instead of glucose phenylhydrazone as might be expected. Mannose, on the other hand, yields only the hydrazone under these conditions.

2. Glucose and fructose phenylhydrazones are converted practically quantitatively to glucosazone on standing in dilute acetic acid. Mannose phenylhydrazone is unchanged by this treatment.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

PHOTOCHEMICAL DECOMPOSITION OF LACTIC ACID

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This study of the photochemical decomposition of lactic acid is part of an investigation of the oxidation of lactic acid by oxygen in the presence of ultraviolet radiation. The investigation was undertaken as a result of a consideration of the theories of physiological chemists in regard to the oxidation of lactic acid in the body. It appeared that a study of the oxidation from a purely chemical viewpoint would be of value in connection with these theories.

Before this could be done a more thorough investigation of the decomposition of the acid, in the absence of oxygen, by ultraviolet radiation was necessary. There is a marked conflict between the results of other investigators over the decomposition of lactic acid in solution by the radiations of a quartz mercury arc. The differences found may be explained, in part, by taking into consideration the fact that some observers exposed the irradiated solution to air and some took the necessary precaution to see that no oxygen was present. Another discrepancy arose from the fact that some observers used glass containers. The wave lengths of radiation that decompose lactic acid are absorbed by glass.

Bolin[1] states that there is no decomposition of lactic acid in glass flasks. Euler's[2] investigation showed that at 70° alcohol and a gas mixture composed of 90% of carbon dioxide and 10% of hydrogen and carbon monoxide resulted. No substance was formed that reduced Fehling's solution. More recently Euler,[3] in experiments carried out both at 30 and 70°, confirms these results. He states that no reaction takes place in glass flasks. In all his experiments he finds an induction period of about two hours. This was, doubtless, the length of time necessary to produce enough carbon dioxide to saturate the solution. Euler's results were confirmed by Scharz[4] with the exception that methane was also found in small

[1] Bolin, *Z. physik. Chem.*, **87**, 490 (1914).

[2] Euler and Lindberg, *Biochem. Z.*, **39**, 410 (1912).

[3] Euler and Ryd, *ibid.*, **51**, 96 (1913).

[4] Scharz, *Arch. ges. Physiol.*, **170**, 650 (1918).

quantities. Neuberg,[5] in criticizing Euler's results, claims that there is no decomposition in quartz flasks when exposed to the radiation from a mercury arc. This conclusion was based on the fact that no evolution of carbon dioxide was observed and that titration of the irradiated solution showed no loss of acid. The failure to obtain carbon dioxide gas could be explained on the basis of the fact that the rather low radiation intensity used would not give enough carbon dioxide to saturate the solution. The fact that the amount of lactic acid remains unchanged is based on the assumption that no other acid is formed under the conditions of his experiment. Baudisch[6] states that no alcohol, no methane and no carbon monoxide were found, but that acetaldehyde was found in large quantities. Neuberg's and Baudisch's results differ greatly from Euler's and those of the present investigator.

Apparatus

The apparatus used in this experiment although designed for the study of the oxidation of lactic acid was fairly well adapted to measuring the decomposition. Two sources of radiation were used. One was a commercial, 220-volt, Cooper-Hewitt quartz mercury arc A operated at 3.1 amperes. This lamp had been used previously for about 500 hours. It was air-cooled by a steady blast at 22°. The other was an iron arc operated at 15 amperes from a 220-volt line. The voltage on the line was held steady by adjusting resistances at the motor generator unit. The visible and ultraviolet radiation from the mercury arc did not vary over 3% in the course of a day. The reaction tube T was placed in a tin-lined thermostat B. The thermostat had a 5 cm. by 15 cm. quartz window Q in the front and a smaller one in the back. In order to remove carbon dioxide from the solution it was found necessary to shake the tube vigorously as well as to evacuate it; otherwise as much as 6 cc. of the gas would remain in the solution. For this reason the reaction tube was mounted on a slide and could be shaken over a 6-cm. stroke at 310 r.p.m. The reaction tube itself was made by the General Electric Company from ground and polished quartz plates fused together to form a square container with internal dimensions of 1.9 × 1.9 × 10.0 cm. At one end a neck 10 cm. long and 0.4 cm. in internal diameter was fused. The tube for the removal of gases was ground into the mouth of the reaction tube and extended the length of the neck. Rubber tubing was wired over the joint; 25 cm. of heavy rubber tubing led from this tube to the 2-mm. bore glass tube from the Töpler pump. The pump delivered the gas directly to the buret of the gas analysis apparatus. Radiation from the arc passed successively through the quartz window, 3.8 cm. of distilled water, the reaction vessel, 0.5 cm. of water and out the

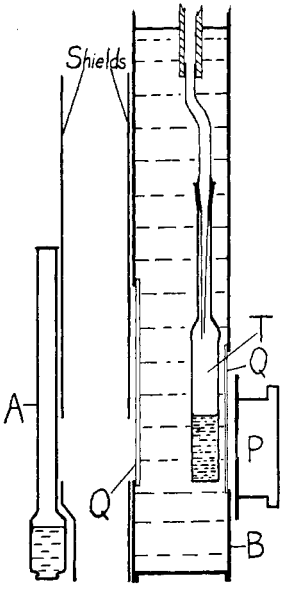

Fig. 1.

[5] Neuberg, *Biochem. Z.*, **13**, 303 (1908); **29**, 279 (1910); **39**, 163 (1912).

[6] Baudisch, *ibid.*, **103**, 59 (1920).

back window. The thermopile P was one made by Coblentz of the Bureau of Standards for the Vermont Agricultural Experiment Station and was loaned by them for this work. The galvanometer was used as a zero instrument, the current from the thermopile being balanced by a certain fraction of a measured current.[7] The thermopile was standardized by a Bureau of Standards standard of radiation. 0.1302×10^{-3} cal. per cm.^{2} per min. gave an e.m.f. of 1.55×10^{-6} volts. This standardization depends somewhat on the assumption that the thin quartz window on the thermopile reflects and absorbs the same amount of radiation from the hot carbon filament of the standard of radiation as it does from the source to be measured.

Experimental Part

Absorption Measurements.—In order to determine the wave lengths absorbed, a series of photographs of the absorption spectrum was made. These were made both with the reaction tube and with a cell the thickness of which could be varied. The results showed that very little radiation of wave lengths longer than 2500 Å. was absorbed and that practically all below that value was absorbed. As most of the radiation from this arc below 2500 Å. was concentrated in five lines between 2330 Å. and 2500 Å., the average wave length of absorbed radiation was taken as 2450 Å.[8] Absorption measurements were made by comparing the amount of radiation transmitted by the reaction tube filled with water and with a lactic acid solution. As the sides of the tube had been slightly distorted when it was fused together, care was taken to see that it was in the same position for each measurement. The arrangement for shaking permitted this without difficulty. Absorption measurements were also made with a 23-mm. tube with quartz windows fastened on by de Khotinsky cement. In this case the radiation was first run through 6.6 cm. of water to remove most of the heat radiated from the lamp. The absorption measurements were all fairly unsatisfactory as the lamp was not steady and showed variations of about 1% over short periods of time. Values were obtained ranging from 3.7 to 4.5%. Most of the measurements were between 4.1 and 4.2%. 4.15% was used as the value. The radiation intensity was measured at the back window. The ratio between this value and that at the position of the reaction cell was determined by experiment.

Lactic Acid.—The lactic acid (Kahlbaum) was prepared by rapid distillation at 5 mm. pressure. Only the constant boiling point fraction was used. After distilling, it was diluted to approximately 1 *N* and refluxed for eight hours to hydrate all lactide.[9] The normality was found to be 1.137 (by oxidation) and 1.140 (by titration with phenolphthalein).

Quantum Yield Determinations.—In the experiments described below the temperature of the thermostat was 25.00° and the gas volumes are corrected to 0° and 760 mm. The lactic acid solution was run into the reaction tube until the bottom of the meniscus was 4.5 cm. from the bottom of the tube. It was then placed in the shaking apparatus in the thermostat. The thermostat was emptied, rinsed out with distilled water and refilled with distilled water. It was found to be important to change the water every run. The tube was evacuated, with shaking between the strokes of the Töpler pump, until no more gas could be pumped out. The shutter in front of the thermostat was then opened to the extent of 4.5 cm., exposing the solution to the quartz mercury arc. A shield was placed close to the arc so that only 4.5 cm. of the tube of the arc was exposed. At the end of the exposure the arc was turned off and the gas pumped out of the solution as described above. This gas was analyzed for carbon dioxide; then oxygen

[7] G. R. Burns, Vermont Agricultural Experiment Station Bulletin, 261 (1927).

[8] "International Critical Tables," Vol. 5.

[9] Dietzel and Krug, *Ber.*, **58B**, 1307 (1925).

was admitted and the mixed gases were run over a hot platinum spiral; the carbon dioxide thus formed was then determined. Typical runs are given in Table I.

TABLE I

QUANTUM YIELDS OF CARBON DIOXIDE

Duration of irradiation, hours	6	6	6
Av. radiation intensity at tube, microvolts	359.5	386.4	372.0
Surface exposed, square centimeters	8.55	8.55	8.55
Carbon dioxide produced, cc.	4.94	5.15	4.90
Decrease on ignition, cc.	0.51	0.53	0.42
Carbon dioxide produced by ignition, cc.	0.50	0.50	0.38
Moles of carbon dioxide found $\times 10^4$	2.220	2.315	2.202
Moles of carbon dioxide calculated $\times 10^4$	3.30	3.55	3.41
Quantum yield on carbon dioxide produced, %	67.4	65.2	64.7

Analysis of Gas.—The gases other than carbon dioxide comprised about 9% of the total volume of gas formed. These gases were investigated as follows. A 54-hour run with the reaction tube three-quarters full and exposed to the full length of the mercury arc gave 168.36 cc. of gas. This was analyzed in a special apparatus with the following results:[10] 153.10 cc. of carbon dioxide, 1.50 cc. of unsaturated compounds, 6.44 cc. of carbon monoxide, 16.99 cc. decrease on ignition with oxygen, 11.08 cc. of carbon dioxide produced by ignition. The ratio, 1.53, between the decrease on ignition and carbon dioxide produced is very close to that which would be produced by 3.67 cc. of methane and 3.67 of ethane. If this mixture of gases had been analyzed by the method customarily used in this investigation, a decrease on ignition of 23.20 cc., and the formation of 20.52 cc. of carbon dioxide would have been found. This ratio is roughly the same as that usually obtained (Table I).

When the iron arc was substituted for the mercury the results in Table II are typical of those obtained.

TABLE II

DECOMPOSITION BY IRON ARC

Carbon dioxide in two hours, cc.	1.40	1.31
Decrease on ignition, cc.	0.24	0.23
Carbon dioxide produced by ignition, cc.	.14	.13

This shows that the higher percentage of short wave lengths from the iron arc produces a different type of decomposition from that produced by the mercury arc. It shows also that the mixture of gases produced above will change in composition with increasing age of the mercury arc. For these reasons, and because the length of time necessary to produce samples of this gas was so great, the experiment was not repeated.

Determination of Ethyl Alcohol.—Ethyl alcohol was found in substantial quantities. The amount was determined by the Bourcart-Kuriloff method.[11] This consists of oxidizing the alcohol to acetic acid by potassium dichromate and sulfuric acid at 100° in a sealed tube, treating the excess dichromate with potassium iodide and sulfuric acid and titrating the iodine by freshly standardized sodium thiosulfate. The applicability of the method to the present type of analysis was as follows. A solution containing 0.020 g. of ethyl alcohol was found to be equal to 8.75 cc. of 0.200 *N* dichromate; calcd. 8.69 cc. This was within the error in weighing out the 2 g. of alcohol from which the alcohol

[10] Analyzed with the aid of Dr. Huffman of this Laboratory, who has had much experience with this type of analysis.

[11] Poznanski, THIS JOURNAL, **50**, 981 (1928).

solution was prepared. It was found that oxidizable material equivalent to 0.33 cc. of 0.200 *N* dichromate would distil from the unirradiated lactic solution. This was due to impurities, as the second fraction distilling showed no reaction with dichromate. That all of the alcohol would distil was shown by putting 0.020 g. of alcohol into 16.2 cc. of lactic acid solution and distilling it according to the procedure below: dichromate used, 9.10 cc.; calcd. 0.33 cc. plus 8.75 cc. = 9.08 cc.

The 16.2 cc. of irradiated lactic acid solution was washed into a 100-cc. flask and 8.0 cc. of 20% sodium hydroxide added. Ten cc. was then distilled off through a short air-cooled reflux condenser in about thirty minutes. Typical determinations are given in Table III.

TABLE III

RATIO OF ALCOHOL TO CARBON DIOXIDE

Carbon dioxide produced in seven hours, cc.	20.10	21.70
0.200 *N* $K_2Cr_2O_7$ used, cc.	21.63	23.64
Moles of carbon dioxide produced $\times 10^4$	9.04	9.74
Moles of alcohol found $\times 10^4$	10.65	11.67
Carbon dioxide/alcohol ratio	1:1.18	1:1.20

Test for Acetaldehyde.—Although no aldehyde could be detected after any run, either in the solution or in the gases pumped out, one quantitative test for it was made. The Schiff's reagent was prepared by Alyea and Bäckström's method.[12] A lactic acid solution was irradiated, after all air had carefully been removed, for six and one-half hours with an intensity great enough to produce 21 cc. of carbon dioxide. The apparatus was so arranged that substances distilling from the solution were condensed and held in an unirradiated trap. The liquid from the trap was then returned to the reaction tube, the tube packed in ice and left for an hour. At the end of this period it was opened, the contents made up to a volume of 25 cc. and 10 cc. of Schiff's reagent added. For purposes of comparison a 0.0006 *M* aldehyde solution and a blank were prepared. To 25 cc. of the former (1.5×10^{-5} mole of aldehyde) 10 cc. of Schiff's reagent were added. The latter consisted of 25 cc. of distilled water plus 10 cc. of Schiff's reagent. The unknown solution developed no color and when compared in a colorimeter was identical with the blank. The 0.0006 *M* aldehyde solution developed a strong pink color.

The amount of carbon monoxide produced in this run must have been about 0.84 cc. If some of the lactic acid had decomposed into carbon monoxide and acetaldehyde this would correspond to a production of 4.0×10^{-5} moles of the aldehyde. It would seem that this amount of aldehyde would give a test even though most of it were destroyed by the action of the radiation.[13]

Discussion of Results

As the decomposition of lactic acid is approximately a quantum reaction, it was not possible to use monochromatic illumination and obtain appreciable quantities of the products. The radiation absorbed comprised so small a portion of the spectrum of the mercury arc that the error from this source in determining the quantum yield was not over 2%. The fact that several wave lengths were absorbed meant that several decomposition reactions were taking place concurrently. Exactly one hundred runs were

[12] Alyea and Bäckström, THIS JOURNAL, **51**, 97 (1929).

[13] Ellis and Wells, "The Chemical Action of Ultra-Violet Rays," **1925**, p. 155.

made, and, in each, as many products were investigated as could be tested in the same experiment. Successive runs only are used as examples in this paper.

Lactic acid, $CH_3CHOHCOOH$, might break up into a carbon dioxide and alcohol. It was found that this was the main decomposition, as 90.9% of the gas given off was carbon dioxide. Vigorous shaking of the reaction tube in addition to evacuation was found to be necessary to remove all of the carbon dioxide from the solution. The neglect of these precautions accounts, in part, for the erratic results of previous investigators. The amount of carbon dioxide found corresponded to a quantum yield of about 0.65 molecule per quantum. As the amount of radiation absorbed could not be satisfactorily determined, the error from this source may be as much as 10%. The other factors necessary to determine the quantum yield were measured to a much higher degree of accuracy.

The amount of alcohol found in the solution was 19% in excess of the quantity required by the assumption that the lactic acid decomposed into equal amounts of alcohol and carbon dioxide. The reason for this discrepancy has not yet been determined. In order to avoid removing alcohol vapor the gases were not as completely removed from the solution in cases where the alcohol content was to be determined as in other instances. The amount of carbon dioxide left in solution was very much less than the amount required to account for this discrepancy. As the alcohol was determined by oxidation of the distillate from a strongly alkaline solution of the reaction mixture, there might have been present other substances which were also oxidized but, as there was no aldehyde, it is difficult to imagine an impurity that could have been present. The method of determining alcohol was accurate to 0.5%. The quantum yield based on the amount of alcohol produced is about 0.77 molecule per quantum.

It is interesting to consider the reactions that took place other than the main decomposition into alcohol and carbon dioxide. The additional substances found in the gas were: (by volume) unsaturated compound (probably ethylene), 0.89%; carbon monoxide, 3.82%; methane (calculated), 2.18%; ethane (calculated), 2.18%. If one molecule of lactic acid is decomposed into ethylene, carbon dioxide would be produced in equal amounts. This would mean that 0.98% of the carbon dioxide came from this decomposition. If methane is one of the products formed, the other might be two molecules of carbon monoxide. The carbon monoxide found was 87% of that required by this decomposition. Carbon monoxide might also be formed by a decomposition giving acetaldehyde as the other product. As a quantity of the aldehyde much less than that required by this reaction could have been detected it was assumed that this decomposition did not take place. One molecule of the acid might give ethane and hydrogen peroxide or its decomposition products. No hydrogen peroxide was

found. Oxygen, in the few cases in which it was found, was accompanied by nitrogen and was assumed to have been the result of air leaking into the apparatus. Ethane might have been formed by the decomposition of two molecules of the acid, yielding ethylene glycol as the other product. No attempt was made to find this trace of ethylene glycol as the author's previous experience with this compound did not lead to the belief that it could be detected.

Summary

1. Lactic acid in water solution is decomposed by radiations of wave lengths shorter than 2500 Å. The chief products of decomposition by radiations from a quartz mercury arc are alcohol and carbon dioxide. Carbon monoxide, saturated hydrocarbons and unsaturated hydrocarbons form about 9% of the gaseous products.

2. Aldehyde, if produced, is present in quantities less than 1% of the total decomposition products.

3. The ratio between the energy absorbed and the carbon dioxide produced corresponds to a quantum yield of approximately 0.65.

4. More ethyl alcohol is produced than is required by the assumption that lactic acid decomposes into equal amounts of alcohol and carbon dioxide.

NEW HAVEN, CONNECTICUT

NEW BOOKS

Das Buch der grossen Chemiker. (The Book of the Great Chemists.) Edited by Dr. GÜNTHER BUGGE with the coöperation of special scholars. Vol. I. From Zosimos to Schönbein. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1929. xii + 496 pp. Illustrated. 16 × 24 cm. Price, unbound, M. 21; bound, M. 24.

This is a book for the chemist's leisure. The publisher's advertisement says that biographical essays in the history of chemistry have not before been published in the German language. The various chapters have been written by scholars who are well known for their researches in the history of chemistry and generally include the latest knowledge on the subjects with which they deal. The first volume brings the account nearly up to the middle of the nineteenth century, and contains chapters on Zosimos (Ruska), Jabir (Ruska), Albertus Magnus (Strunz), Roger Bacon (Strunz), Raymund Lull (Strunz), pseudo-Geber (Ruska), Biringuccio (Johannsen), Paracelsus (Strunz), Agricola (Darmstaedter), Libavius (Darmstaedter), pseudo-Basil Valentine (Fritz), Van Helmont (Strunz), Glauber (Walden), Boyle (Färber), Stahl (Koch), Boerhaave (Speter), Goeffroy the Elder (Speter), Marggraf (Speter), Black (Speter), Cavendish (Lockemann), Priestley (Lockemann), Scheele (Lockemann), Leblanc (Bloch), Lavoisier