

substance answering the description given by Wagner and Tollens is formed by the action in sealed tube of cold, liquid, anhydrous ammonia upon  $\alpha,\beta$ -dibromopropionic acid. The latter fact points to the possibility of decomposing the dibromopropionic acid by ammonia and forming polymeric compounds of colloidal nature by passing through  $\alpha$ -bromoacrylic and propiolic acids.

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## THE OXIDATION OF PROPYLENEGLYCOL. I. THE ACTION OF ALKALIN POTASSIUM PERMANGANATE GIVING CARBONIC, ACETIC AND OXALIC ACIDS.

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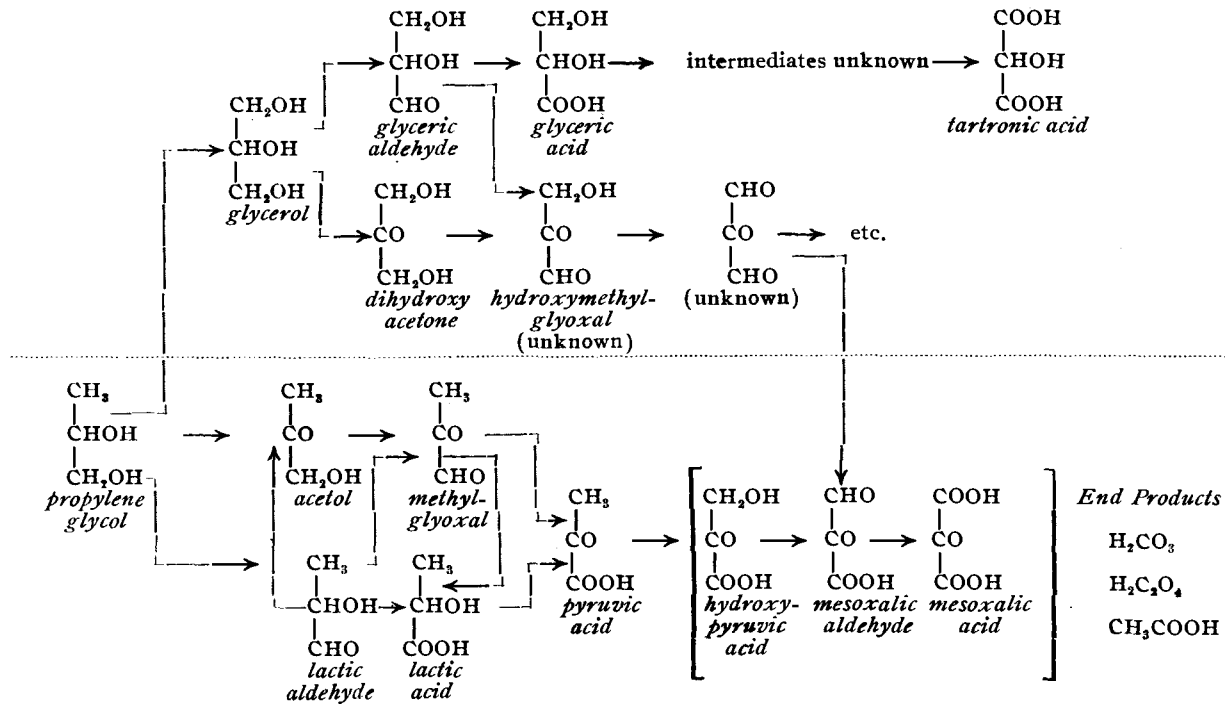
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The purpose at the beginning of these experiments was to find some conditions under which lactic aldehyde,  $\text{CH}_3\text{CHOH}\cdot\text{CHO}$ , is formed by the oxidation of propylene glycol,  $\text{CH}_3\text{CHOH}\cdot\text{CH}_2\text{OH}$ . Lactic aldehyde has never been prepared by direct oxidation. It was, however, synthesized in 1908, by A. Wohl and M. Lange.<sup>1</sup> They took dichloroacetic acid which with sodium ethylate gave ethyl diethoxyacetate; this, when condensed with piperidine, gave a piperidide, which on treatment with  $\text{MgICH}_3$  by Grignard's general method, gave methylglyoxalacetal,  $\text{CH}_3\text{COCH} : (\text{OC}_2\text{H}_5)_2$ . The glyoxal derivative reduced with sodium gave the acetal of lactic aldehyde, which, when hydrolyzed with 0.1*N* sulfuric acid, gave the free aldehyde. The derivatives and properties of lactic aldehyde recorded by these workers make the identification of lactic aldehyde relatively simple. Lactic aldehyde has also been synthesized more recently by Dr. Cyrill Krauz of Prague.<sup>2</sup> He took *unsym*-dichloroacetone from which pyruvic aldehyde acetal was prepared. This, on reduction of the ketone group and on subsequent hydrolysis gave lactic aldehyde. In cases where it is impossible to find lactic aldehyde in the oxidation products it would be interesting to learn if this substance represents one of the intermediate stages of oxidation.

In the accompanying table the possible oxidation products of propylene glycol are given. No reference was found in the literature concerning the oxidation of propylene glycol to glycerol. The second stage, glyceric aldehyde and dihydroxyacetone from glycerol, has been brought about variously by the action of nitric acid, platinum black, hydrogen peroxide in the presence of ferrous iron, bromine and soda, bromine vapor on lead glycerate, action of quinone on aqueous solutions in the sunlight or the illumination

<sup>1</sup> *Ber.*, 41, 3612.

<sup>2</sup> *Chemische Listy*, 5, 323-7; *C. A.*, 6, 739.



of glycerol solutions containing uranyl sulfate as an oxygen carrier.<sup>1</sup> The transformation of glycerol to glyceric acid has been accomplished by means of nitric acid, mercuric oxide and barium hydroxide or silver chloride and sodium hydroxide.<sup>2</sup> Tartronic acid, in small amounts, is obtained by the oxidation of glycerol with aqueous potassium permanganate,<sup>3</sup> and by the use of nitric acid.<sup>4</sup> The other possible oxidation products of glycerol are unknown and therefore only a few of them are given in the table. It is evident that the formation of the whole series of compounds lying above the dotted line would involve the oxidation of a methyl group in preference to a secondary alcohol,  $\text{CHOH}$ , or primary alcohol,  $\text{CH}_2\text{OH}$ , group in the propyleneglycol molecule. This kind of a case seems very rare, if known at all. Weyl<sup>5</sup> states that the direct oxidation of a methyl group to a *secondary* alcohol group is impossible and that the oxidation of a methyl group to an aldehyde group is very rarely carried out in the aliphatic series. The one exception mentioned is the oxidation of acetaldehyde,  $\text{CH}_3\text{CHO}$ , to glyoxal,  $\text{CHO-CHO}$ , by means of nitric acid.<sup>6</sup> It is also stated that the smooth oxidation of a methyl group to a carboxyl group is seldom observed in the aliphatic series.<sup>7</sup> Hetper, in recent work on the oxidation of a very large number of organic compounds with potassium permanganate in the presence of phosphoric acid, found that the methyl groups tend to persist as acetic acid and that the acetic acid formed could be used to determine the number of such methyl groups originally in the compound.<sup>8</sup> It is therefore clear that the oxidation above the dotted line will not be of frequent occurrence.

If we assume that the secondary alcohol group is first oxidized, leaving the rest of the molecule intact, we get acetol. Kling<sup>9</sup> oxidized propyleneglycol to a mixture of acetol and some methyl glyoxal by the action of bromine in sunlight. The methylglyoxal was identified by means

<sup>1</sup> See Deen, *Jahresber.*, 1863, 501; Fischer and Tafel, *Ber.*, 20, 1089, 2566, 3384; 21, 2634; 22, 106; Grimaux, *Compt. rend.*, 104, 1276 (1887); Stone and McCoy, *Am. Chem. J.*, 15, 656; Harries, *Ber.*, 36, 1936; Tarugi, *Gazz. chim. ital.*, 36, I, 343 (1906); Fenton and Jackson, *J. Chem. Soc.*, 75, 4; Ciamician and Silber, *Atti Accad. Lincei*, [5] 10, I, 93; Wohl and Neuberg, *Ber.*, 33, 3098, 3109; Piloty and Ruff, *Ber.*, 30, 1663; Neuberg, *Biochem. Z.*, 13, 316 (1908).

<sup>2</sup> *Ber.*, 9, 1902; 10, 267; 14, 2071; 18, 3357; 29, R. 545.

<sup>3</sup> Campani and Rizzari, *Jahresber. Fortschr. Chem.*, 1880, 787; *Gazz. chim. ital.*, 12, 1.

<sup>4</sup> Sadler, *Ber.*, 8, 1456.

<sup>5</sup> "Methoden der Organ. Chem.," Bd. 2, I Abt. p. 5, Verlag von Georg Thieme (Leipzig), (1911).

<sup>6</sup> de Forcrand, *Bl.*, 41, 240 (1884); *Ber.*, 17, 168 (1884).

<sup>7</sup> Weyl, *Loc. cit.*, p. 9.

<sup>8</sup> *Bull. Intern. Sci. Cracovie*, 1910, A. 601; *Z. anal. Chem.*, 50, 343-70; *C. A.*, 5, 2845.

*Compt. rend.*, 129, 220.

of its oxime. Methylglyoxal has been prepared in quantities by Denis<sup>1</sup> by the action of cupric acetate on acetol at room temperature. Methylglyoxal, even in its polymeric form, has a great tendency to rearrange<sup>2</sup> into lactic acid<sup>3</sup> even in the presence of oxidizing agents. Pyruvic acid has not been prepared from methylglyoxal, from propylene glycol nor from acetol, but there seems to be no good reason why it could not. However, lactic acid has been oxidized by Beilstein and Weigand<sup>4</sup> to pyruvic acid by the action of insufficient potassium permanganate on calcium lactate.

If, on the other hand, we assume that the primary alcohol group,  $\text{CH}_2\text{OH}$ , is first oxidized in preference to the other two groups, the first oxidation stage must be lactic aldehyde. There is no *a priori* reason why this could not take place. This type of reactions is carried out very frequently and easily in the case of the higher aliphatic alcohols in the preparation of the corresponding acids (see preparation of mannonic acid from mannitol, gluconic acid and gulonic acid from sorbitol and many others; also glyceric acid from glycerol). Nef<sup>5</sup> states that if lactic aldehyde were formed as an oxidation product it would immediately rearrange to acetol. He believes that he found traces of lactic acid on oxidizing propylene glycol with silver chloride in the presence of alkalis,<sup>6</sup> but attributes its formation to the oxidation of small amounts of lactic aldehyde before rearrangement took place. Finally, Würtz<sup>7</sup> found that platinum black acting on propylene glycol gave lactic acid.

In pyruvic acid everything is oxidized except the methyl group. If we disregard the statements made above and assume that the methyl group is oxidized without disruption of its molecule, we would get hydroxypyruvic acid, which is known,<sup>8</sup> but has never been prepared in this way, then mesoxalic aldehyde, which is unknown, and finally mesoxalic acid. This explanation of the oxidation of compounds such as acetol, lactic acid, pyruvic acid, etc., is favored by Denis.<sup>9</sup> Against this supposition is the statement<sup>10</sup> that the only possible oxidation products of dihydroxy-primary-secondary alcohols are aldehyde-alcohols, ketone-alcohols, ketone-aldehydes, alcohol-acids and ketone-acids. Moreover,

<sup>1</sup> *Am. Chem. Jour.*, **38**, 583.

<sup>2</sup> See Nef, *Ann.*, **335**, 271, 272; **357**, 215, 231, 299, 302, etc.; Evans, *Am. Chem. J.*, **35**, 115; Evans and Brooks, *THIS JOURNAL*, **30**, 404; Evans and Witzemann, *Ibid.*, **33**, 1772.

<sup>3</sup> Denis, *Ibid.*, 584-5.

<sup>4</sup> *Ber.*, **17**, 840. Compare *Am. Chem. J.*, **35**, 130.

<sup>5</sup> *Ann.*, **335**, 313.

<sup>6</sup> *Ibid.*, 315.

<sup>7</sup> *Ann. chim. phys.*, [3] **55**, 443 (1859).

<sup>8</sup> *Ber.*, **24**, 401.

<sup>9</sup> *Am. Chem. J.*, **38**, 575.

<sup>10</sup> Bernthsen, *Kurzes Lehrbuch der Org. Chem.*, 9th ed., p. 220.

it is expressly stated that dibasic acids  $C_n$ , or dialdehydes  $C_n$ , are not formed. This would exclude mesoxalic acid.

Other oxidations of propyleneglycol which have been made in which the three carbon atom molecule is broken up, with the formation of acetic or oxalic acids and carbon dioxide, are as follows: With nitric acid<sup>1</sup> propyleneglycol gives oxalic acid (and presumably carbon dioxide) exclusively. When treated with potassium permanganate,<sup>2</sup> acetic and carbonic acids are obtained. Flawitzky,<sup>3</sup> by the use of potassium dichromate, and Nef,<sup>4</sup> by the use of silver chloride and silver oxide with and without alkali, obtained the same.

#### Experimental Part.

*Methods of Analysis.*—The methods of analysis were all simple applications of well known methods and facts to the immediate requirements of these experiments.<sup>5</sup> Unless otherwise stated, in all cases in which the quantitative method used did not prove the identity of the substance, the products found were identified by their usual qualitative reactions.

The carbonic acid was always determined by precipitating barium carbonate from saturated barium hydroxide solution.<sup>6</sup> A 500 cc. balloon flask was supplied with a rubber stopper containing a glass tube and a dropping funnel, both of which extended to the bottom of the flask, and a return flow condenser. The top of the condenser was connected with five gas wash bottles, containing saturated barium hydroxide, the last one being connected with a suction pump. The air which was circulated through the apparatus entered the balloon flask by way of a long tube filled with soda lime and three gas wash bottles charged with concentrated sodium hydroxide solution. Blanks run with the apparatus from time to time showed that the carbon dioxide of the air was effectively excluded. Test experiments with known amounts of sodium carbonate showed that results obtained by filtering off the barium carbonate formed, and weighing in a tared filter paper were easily obtained accurate to one or two per cent. of the carbon dioxide being determined.

The acetic acid was determined by taking a known portion of the solution to be tested, adding an excess of 0.5 *N* hydrochloric acid and distilling the solution in the ordinary vacuum distillation apparatus, using a long, well cooled condenser. The distillate was carefully titrated with standardized potassium hydroxide solution, a known portion of this was taken, the color of phenolphthalein was discharged with a small drop of very dilute sulfuric acid, 1.0 cc. of 5% potassium chromate solution was

<sup>1</sup> Beilstein, Vol. I, 261.

<sup>2</sup> Würtz, *Ann. chim. phys.*, [3] 55, 447.

<sup>3</sup> *Ber.*, 11, 1256.

<sup>4</sup> *Ann.*, 335, 312-4.

<sup>6</sup> See also Denis, *Am. Chem. J.*, 33, 562.

<sup>5</sup> This is a slight modification of Nef's method, *Ann.*, 357, 220.

then added and the solution titrated for chlorides by the well known method, using 0.50 *N* silver nitrate solution. The silver nitrate was calculated to its hydrochloric acid equivalent and subtracted from the potassium hydroxide. This would leave the rest of the potassium hydroxide to be calculated to acetic acid, provided it was known that no formic acid was present. Moreover, the application of this method depended on preliminary qualitative tests as to the presence of other interfering compounds. Check experiments with known amounts of sodium carbonate, sodium acetate and oxalic acid proved the method to be correct within one to two per cent of the acetic acid present.

Formic acid was tested for in every case by using a modification of Jones' method<sup>1</sup> on a portion of the neutralized distillate by making the solution alkaline with about 1.0 gram sodium carbonate and adding standard potassium permanganate till a pink color permanent in warm solution was obtained. The method would have been more simple if it had been possible to add an excess of potassium permanganate and titrate back with oxalic acid in the presence of sulfuric acid, but this was not permissible because acetic acid is only stable to potassium permanganate in alkaline solution. Formic acid in the presence of acetic acid was, however, not found in the experiments with potassium permanganate.

To determine the oxalic acid the residue from the acetic acid was dissolved in water to which an excess of a calcium acetate solution was added. The mixture was warmed until the precipitate became crystalline. It was then filtered off, dissolved in dilute sulfuric acid and titrated for oxalic acid by the well known method. Test experiments proved the method to be accurate to within one to two per cent of the amount present.

The distillation is carried out *in vacuo* because the error due to a solution of carbon dioxide in the condensate is thus avoided. The loss of acetic acid due to the loss of vapor by the use of suction is negligible in these experiments because the acetic acid never exceeded 0.1 to 0.2% of the water in the solution. This error increases systematically as the percentage of acetic acid in the solution increases, so that the application of the method in this way is limited to cases where the constituents are known and the percentage of acetic acid very small. Hydrochloric acid was used to decompose the salts because it would not affect the nonvolatile products chemically as the solution becomes concentrated. The oxalic acid was precipitated in order to remove it from other oxidizable compounds which might be formed in the oxidation. The calcium salt was selected because it was found by experiment that the calcium salts of lactic and pyruvic acids are soluble under these conditions and would therefore not be confused with oxalic acid.

<sup>1</sup> *Am. Chem. J.*, 17, 539; also *Ber.*, 27, 1061; *Ann. chim. phys.*, [3] 55, 374 (1859). *Monatsh.*, 14, 746 (1893).

### Action of Potassium Permanganate on Propyleneglycol in Alkaline Solution.

In attempting to establish the conditions whereby propyleneglycol might yield lactic aldehyde, oxidation studies were first undertaken in order to throw light on the mechanism of the reaction. It is then intended to follow these with experiments in which milder oxidizing agents will be used.

The first oxidizing agent studied was potassium permanganate in potassium hydroxide solution. The conditions of the experiments and the results obtained follow: From previous experiments of other workers on propyleneglycol,<sup>1</sup> and especially on related substances<sup>2</sup> there was every reason to expect carbonic, acetic and oxalic acids as the sole products of the oxidation. Würtz did not work with alkaline solution and therefore probably did not obtain oxalic acid. In fact, the only reagent on record which is known to give oxalic acid as an oxidation product of propyleneglycol is nitric acid.<sup>3</sup>

*Potassium Permanganate, Potassium Hydroxide and Propyleneglycol.*—

(a) A solution of 4.48 grams (1 mol.) of propyleneglycol in 30 cc. of water was added slowly to a mixture of 28.62 grams of potassium permanganate and 24.75 grams (7.5 mols.) of potassium hydroxide dissolved in 1000 cc. of water. The time required for this procedure was 45 minutes, the temperature at the beginning of the experiment being 16°, while at the close it was 31°. The reaction mixture having stood at room temperature for two days, at the end of which time the green color of the potassium manganate had disappeared, the oxide of manganese was filtered off. The volume of the filtrate and washings came to 1165 cc. On analysis 100 cc. of this solution yielded 0.91 gram of barium carbonate<sup>4</sup> or 2.26 grams of carbon dioxide in all. The distillate, obtained by treating another 100 cc. of the filtrate with hydrochloric acid, as indicated in the above method of analysis, required 15.05 cc. of 0.87 *N* potassium hydroxide solution for neutralization, and 12.93 cc. of 0.87 *N* silver nitrate solution for the complete precipitation of the chlorine as silver chloride. Therefore, 2.12 cc. of 0.87 *N* potassium hydroxide was required for the acetic acid, or a total of 1.284 gram of acetic acid. The residue from

<sup>1</sup> Würtz, *Ann. chim. phys.*, [3] 55, 447 (1859).

<sup>2</sup> Cochenhausen, *J. prakt. Chem.*, [2] 58, 454; *Z. angew. Chem.*, 1899, 110; Dumas, Stas, Gottlieb, *Ann.*, 52, 130; Hercz, *Ann.*, 165, 257; Ulzer and Seidel, *Monatsh.*, 18, 138; Baeyer, *Ann.*, 131, 298; Nef, *Ann.*, 335, 191-333; Beilstein, *Ber.*, 17, 841; Denis, *Am. Chem. J.*, 38, 561-94, etc.

<sup>3</sup> Beilstein, Vol. I, 261.

<sup>4</sup> 13.13 grams of the potassium hydroxide used gave 0.24 gram of barium carbonate. In all determinations of carbon dioxide the amount of barium carbonate corresponding to the KOH used in the experiment was subtracted from the total barium carbonate found.

the distillation contained oxalic acid equivalent to 48.65 cc. of 0.0987 *N* potassium permanganate solution, or a total of 2.461 grams of oxalic acid. In this experiment the carbon content of the products of reaction is equal to 84% of that of the propyleneglycol used. A repetition of the experiment with a temperature range of 20° to 28° yielded 1.841 grams of carbon dioxide, 1.325 grams of acetic acid and 2.56 grams of oxalic acid, or a total equivalent to 81% of the propyleneglycol used.

(b) Having thus found that the results in the case of propyleneglycol are the same as those obtained with related substances when oxidized with alkalin solutions of potassium permanganate, it was thought desirable to learn if the experiences of Cochenhausen with acetone<sup>1</sup> would be true for propylene glycol. Attempts to determine quantitatively the unchanged propyleneglycol in the above experiments were not successful. The Baumann-Schotten reaction as used for the determination of glycerol by Piloty<sup>2</sup> and others gave a solid benzoyl derivative but not sufficiently quantitative in yield for these experiments. It was therefore necessary to add no more propyleneglycol than was needed to consume the oxidizing agent. For this purpose an oxidizing solution was prepared containing 28.62 grams of potassium permanganate and 49.50 grams of potassium hydroxide dissolved in the minimum amount of water (1162 cc.). To 500 cc. of this reagent, corresponding to 12.31 grams of potassium permanganate and 21.29 grams of potassium hydroxide, was added a solution of 2.24 grams of propyleneglycol dissolved in 25 cc. of water, the temperature ranging from 15° to 20°. After the reaction was complete the filtrate (665 cc.) from the oxide of manganese was found to possess no characteristic odor. On analysis, 100 cc. of the solution yielded 0.70 gram of barium carbonate, corresponding to a total of 0.953 gram of carbon dioxide (74.4% of one-third of the carbon). The distillate obtained from an acidulated portion of 100 cc. of the filtrate required 13.5 cc. of 0.87 *N* potassium hydroxide solution for neutralization and 12.17 cc. of 0.87 *N* silver nitrate solution for the chlorine. The acetic acid therefore required 1.33 cc. of 0.87 *N* potassium hydroxide solution, or a total of 0.465 gram (theory = 1.76 grams) of acetic acid (26.4%). The oxalic acid in the residue required 44.4 cc. of 0.0987 *N* potassium permanganate, or a total of 1.3 grams (theory = 2.65 grams) of oxalic acid. The total products are equivalent to 74.5% of the propyleneglycol used. When the products are calculated to the amount of potassium permanganate necessary to produce them, it is found that 3.28 grams are required for the acetic acid and 10.68 grams for oxalic acid, or a total of 13.91 grams, which is 1.60 grams in excess of the amount used.

<sup>1</sup> *J. prakt. Chem.*, [2] 58, 454.

<sup>2</sup> *Ber.*, 30, 3167 (1897).



(c) The question now arose as to whether a varying concentration of the alkali might not diminish the amount of acetic acid formed. Owing to the small solubility of potassium permanganate it is obvious that a greater concentration of the reagents than used in the above experiment could not be obtained in cold water. Therefore the procedure used in the following experiment was adopted: To a solution of 65 grams of potassium hydroxide in 500 cc. of water were added 2.46 grams of propyleneglycol. Potassium permanganate was added to this mixture at the rate of one or two crystals at a time until no more was dissolved by the solution. The reaction mixture was shaken frequently as the potassium permanganate tended to become covered with the oxide of manganese, thus hindering solution. After two months of slow reaction in this way, it was found that potassium permanganate was no longer being used, and the oxide of manganese was filtered off, the total volume of the filtrate being 500 cc. On analysis, an aliquot part of this solution was found to contain 1.41 grams of carbon dioxide, an amount which is 99% of that demanded by the theory. When 50 cc. of the filtrate were treated with an excess of hydrochloric acid and distilled *in vacuo*, 18.1 cc. of 0.0857 *N* potassium hydroxide solution were required for neutralization, and 11.1 cc. of 0.0867 *N* silver nitrate solution for the chlorine determination, thus giving 7 cc. of the alkali solution for the acetic acid or a total of 0.364 gram. The residue gave oxalic acid equivalent to 53.96 cc. of 0.969 *N* potassium permanganate solution, or 2.36 grams of oxalic acid in all. This is 18.7% of the theoretical amount of acetic acid and 81% of the theoretical amount of oxalic acid. When the products are again calculated to the amount of potassium permanganate necessary to produce them there is obtained 2.55 grams for acetic acid, 19.3 grams for oxalic acid, or a total of 21.85 grams. This is 21% in excess of the amount used.

(d) The following experiment was carried out to determine the influence of temperature on the character of the products formed and also to completely oxidize the propyleneglycol used. To a solution of 24.62 grams of potassium permanganate and 42.58 grams of potassium hydroxide in 1000 cc. of water was added 3.36 grams of propyleneglycol dissolved in about 30 cc. of water. The reaction mixture immediately became warm and after standing at room temperature for an hour was placed on the hot plate (55°–70°) until the solution had decolorized. An additional amount (1.5 grams) of potassium permanganate was added in small portions till the color became just permanent. The filtrate and washings came to 1000 cc. The distillate from acidulating 50 cc. of the filtrate as above required 1.92 cc. of 0.435 *N* potassium hydroxide solution for the acid and 8.27 cc. of 0.05 *N* silver nitrate solution for the chlorine. This corresponds to a total of 0.504 gram of acetic acid (theory

= 2.64 grams). The oxalic acid in the residue required 29 cc. of 0.0969 *N* potassium permanganate, which corresponds to a total of 2.53 grams (theory = 3.97 grams) of oxalic acid. When analyzed for carbon dioxide, 50 cc. yielded 0.62 gram of barium carbonate, or 2.6 grams of carbon dioxide in all. When the total carbon content (1.58 grams) of the products obtained is compared with that of the propyleneglycol used (1.59 grams) it is seen that the reaction is practically quantitative (99.3%). An examination of the results of this experiment shows that the total yield of oxalic and acetic acids is but 82.8% of that demanded on the assumption that two-thirds of the carbon content of the propyleneglycol used is converted to equivalent amounts of these acids, while one-third is converted to the equivalent amount of carbon dioxide. Furthermore, it is seen that the carbon content (0.71 grams) of the carbon dioxide obtained is 46.4% of that of the propyleneglycol used and not 33.3% as demanded by the above assumption. That the excess of carbon dioxide cannot come from the oxidation of potassium acetate formed in the reaction is rigidly proven by the experiment of Denis,<sup>1</sup> which has been repeated and confirmed during the progress of this work. The amount of potassium permanganate required for each of the above substances is as follows: for acetic acid 3.49 grams, for oxalic acid 20.7 grams, for carbon dioxide 6.7 grams, or a total of 30.8 grams, or 6.22 grams in excess of the amount used.

#### Partial Summary.

No.	Propylene grams.	KOH grams.	KMnO <sub>4</sub> grams.	H <sub>2</sub> O cc.	CO <sub>2</sub> grams.	Acetic acid grams.	Oxalic acid grams.	Percentage recovered
a.....	4.48	24.75	28.62	1000	2.26	1.284	2.461	84.0
	4.48	24.75	28.62	1000	1.84	1.325	2.56	81.0
b.....	2.24	21.29	12.31	500	0.953	0.465	1.3	74.0
c.....	2.46	65.0	17.95	500	1.41	0.364	2.36	100.0
d.....	3.36	42.58	24.62	1000	2.60	0.504	2.53	99.0

The numerical results of the above experiments are summarized in the table. From them we may draw the following conclusions:

(1) That the results obtained in the oxidation of propyleneglycol are the same as those obtained with related substances when oxidized with alkaline permanganate: namely, that the sole end products are carbon dioxide and acetic and oxalic acids.

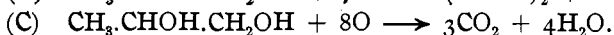
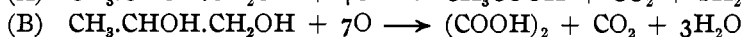
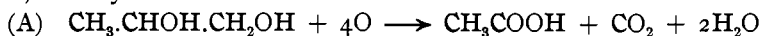
(2) That the ratio of oxalic acid to acetic acid (as in (a)) can be increased by the addition of more alkali as shown by experiments (b) and (c). This verifies Cochenhausen's experiments with acetone,<sup>2</sup> in which he found that he could increase the ratio of oxalic acid to acetic acid but could not get 100% of the possible oxalic acid, assuming the products to be only oxalic and carbonic acids.

<sup>1</sup> *Am. Chem. J.*, **38**, 572.

<sup>2</sup> *J. prakt. Chem.*, [2] **58**, 454.

(3) That when the alkali concentration is high and the temperature high as in experiment (*d*), the molecule of propyleneglycol tends to break up and a disproportionate amount of carbon dioxide is formed. This result was entirely unexpected.

(4) That since potassium oxalate and potassium acetate are both stable toward potassium permanganate and since therefore the former cannot be produced by the oxidation of the latter, under these conditions, and because of the observation noted in (3), there must be at least three reactions taking place in such an experiment as (*d*), and two (A and B) in the others, namely:



(5) It is evident that if lactic aldehyde is one of the intermediate products in the oxidation of propyleneglycol with potassium permanganate in alkaline solution, it must undergo immediate oxidation to carbon dioxide, oxalic and acetic acids.

The formation of an excess of carbon dioxide in Experiment (*d*) furnished a suggestion which was worked out as follows:

#### **Action of Potassium Permanganate on Lactic and Pyruvic Acids in Alkaline Solution.**

Similar experiments to the above were carried out on lactic and pyruvic acids in the hope that the results would serve as a key to the mechanism of the oxidation of propylene and its intermediate products.

If it could be shown, for example, that lactic acid does not give the excess of carbon dioxide but that pyruvic acid does, then it would be clear that lactic acid is not an intermediate stage in the oxidation of propyleneglycol under these conditions. If, on the other hand, both should fail to give the excess of carbon dioxide, then it would appear that lactic aldehyde could not be an intermediate product in the reaction producing this excess of carbon dioxide. Also other important conclusions concerning the course of the reaction in the formation of acetic and oxalic acids could be arrived at.

The best results of this kind that are given in the literature are those of Denis.<sup>1</sup> "Lactic acid, 11.1 grams of 87.1% acid, in 50 cc. water, was added to a solution of 57 grams of potassium permanganate and 54.6 grams (9 mols.) potassium hydroxide in 1.1 liters water. . . . . after two days standing the mixture was heated for two hours in a bath kept at 60°. The amount of carbon dioxide formed was not determined, but 12.6 grams of crystallized oxalic acid, which is 94% of the amount demanded by theory, were obtained."

<sup>1</sup> *Am. Chem. J.*, 38, 577.

(e) Since it was essential to know the amount of carbon dioxide formed, the above experiment was repeated, using the same amount of reacting materials except that 13.25 grams of a 73% lactic acid solution (determined by titration of the free acid) known as Merck's Highest Purity (75%) was used. On the addition of the lactic acid the flask became almost too warm to hold with comfort. After cooling and allowing to stand for two days, during which time one gram more of potassium permanganate was added and was promptly decolorized, thus showing that oxidation of the lactic acid was not complete, the manganese dioxide was filtered off. The filtrate and washings from the manganese dioxide totaled 1150 cc. When 50 cc. were analyzed in the usual way for acetic acid 10.05 cc. of 0.091 *N* potassium hydroxide solution and 10.65 cc. of 0.05 *N* silver nitrate solution, or a total of 0.54 gram of acetic acid, was found (theory = 6.44 grams, therefore 8.3%). This result was repeatedly obtained. The residue from the distillation required 80.65 cc. of 0.096 *N* potassium permanganate solution. As a check it was found that the oxalic acid in 100 cc. of the above filtrate required 161.13 cc. of potassium permanganate solution, these results corresponding therefore to 8.10 grams and 8.06 grams of oxalic acid, respectively (theory = 9.67 grams), or 83.7% of that possible. The carbon dioxide in 50 cc. yielded 1.22 grams of barium carbonate, or, after deducting for the carbon dioxide of the potassium hydroxide, 5.99 grams of carbon dioxide from the lactic acid used. As a check on the above analysis, the amounts of potassium permanganate necessary to produce each of the above substances were found to be 1.87 grams for the acetic acid, 47.39 grams for the oxalic acid, and 7.91 grams for the carbon dioxide, or 57.17 grams in all as compared with 58 grams used.

On the assumption that the amount of carbon dioxide formed should be equivalent to one-third of the carbon content of the lactic acid used, the above amount of carbon dioxide (5.99 grams) is 1.28 grams in excess. This excess of carbon dioxide was not expected.

From the fact that oxidation in the above experiment was incomplete it was supposed that there was some dehydration product of lactic acid present which caused an error in the determination of the strength of the acid found by acidimetry. This may have been due to lactide,

$$\begin{array}{c} \text{CO.O.CH.CH}_3 \\ | \qquad | \\ \text{CH}_3\text{.CH.O.CO} \end{array}$$

which is formed in the distillation of lactic acid,<sup>1</sup> or on heating to 150° and passing dry air through it,<sup>2</sup> or it may have been lactic anhydride which is formed on heating lactic acid to 130–140°<sup>3</sup>, or

<sup>1</sup> J. Gay-Lussac, Pelouze, *Ann.*, 7, 43; Pelouze, *Ann.*, 53, 116; Englehardt, *Ann.*, 70, 243, 245.

<sup>2</sup> Wislicenus, *Ann.*, 167, 318.

<sup>3</sup> Pelouze, *Ann.*, 53, 114; Englehardt, *Ibid.*, 70, 242.

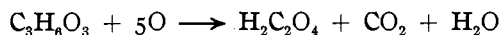
even in the cold,<sup>1</sup> but which goes back to lactic acid at once in the presence of alkali. Or it may have been due to both. In order to be certain that it was not the presence of one or both of these compounds that caused the formation of the small amount of acetic and the excess of carbon dioxide the following experiment was performed:

(f) Zinc lactate<sup>2</sup> was prepared by dissolving zinc carbonate in the lactic acid referred to above. This solution was filtered and the salt was purified by fractionally crystallizing from a hot concentrated solution. This operation was repeated several times. For the experiment, 9.95 grams of zinc lactate, which had been dried to constant weight, were dissolved in about 200 cc. of water and treated with an excess of sodium carbonate solution. After removing the zinc carbonate by filtration, acidifying the filtrate with hydrochloric acid and boiling to get rid of last traces of carbon dioxide, the resulting solution was made just alkaline with potassium hydroxide. After diluting with water to 837 cc., 41.3 grams of potassium hydroxide were added and the resulting solution heated to 60–80° at which temperature it was kept throughout the oxidation. This temperature was deliberately selected because it was thought that perhaps in this way acetic acid formation could be prevented. Meanwhile, 44.1 grams of potassium permanganate crystals were added, a few grams at a time, until the violet color only disappeared on long standing (about two days). After removing the oxide of manganese, the filtrate (1100 cc.) was analyzed by the usual method. The oxalic acid in 50 cc. required 66.79 cc. of 0.096 *N* potassium permanganate solution, which is equivalent to a total of 6.4 grams of oxalic acid (86.9% of theory). The oxalic acid in 50 cc. corresponded to 0.26 cc. of 0.435 *N* potassium hydroxide solution, or a total of 0.15 gram of acetic acid; or for 100 cc., 0.46 cc. of potassium hydroxide solution which is equivalent to 0.133 gram of acetic acid. This gives an average of 0.142 gram (theory = 4.906 grams), therefore 2.9%. When 50 cc. were analyzed for carbon dioxide, 0.94 gram of barium carbonate was obtained, or 20.46 grams in all, which is equivalent to 4.40 grams of carbon dioxide, after having deducted for the potassium hydroxide used. The amount of carbon dioxide equivalent to the acetic acid and oxalic acid found is 3.24 grams, thus leaving 1.16 grams unaccounted for. If it is assumed that 10.2% of the lactic acid not accounted for as acetic and oxalic acids is oxidized to carbon dioxide, this would be 1.1 grams, which is in close agreement with the result stated above. The amounts of potassium permanganate necessary to produce the above oxidation products from lactic acid are

<sup>1</sup> Wislicenus, *Ann.*, 164, 181.

<sup>2</sup> *Ann.*, 63, 88; 104, 192; *Ber.*, 19, 2454; 41, 34; *Monatsh.*, 22, 348; *Bull. soc. chim.*, [3] 27, 803; *Chem. Zent.*, 1905, II, 881; *Chem.-Ztg.*, 30, 40; *Arch. Pharm.*, 246, 488; Meyer and Jacobson, *Lehrbuch*, I, Vol. II, p. 557, new ed.

as follows: for acetic acid 0.49 gram, for oxalic acid 37.5 grams, for the carbon dioxide found in excess of that equivalent to one-third the carbon content of the lactic acid used 5.53 grams, or a total of 43.52 grams as against 44.1 grams of the reagent used (*i. e.*, 98.7% has been accounted for). At the temperature employed it had been hoped to obtain only oxalic acid, and, if any at all, merely a trace of acetic acid and an amount of carbon dioxide corresponding to these two. The experiment therefore shows that the lactide was not entirely responsible for the excess of carbon dioxide and acetic acid but it is probably oxidized in about the same manner as lactic acid itself. The amount of potassium permanganate required for the oxidation of the lactic acid according to the following equation:



is 43.1 grams, while the products are equivalent to 43.52 grams (5.05 atoms of O) and the amount actually used was 44.1 grams (5.13 atoms of O).

*Pyruvic Acid, Potassium Permanganate and Potassium Hydroxide.*—Denis<sup>1</sup> found that "pyruvic acid when titrated with potassium permanganate in an aqueous solution containing an excess of sodium hydroxide or sodium carbonate, uses up only 3.49 to 3.56 atoms of oxygen, instead of 4 atoms, as demanded by theory, for each molecule of pyruvic acid taken." Denis<sup>2</sup> also found that pyruvic acid, when oxidized with potassium permanganate and potassium hydroxide, gave a yield of 82% of oxalic acid. The carbon dioxide was not reported. The latter experiment cited above was repeated using double quantities except that 4.1 grams of pyruvic acid were used. After standing one hour the reaction mixture was red in color and possessed a jelly-like consistency, which on warming assumed the usual form of the precipitated manganese dioxide. The filtrate from the latter was 925 cc. To determine acetic acid, 100 cc. of the filtrate when treated by the usual method required 153.4 cc. of 0.091 *N* potassium hydroxide solution diluted to 412 cc., of which 50 cc. required 32.57 cc. of 0.05 *N* silver nitrate solution. This corresponds to 61.05 cc. of 0.091 *N* potassium hydroxide for all, which is equivalent to 0.334 gram of acetic acid (theory = 2.79 grams, therefore 11.9%). For 50 cc. the oxalic acid required 27.95 cc. of 0.097 *N* potassium permanganate solution, which corresponds to 2.21 grams of oxalic acid (theory = 4.19 grams, therefore 52.74%). From 50 cc. of the filtrate 0.52 gram of barium carbonate was obtained, which corresponds to 2.14 grams of carbon dioxide (theory = 2.05 grams). The amount of carbon dioxide equivalent to the amounts of acetic and oxalic acids obtained is 1.32 grams, thus leaving 0.82 (2.14-1.32) gram of carbon dioxide unaccounted for

<sup>1</sup> *Am. Chem. J.*, 38, 577.

<sup>2</sup> *Loc. cit.* .

on the assumption that one-third of the carbon content of the pyruvic acid molecule yields an equivalent amount of carbon dioxide. In order to check these analyses, the products were calculated to the potassium permanganate required for their production; for acetic acid 0.593 gram, for oxalic acid 10.4 grams, for carbon dioxide 3.22 grams, or a total of 14.213 grams as against 14.372 grams used. A consideration of the demands of the analytical methods shows that this experiment is practically quantitative.

A portion (500 cc.) of the above filtrate was treated with a small excess of hydrochloric acid and distilled *in vacuo* as usual. The distillate thus obtained was boiled with an excess of well washed silver oxide. When the solution was neutral the excess of silver oxide was filtered off and the filtrate was evaporated almost to dryness on the water bath. There was no apparent decomposition nor formation of silver mirrors at any point, thus showing the absence of formic acid in the process. Portions of the crystals formed were treated for pyruvic acid as follows: with ferric chloride and sulfuric acid, which gives the violet color for aldehyde with pyruvic acid; with sodium nitroprusside, and also with phenylhydrazine. These tests, in spite of their delicacy, failed to show the presence of the pyruvic acid. It is necessary to establish the absence of the keto acid because the amounts of oxalic and acetic acids obtained in the experiment are equivalent to only 3.2 grams (amount used = 4.1 grams). A portion of the crystals and also the mother liquor were examined for acetic acid by the ethyl acetate method. The odor of the ester was definitely identified, thus showing that acetic acid was formed.

Under the conditions employed above, the results of the experiments with lactic and pyruvic acids show:

(1) That acetic acid is a definite product of the oxidation of these acids with alkaline potassium permanganate solution.

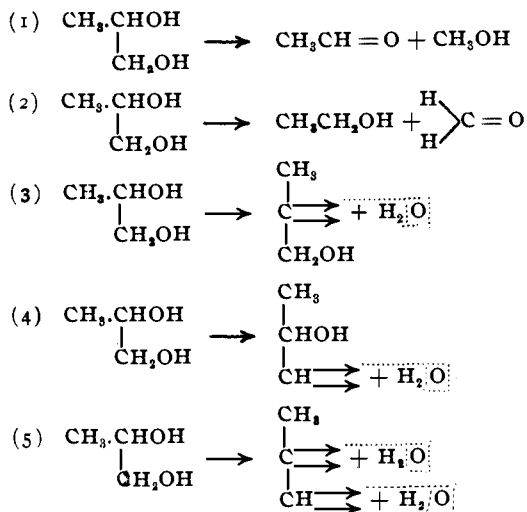
(2) That in effect there is a total oxidation of part of the molecules of the two acids to carbon dioxide only.

(3) That we have in these cases also, as was found with propylene-glycol (page 1096) no less than three definite reactions taking place simultaneously producing acetic acid, oxalic acid and carbonic acid, respectively.

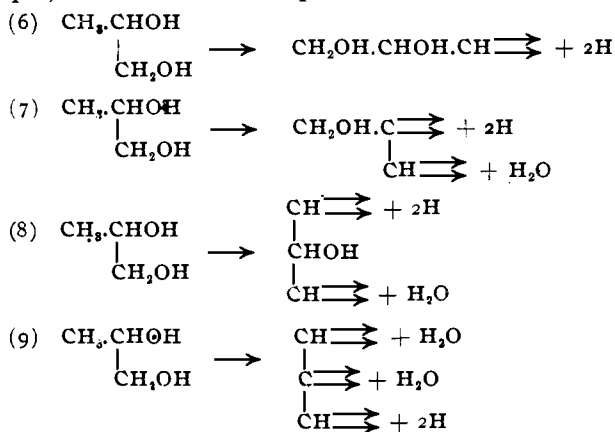
(4) That in experiment (d), under propyleneglycol and in those on lactic acid and pyruvic acid, exactly the same oxidation products are obtained; namely, carbonic, acetic and oxalic acids; and, furthermore, the theoretically possible intermediate acids yield the same products and also like propyleneglycol, yield an amount of carbon dioxide in excess of that equivalent to one carbon atom.

If we assume that propyleneglycol dissociates<sup>1</sup> in accordance with Nef's theories we have the following possibilities:

<sup>1</sup> Compare Nef, *Ann.*, 335, 191.



If we assume that the  $-\text{CH}_3^1$  group takes part in the dissociation (which assumption has been excluded on other grounds in the introductory part of this paper) we have four more possibilities:



If we consider the first dissociation to take place we would have as its products acetaldehyde and methyl alcohol. Experiments by Denis<sup>2</sup> show that acetaldehyde with potassium permanganate in the presence of potassium hydroxide gives carbon dioxide, oxalic and acetic acids. Our own experiments with methyl alcohol show that it is quantitatively changed to carbon dioxide under these conditions. Therefore this possibility remains.

If we examine equation (2), ethyl alcohol and formaldehyde would be

<sup>1</sup> Compare Nef, *THIS JOURNAL*, 26, 1555, 1566, etc.

<sup>2</sup> *Am. Chem. J.*, 38, 509.



the products. With ethyl alcohol Denis<sup>1</sup> obtained carbon dioxide, oxalic acid and acetic acid. Formaldehyde, according to Jones and others,<sup>2</sup> and our own experiments, is oxidized quantitatively to carbon dioxide under these conditions. Therefore this possibility remains.

The product of the reaction indicated in (3) would be acetol. This substance was found by Denis to give<sup>3</sup> acetic and oxalic acids as well as carbon dioxide.

The lactic aldehyde of (4) has not been tried.

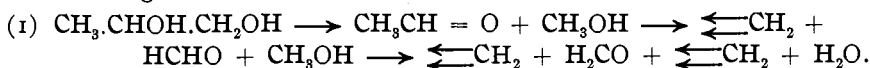
Pyruvic aldehyde, which is the product obtained from (5), has not been tried so far as is known. Pyruvic acid, however, was found to give both acetic and oxalic acids, besides carbon dioxide.

From the above statements it is evident that not a single one of the first five possibilities can be excluded. A comparison of the list of the products of oxidation with the dissociation possibilities listed above brings out the following facts:

(a) That the oxidation could not have taken place in experiment (d) entirely according to dissociations (1) and (2).

(b) If we assume that the oxidation first takes place on the two alcohol groups, giving finally acetol, lactic aldehyde or pyruvic aldehyde and that this, or these, provided all are formed, or their final oxidation product, if it is first formed, dissociate in accordance with schemes like 6, 7, 8 or 9, or undergo oxidation in the  $-\text{CH}_3$  group to hydroxypyruvic acid and subsequently to mesoxalic acid, which has been shown to give oxalic acid and carbon dioxide under these conditions,<sup>4</sup> we would have a satisfactory explanation of the formation of oxalic and carbonic acids. This would not, however, account for the excess of carbon dioxide so often observed.

(c) Since potassium permanganate is not reduced at all on boiling a solution of oxalic acid containing an excess of potassium hydroxide<sup>5</sup> and, since the same is true of acetic acid, the excess of carbon dioxide cannot arise from an oxidation of these. In view of these facts and also in view of the results stated in (a), it becomes apparent that a portion of the products of dissociation of the propyleneglycol molecule in 1 and 2 must undergo a further dissociation as follows:



i. e., the equivalent of three molecules of formaldehyde and one of water:

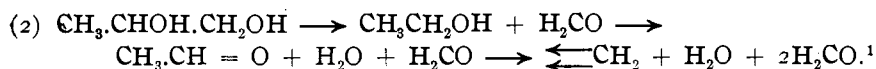
<sup>1</sup> *Am. Chem. J.*, **38**, 568.

<sup>2</sup> *Ibid.*, **17**, 539; *Ber.*, **27**, 1061; *Ann. chim. phys.*, [3] **55**, 374 (1859); *Monatsh.*, **14**, 746.

<sup>3</sup> *Am. Chem. J.*, **38**, 575.

<sup>4</sup> Baeyer, *Ann.*, **131**, 298; Denis, *Am. Chem. J.*, **38**, 578.

<sup>5</sup> Benedikt-Zsigmondy, *Z. anal. Chem.*, **25**, 588.



*i. e.*, the equivalent of three molecules of formaldehyde and one of water. Then the formaldehyde molecules undergo oxidation with alkalin potassium permanganate to carbon dioxide. Furthermore, it is apparent that the first products of dissociation in 3, 4, and 5 could in like manner undergo similar secondary dissociations and might equally well account for the excessive amount of carbon dioxide not only in propylene glycol, but also in the separate oxidation of lactic acid and pyruvic acid as indicated above.

Before concluding it will be well to point out that the above results on the oxidation of lactic acid and pyruvic acid are important in another direction. There are a number of methods for the analysis of compounds of this kind in which apparently no careful study of the products of the reaction has been made. The following brief discussion of lactic acid will show how the results given above can affect such analytical procedures.

#### Analysis of Lactic Acid.

Among the more recent methods for the quantitative determination of lactic acid<sup>2</sup> the method of Ulzer and Seidel,<sup>3</sup> in which the oxalic acid formed by oxidation with alkalin potassium permanganate is determined, is given.

Ulzer and Seidel had occasion to determine the strength of a sample of lactic acid. They first titrated with alkali, using phenolphthalein as an indicator. Then they added excess of alkali, boiled, and titrated back with acid. This gave a higher value, which they attributed to the decomposition of the lactide present. In order to learn which result was correct, they applied Benedikt-Zsigmondy's potassium permanganate method for glycerol in dilute aqueous solution<sup>4</sup> to the analysis of lactic acid. They proceeded as follows: Take about 1 gram of the lactic acid sample, dissolve in 100 cc. of water, add a concentrated solution of 3 grams of potassium hydroxide and then a five per cent aqueous solution of potassium permanganate with constant shaking until the solution is no longer green, but is blue black in color, which color does not disappear. Now heat to boiling, the blue black color must be retained and MnO<sub>2</sub> will be precipitated. After the solution has cooled somewhat, hydrogen peroxide or sulfurous acid is added until it becomes colorless. The precipitate is filtered off and washed with boiling water. In the filtrate the oxalic

<sup>1</sup> Compare, Denis, *Am. Chem. J.*, 38, 569.

<sup>2</sup> Beilstein, *Ergänzungsband*, I (1901).

<sup>3</sup> *Monatsh.*, 18, 138.

<sup>4</sup> *Chem.-Ztg.*, 9, 975, or see Benedikt-Ulzer, *Analyse der Fette und Wachstern*, 5th Ed., p. 480 (1908); see also Filsinger, *Z. öffentl. Chem.*, 3, 97-101; *Chem. Zent.*, 1897, I, 888.

acid is precipitated with calcium acetate after acidifying with acetic acid, and the precipitate is titrated with standard hydrochloric acid. Or the method frequently used was to acidify the filtrate strongly with sulfuric acid and titrate with potassium permanganate. The potassium permanganate used is calculated to oxalic acid.

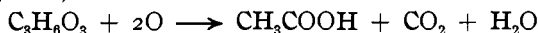
Dr. Denis states that the above work<sup>1</sup> was confirmed repeatedly. She also made titrations of lactic acid by adding 0.1 *N* potassium permanganate to the alkalin solution. When no more potassium permanganate was reduced the solution was strongly acidified and the manganese dioxide reduced with 0.2 *N* oxalic acid. These experiments showed that 4.84 and 4.87 atoms of oxygen were consumed instead of 5 atoms per molecule, as demanded by the equation. The average difference of 3.4% was no doubt attributed to error. In experiment (*f*) above on zinc lactate the products accounted for 5.05 atoms of oxygen per molecule of lactic acid. This is an excess of 1%. The amount of potassium permanganate used was equivalent to 5.13 atoms of oxygen or 2.6% in excess. In experiment (*e*) the conditions used were much the same as those used by Ulzer and Seidel and the amount of acetic acid formed was larger.

Our own experiments have shown that the reaction is not as simple as was assumed by the former workers. The analytical error in working by Ulzer and Seidel's method may vary a great deal, depending on the temperature, the dilution, the concentration of the alkali, etc. The error in Denis' adaptation of it would never be so large because the potassium permanganate used in the oxidation is the basis of calculation.

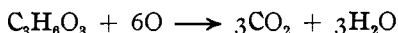
Instead of having only the reaction



the following, also,



and



take place.

Further work along these lines on acetone, lactic acid and glycerol is now under way.

COLUMBUS, OHIO.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 208.]

### STUDIES ON AMYLASES: IV. A FURTHER INVESTIGATION OF THE PROPERTIES OF PANCREATIC AMYLASE.<sup>2</sup>

By H. C. SHERMAN AND M. D. SCHLESINGER.

Received May 31, 1912.

In a previous paper,<sup>3</sup> we have described the preparation of several

<sup>1</sup> *Am. Chem. J.*, **38**, 576.

<sup>2</sup> Read before the New York Section, May, 1912.

<sup>3</sup> *THIS JOURNAL*, **33**, 1195.