
*A. Reduction in Sodium Hydroxide Solution.*

*Experiment 1.*—The following material was employed:

Pyroracemic acid.....	5 grams.
Alcohol.....	50 cc.
Water.....	50 cc.
Sodium hydroxide.....	8 grams.
Temperature.....	Ordinary.
Time.....	7 hours.
N. D. <sub>100</sub> .....	0.45 ampere.
Voltage.....	3 $\frac{1}{2}$ volts.

The lactic acid in the cathode liquid was estimated according to the directions in Beilstein's "Handbook" as follows: It was acidulated with dilute sulphuric acid and extracted with ether several times. The ether was evaporated and the residual liquid heated in a porcelain dish for some minutes on a water-bath to expel any dissolved ether. Lead acetate was added to remove any sulphuric acid present. The lead sulphate formed was filtered off and more lead acetate added together with alcoholic ammonia (alcohol 90 per cent., ammonia 10 per cent.) until no further precipitation was noticed. A white, slimy precipitate was obtained, which, according to Beilstein, has the composition,  $3\text{PbO}\cdot\text{C}_3\text{H}_6\text{O}_3$ . This was filtered off, washed with alcohol, dried at  $100^\circ\text{C}$ ., and weighed. The same writer mentions that this precipitate contains 78.5 per cent. lead oxide; therefore there is 21.5 per cent. free lactic acid contained in it. The precipitate in this case weighed 2.595 grams, corresponding to 0.5579 gram of lactic acid.

According to the equation



10.91 per cent. of the theoretical yield was obtained.

*Experiment 2.*—Here I used:

Pyroracemic acid.....	5 grams.
Alcohol.....	75 cc.
Water.....	50 cc.
Sodium hydroxide.....	10 grams.
Temperature.....	Ordinary.
Time.....	5 hours.
N. D. <sub>100</sub> .....	0.8 ampere.
Voltage.....	4 volts.

The cathode liquid was acidulated and treated as above. The precipitate weighed 6.7581 grams, equivalent to 1.4529 grams of lactic acid, or 28.43 per cent. of the theory.

*Experiment 3.*—The material was:

Pyroracemic acid.....	5 grams.
Sodium hydroxide.....	8 grams.
Alcohol.....	50 cc.
Water.....	50 cc.
Temperature.....	50° C.
Time.....	6 hours.
N. D. <sub>100</sub> .....	0.7 ampere.
Voltage.....	4 volts.

The cathode liquid under the prescribed treatment yielded 3.9592 grams of precipitate, corresponding to 0.8512 gram lactic acid, equivalent to 16.65 per cent. of theory.

In the preceding experiments platinum electrodes were employed.

*Experiment 4.*—Lead electrodes were used in this experiment with conditions as follows:

Pyroracemic acid.....	20 grams.
Sodium hydroxide.....	10 grams.
Alcohol.....	100 cc.
Water.....	110 cc.
Temperature.....	60° C.
Time.....	5 hours.
N. D. <sub>100</sub> .....	0.9 ampere.
Voltage.....	5-6 volts.

The cathode liquid, treated as usual, gave 4.5860 grams of the lead salt, corresponding to 0.9859 gram of lactic acid, equivalent to 9.64 per cent. of theory.

#### B. Reduction in Sulphuric Acid Solution.

*Experiment 1.*—Here I used:

Pyroracemic acid.....	10 grams.
Alcohol.....	75 cc.
Sulphuric acid (conc.).....	20 cc.
Temperature.....	30° C.
Time.....	21 hours.
N. D. <sub>100</sub> .....	0.45 ampere.
Voltage.....	3 volts.

The cathode liquid was directly shaken out with ether, as it was an acid solution, otherwise treatment was the same as when working in an alkaline solution. It yielded 3.0499 grams of the lead salt, corresponding to 0.6557 gram of lactic acid, equivalent to 6.41 per cent. of the theory.

*Experiment 2.*—The following was used:

Pyroracemic acid.....	10 grams.
Sulphuric acid (conc.).....	20 cc.
Alcohol.....	75 cc.
Temperature.....	30° C.
Time.....	9 hours.
N. D. <sub>100</sub> .....	0.45 ampere.
Voltage.....	3 volts.

The cathode liquid gave 7.1718 grams of the lead salt, corresponding to 1.5417 grams of lactic acid, equivalent to 15.08 per cent. of the theory.

*Experiment 3.*—Here I used:

Pyroracemic acid.....	5 grams.
Sulphuric acid (conc.).....	20 cc.
Alcohol.....	75 cc.
Temperature.....	30° C.
Time.....	6 hours.
N. D. <sub>100</sub> .....	0.6 ampere.
Voltage.....	3 $\frac{1}{3}$ volts.

The usual treatment gave 5.3731 grams of the lead salt, corresponding to 1.1552 grams of lactic acid, equivalent to 22.60 per cent. of the theory.

*Experiment 4.*—Here the following were used:

Pyroracemic acid.....	5 grams.
Water.....	50 cc.
Sulphuric acid (conc.).....	25 cc.
Alcohol.....	50 cc.
Time.....	6 hours.
Temperature.....	35° C.
N. D. <sub>100</sub> .....	0.8 ampere.
Voltage.....	3 $\frac{1}{3}$ volts.

This yielded 6.4670 grams of the lead salt, corresponding to 1.3904 grams of lactic acid, equivalent to 27.19 per cent. of the theory. Platinum electrodes were used in these experiments.

*Experiment 5.*—Lead electrodes were used in this experiment with the following conditions:

Pyroracemic acid.....	10 grams.
Sulphuric acid (conc.).....	10 cc.
Alcohol.....	100 cc.
Temperature.....	50° C.
Time.....	4 $\frac{1}{2}$ hours.
N. D. <sub>100</sub> .....	0.85 ampere.
Voltage.....	5-6 volts.

The yield was 3.3203 grams of the lead salt, corresponding to 0.7138 gram of lactic acid, equivalent to 6.97 per cent. of the theory.

*Experiment 6.*—Carbon electrodes were employed here with the following conditions:

Pyroracemic acid.....	10 grams.
Sulphuric acid (conc.).....	15 cc.
Alcohol.....	100 cc.
Water.....	50 cc.
Temperature.....	60° C.
Time.....	4½ hours.
N. D. <sub>45</sub> .....	0.9 ampere.
Voltage.....	3.5 volts.

The cathode liquid gave 3.7693 grams of the lead salt, corresponding to 0.8103 gram of lactic acid, equivalent to 7.93 per cent. of the theory.

It might be well to state the maximum and minimum yields of lactic acid.

In alkaline solution under the conditions of experiment (2) the maximum was obtained, under those of (4), the minimum. The figures are 28.43 and 9.64 per cent. of the theoretical yields.

In sulphuric acid solution, under experiment (4), the maximum 27.19 per cent., and under experiment (1), the minimum, 6.41 per cent., of the theoretical was obtained.

In the reduction of pyrорacemic acid by electrolytic hydrogen, it seems natural that lactic acid should be the first product of the reduction; also, that by further reduction propionic acid should be obtained.

The latter, in my opinion, is formed at least in small quantities and probably, if exceedingly large quantities of pyrорacemic acid were electrolyzed and treated as described, it would be found.

Further, it is noticed in this part also, that the change in the kind of electrodes causes no marked difference.

As a final conclusion it may be stated that this study reveals as products of the electrolytic oxidation and reduction of pyrорacemic acid—acetaldehyde, acetic acid, acetic ester, and lactic acid with some probability of diacetyl and propionic acid.