tion, 6.5 g. of 4,4-dimethylpentine-1 and 5.2 g. of ethyl benzoate there was obtained 3.8 g. of a product boiling at 135–137° at 0.4 mm. pressure: d_4^{20} 0.9325; n_D^{20} 1.5080.

Anal. Subs., 0.2139: CO_2, 0.5979; H_2O, 0.1391. Calcd. for $C_{21}H_{28}O$: C, 85.14; H, 9.46. Found: C, 84.60; H, 9.59.

Diphenyl-ω-cyclohexylpropinylcarbinol.—From 21.6 cc. of 3.8 *N* ethylmagnesium bromide solution, 10.5 g. of cyclohexylpropine and 14.5 g. of benzophenone there was obtained 6 g. of product which boiled at 210–215° at 1.1 to 1.3 mm. pressure; d_4^{20} 1.058; n_D^{20} 1.5750. This product was redistilled at 0.003 mm. pressure and then boiled at 165–166°.

Anal. Subs., 0.2043: CO_2, 0.6505; H_2O, 0.1459. Calcd. for $C_{22}H_{24}O$: C, 86.84; H, 7.89. Found: C, 86.85; H, 7.99.

Phenyl-di-ω-cyclohexylpropinylcarbinol.—From 35 cc. of 4.2 *N* ethylmagnesium bromide solution, 18.5 g. of cyclohexylpropine and 11.4 g. of ethyl benzoate there was obtained 4 g. of this carbinol; b. p. 180–185° at 0.017 mm. pressure; d_4^{20} 1.014; n_D^{20} 1.5390.

Anal. Subs., 0.1986: CO_2, 0.6258; H_2O, 0.1635. Calcd. for $C_{25}H_{32}O$: C, 86.20; H, 9.19. Found: C, 85.94; H, 9.21.

Summary

1. Hexa-ω-*tert.*-butylpropinylethane has been prepared and has been found to be less readily cleaved by alkali metals than hexa-*tert.*-butylethinylethane. However, it decomposes with greater rapidity in the air.

2. Some new acetylenic carbinols having primary alkyl groups next to the acetylenic linkage have been described.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

PHOTOCHEMICAL OXIDATION OF LACTIC ACID[1]

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The present study is a development and a continuation of an investigation of the action of ultraviolet radiation on lactic acid. In the absence of oxygen it has been shown that the main products of the decomposition are ethanol and carbon dioxide.[2] It was felt that the conflicting results obtained by other investigators[3] of this decomposition were due to the presence of oxygen dissolved in the solution.

The decomposition of lactic acid in the presence of oxygen has never been fully investigated. Some workers[4] in this field have exposed solutions of lactic acid to sunlight and air and have obtained qualitative tests

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[1] A part of a paper presented at the Cincinnati meeting of the American Chemical Society.

[2] Burns, THIS JOURNAL, **51**, 3165 (1929).

[3] See Neuberg, *Biochem. Z.*, **39**, 163 (1912); Baudisch, *ibid.*, **103**, 59 (1920).

[4] See Ganassini, *Chem. Zentr.*, I, 387 (1913); I, 729 (1910); *Chemical Abstracts*, **5**, 3236 (1911); Ciamician and Silber, *Ber.*, **46**, 1558 (1913).

for acetic acid, pyruvic acid, acetaldehyde and carbon dioxide. Others[5] have exposed solutions of lactic acid containing uranyl sulfate and measured the amount of uranyl sulfate reduced and the amount of acetaldehyde formed.

In the present investigation a solution of lactic acid was shaken with oxygen while being exposed to the visible and ultraviolet radiation from a quartz mercury lamp. Radiation of wave length longer than 2890 Å. was only slightly absorbed. Thermochemical data[6] show that the decomposition of a dilute solution of lactic acid into dilute ethanol and a saturated solution of carbon dioxide evolves about 3.7 kilogram calories. The longest wave length of radiation that accomplishes this change is equivalent to 112 kilogram calories. It is not surprising that the ethanol formed under these conditions reacts with oxygen dissolved in the solution. The main products of the reaction are acetaldehyde, a peroxide and acetic acid. Quantitative data were obtained on all the above products, as well as on the other substances formed in smaller amounts. Ethanol and pyruvic acid were not found in the reaction mixture. The amount of oxygen used was determined.

Apparatus.—The apparatus was substantially the same as that previously described.[2] A Hullet gas buret[7] was introduced between the reaction vessel and the Töpler pump by means of a three-way stopcock in order to measure the amount of oxygen introduced. This buret and the gas analysis buret were in a water-bath kept at 25.0° by a thermostat. The shields between the mercury arc and the reaction vessel were removed so that the latter received the same amount of radiation over the full length of its stroke.

Experimental Part

Before all experiments, the quartz windows were cleaned with cleaning solution, the thermostat filled with distilled water, and the temperature brought to 25.0°. The reaction tube contained 21.38 cc. of 1.140 *N* lactic acid, enough to make it about half full. The rate of shaking was 310 r. p. m. with a 6-cm. stroke. With a total pressure of oxygen and water vapor of 760 mm., the solution dissolved 0.70 cc. (2.8×10^{-5} mole) of oxygen. The usual procedure was to evacuate the system, after the reaction vessel containing the solution had been attached, then to introduce a measured quantity of oxygen, start the shaking and illuminate the solution for one hour. During this time the pressure was held at 760 mm. and the decrease in the gas volume observed. Inasmuch as from 5 to 17 cc. of carbon dioxide remained dissolved in the solution, the decrease in volume was large. At the end of an hour the gas was about 50% oyxgen. The gas was then pumped into the gas analysis buret, the reaction vessel being shaken to remove the carbon dioxide in solution, and analyzed for carbon dioxide, decrease in volume on ignition, and carbon dioxide produced by ignition. The oxygen used was

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[5] See Neuberg, *Biochem. Z.*, **13**, 305 (1908); **29**, 279 (1910); Bolin, *Z. physik. Chem.*, **87**, 490 (1914); Müller, *Biochem. Z.*, **178**, 77 (1926).

[6] Meyerhoff, *ibid.*, **129**, 594 (1922); "International Critical Tables," Vol. V.

[7] Taylor and R. M. Burns, This Journal, **43**, 1275 (1921).

assumed to be the volume introduced minus the volume recovered. The volume recovered was taken to be the volume of the gases after the removal of the carbon dioxide minus the volume of carbon dioxide produced on ignition. The aldehyde produced had no effect on the gas analysis in the one-hour runs. In the following tables all gas volumes are corrected to the dry gas at 0° and 760 mm. All distillations and analyses were carried out in all-glass apparatus.

Dark Reaction Rate.—As far as could be observed there was no reaction in the dark.

Oxygen–Carbon Dioxide Ratio.—On illumination, the volume of the gas in the system was found to decrease with a slowly diminishing rate for about eighty-five minutes, followed by a sudden evolution of about 4 cc. of gas. For this reason the runs were limited to sixty minutes. Numbers 1 and 2 in Table I are the results of two runs which were continued for five hours with the gas in the system analyzed and fresh oxygen introduced each hour. Run 3 was made with 50% lactic acid. Tables II and IV include one-hour runs.

TABLE I

VALUES IN CC.

	Run 1				
	1st hour	2d hour	3d hour	4th hour	5th hour
Oxygen absorbed	16.7	21.9	23.7	26.0	27.4
Carbon dioxide produced	13.62	19.87	23.07	26.01	28.08
Decrease on ignition	0.13	0.13	0.27	0.28	0.30
Carbon dioxide by ignition	.20	.20	.25	.25	.31
	Run 2				
Oxygen absorbed	16.6	21.0	23.0	24.4	25.8
Carbon dioxide produced	13.16	19.43	22.04	24.00	25.07
Decrease on ignition	0.08	0.13	0.22	0.22	0.26
Carbon dioxide by ignition	.16	.16	.19	.21	.27
	Run 3				
Oxygen absorbed	38.5	34.2	35.2		
Carbon dioxide produced	27.17	29.53	33.47		
Decrease on ignition	0.18	0.27	0.28		
Carbon dioxide by ignition	.36	.62	.34		

Carbon Dioxide–Acetic Acid Ratio.—After the aldehyde and the alcohol had been removed from the reaction mixture by distillation through a fractionating column, the residue and washings of the column were made up to 100 cc. and distilled. Water was admitted as fast as it distilled out and the process continued until 300 to 500 cc. of distillate had collected. Preliminary experiments showed that the greater part of the acetic acid distilled with the first 250 cc. This distillate was divided into two equal portions, one titrated with barium hydroxide to find the total acidity, the other oxidized by the Bourcart–Kuriloff[8] method to determine the lactic acid which had also distilled. Under these conditions this amounted

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

to about one-third of the total acid distilling. Table II gives the results of one-hour runs. In order to be sure that the rate of shaking was not a limiting factor, Experiments 3 and 4 of Table II were carried out with half the usual quantity of lactic acid and with the shaking rate increased from 310 to 375 r. p. m. In five one-hour runs on the same sample of lactic acid, the yield of acetic based on carbon dioxide was 70.3%.

TABLE II

VALUES IN MOLES × 10^{-6}

Run number	1	2	3	4
Oxygen absorbed	888	819	670	585
Carbon dioxide produced	719	674	577	520
Decrease on ignition	3.5	4		
Carbon dioxide by ignition	6.3	7.6		
Acetic acid formed	536	507	452	400
Yield of acetic on carbon dioxide, %	74.5	75.2	78.4	77.0

Acetaldehyde–Acetic Acid Ratio.—No gas analyses were made in these experiments because of the danger of removing some of the aldehyde. The aldehyde and the alcohol were removed by distillation through a 15-cm. glass bead rectifying column and the residue analyzed in the usual manner. Half the aldehyde–alcohol mixture was analyzed by oxidation, half was analyzed for alcohol after the aldehyde had been removed by distillation from sodium bisulfite and the sulfurous acid removed by distillation from basic solution. At the same time two samples of lactic acid were similarly analyzed for alcohol. No correction was made for the amount of formaldehyde in the acetaldehyde. Colorimetric determinations indicated that a series of five one-hour runs produced over five times the amount of acetaldehyde that was produced in one hour.

TABLE III

VALUES IN MOLES × 10^6

Acetaldehyde	236	228
Ethanol	14	13
Ethanol in lactic acid	14	14
Acetic acid formed	597	612
Acetaldehyde oxidized to acetic acid, %	71.7	72.8

Peroxide Formation.—As soon as the period of illumination was over the contents of the tube were run into an acid solution of potassium iodide. At the end of an hour the liberated iodine was titrated. I and II were one-hour runs, III was a five-hour run with fresh oxygen supplied every hour.

I	5.12 cc. of 0.098 N $Na_2S_2O_3$ or 0.000251 moles of peroxide
II	5.40 cc. of .100 N $Na_2S_2O_3$ or .000270 moles of peroxide
III	4.56 cc. of .123 N $Na_2S_2O_3$ or .000280 moles of peroxide

When the reaction mixture was allowed to stand for forty-eight hours before analysis the peroxide content dropped to 0.00010 mole and the aldehyde to 0.00012 mole.

Formaldehyde.—The aldehyde fraction of the distillate from the reaction mixture turned Schiff's reagent blue in the presence of sulfuric acid. Formaldehyde gives this reaction while acetaldehyde does not. The approximate amount of formaldehyde present was determined by a colorimetric method based on this reaction. To one-quarter (5 cc.) of the distillate were added 5 cc. of 1 to 3 sulfuric acid and 5 cc. of basic fuchsin almost decolorized by sulfurous acid. The color developed was compared with that developed by 5 cc. of standard formaldehyde solution treated in the same manner. The concentration of the standard solution was determined by oxidation.

One-quarter of distillate was 1.24 stronger than the standard
One-quarter of distillate was 1.23 stronger than the standard
80 cc. standard = 0.56 cc. of 0.200 N $K_2Cr_2O_7$ or 0.000009 mole
10 cc. standard = 0.066 cc. of 0.200 N $K_2Cr_2O_7$ or 0.000008 mole

The residue from the distillation gave a test with Schiff's reagent. The substance giving this test was not identified.

Formic Acid.—No satisfactory test for formic acid in the presence of lactic and acetic acid was found. Formic acid reduces silver nitrate in acid solution while none of the known constituents of the reaction mixture does. The reaction mixture reduces silver nitrate, producing less silver than that reduced by 0.000004 mole of formic acid in a mixture containing lactic acid, formaldehyde and acetaldehyde in the same proportions as the reaction mixture. The residue of the reaction mixture which was left after steam distillation of the acetic acid did not reduce silver nitrate, while the distillate did so.

Quantum Yield.—The quantum yield in the decomposition reaction is probably between 0.5 and 1.0. Absorption measurements on the oxidation reaction mixture show that, after one hour of illumination, it absorbs about 35% more radiation than the lactic acid. These measurements were made with two thermopiles and galvanometers so that the amount of radiation from the lamp and the amount transmitted by the solution could be determined simultaneously. Several pairs of determinations were made in which the solution was exposed without oxygen for one hour, then oxygen was admitted and the solution exposed for another hour. An attempt was made to keep the radiation constant for each pair of runs. The results are given in Table IV.

Wave Lengths Absorbed.—The following absorption measurements were made in the reaction tube as soon as it was removed from the thermostat. Unoxidized lactic acid absorbed completely to 2535° Å. After one hour of oxidation it absorbed to 2894° Å., after five hours some of the

Table IV

Values in Cc.

	No O_2	O_2	No O_2	O_2	No O_2	O_2
	I		II		III	
Oxygen	..	16.3	..	14.7	..	15.4
Carbon dioxide	4.07	13.57	3.78	12.63	3.77	13.62
Decrease on ignition	0.54	0.18	0.52	0.11	0.40	0.13
Carbon dioxide by ignition	.63	.15	.63	.18	.48	.20
Times increase of carbon dioxide		3.33		3.34		3.61
Times increase in moles of gases		3.02		3.02		3.34

line at 2967 Å. The 50% lactic acid absorbed some of the 2700 Å. line at the start. The alkaline solution of sodium lactate absorbed some of the 3300 Å. line after four hours of oxidation.

Oxidation of the Lactate Ion.—A solution was prepared which contained two equivalents of sodium hydroxide to one of lactic acid, the lactic acid being in the same concentration as in the previous runs. The quantities of oxygen used per hour in a four-hour run were: 3.81, 3.12, 3.29, 2.96 cc.

Subsequent Dark Reactions.—After the gases had been removed the reaction mixture was allowed to stand in the dark for twenty-four hours, the gas formed during this time was removed, and the process repeated at the end of the next twenty-four hours.

Table V

Values in Cc.

	Run 1		Run 2	
	24 hours	48 hours	24 hours	48 hours
Carbon dioxide	2.36	0.65	1.86	0.66
Ignition	0.36	.06	0.38	.19
Carbon dioxide on ignition	.18	.03	.18	.10

Pyruvic Acid.—No pyruvic acid was found in the reaction mixture although the test used would have shown the presence of 5×10^{-5} mole.

Discussion of Results

On the basis of the amount of carbon dioxide evolved: the oxygen used was 118%; peroxide formed, 32%; pyruvic acid, none; carbon monoxide, 0.4%. As the oxidation was continued for longer periods, the carbon dioxide given off became equal to the oxygen used. The amount of peroxide in the solution remained constant after the first hour of oxidation. The aldehyde concentration increased. The above results are the only ones that represent the condition of the reaction mixture at the end of the period of irradiation. In the distillation which is necessary for the analysis of the other products, the peroxide may decompose or may react with certain constituents of the reaction mixture. The products isolated by distillation were acetic acid, 75% (on carbon dioxide);

acetaldehyde, 28%; formaldehyde, 1%; ethanol, none; formic acid, not more than 0.4%. When the solution was allowed to stand for forty-eight hours before analysis, an additional 12% of carbon dioxide was evolved, the peroxide content dropped to 10% and the aldehyde to 12%. The quantum yield in this reaction is several times that of the decomposition reaction without oxygen. The above figures are unavoidably subject to certain errors inasmuch as the amount of lactic acid decomposed was extremely small and the separation of the decomposition products from the undecomposed acid and from each other was difficult.

The results do not exclude the possibility that one of the reactions follows this course: the lactic acid is first decomposed into carbon dioxide and ethanol. The ethanol, which must contain part of the energy from the absorbed radiation, is then oxidized to acetaldehyde. This acetaldehyde is oxidized to acetyl peroxide, probably after the absorption of additional radiation. Bowen[9] has recently shown this to be the case with acetaldehyde and oxygen alone. The acetyl peroxide subsequently reacts with acetaldehyde to give acetic acid. In order to account for the amount of oxygen used it would be necessary to assume the formation of some compound other than those described. No such compound could be identified although the reaction mixture contained a non-volatile reducing agent. Work is now being undertaken on propionic acid in the hope that this point will be cleared up. A similar decomposition of pyruvic acid shows that the reaction proceeds in a manner which is entirely unlike that of lactic acid.

Summary

1. When lactic acid is decomposed by ultraviolet radiation in a solution containing dissolved oxygen, the chief products are carbon dioxide, acetaldehyde, a peroxide and acetic acid. The amount of each of these decomposition products has been measured.

2. Neither ethanol nor pyruvic acid is formed.

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[9] Bowen and Tietz, *J. Chem. Soc.*, **132**, 234 (1930).