were analyzed for calcium, magnesium, phosphorus, silicon and potassium. The results are shown in the following table:

Table I.—Analyses of Crab Grass Ash.

	Grown in garden soil. G.	Grown in limestone roadway. G.	Percentage difference.
Wt. of air-dried sample	7.9833	7.8307	..
Wt. of ash of air-dried sample	1.6640	1.3695	..
	%.	%.	
Ash in the air-dried sample	20.84	17.49	—16.1
P_2O_5 in the ash	4.01	4.92	+22.7
SiO_2	14.60	14.50	..
CaO	3.75	5.40	+44.0
MgO	2.68	3.42	+27.6
K_2O	39.86	32.38	—18.8

It will be seen from these figures that the intake of inorganic material was not the same in the two specimens. It is interesting to note that the sample of grass grown in the middle of a comparatively new limestone roadbed which was from 4 to 5 inches in thickness contained approximately 16% less ash than did a similar sample grown in garden soil and that the quantity of K_2O was 18.8% less in the first mentioned. In opposition to this it is seen that the ash of the sample grown in the limestone contained 22.7% more P_2O_5, 44.0% more CaO and 27.6% more MgO. That the percentage of silica is approximately the same in these two samples is likewise worthy of note.

The outstanding feature in connection with the growth of these two samples of crab grass is that the absorption and retention of these different amounts of calcium, magnesium, phosphorus and potassium cause no observable difference in their external appearance.

Lexington, Ky.

[Contribution from the Chemical Laboratory of the Ohio State University.]

THE OXIDATION OF ORGANIC COMPOUNDS WITH ALKALINE POTASSIUM PERMANGANATE.

Part I.—The Oxidation of Acetaldehyde. Part II.—The Oxidation of Glycol, Glycollic Aldehyde, Glyoxal, Glycollic Acid and Glyoxalic Acid.

By William Lloyd Evans and Homer Adkins.

Received June 20, 1919.

The problem of the alkaline oxidation with potassium permanganate of some of the simple alcohols, aldehydes, ethers, ketones and acids has been quantitatively studied by a number of investigators.[1] In much of the work which has been done on the alkaline oxidation of organic com-

---

[1] Nef, *Ann.*, 335, 269 (1904); Denis, *Am. Chem. J.*, 38, 561 (1907); Evans and Witzemann, This Journal, 34, 1086 (1912); Witzemann, *Ibid.*, 38, 150 (1916); 39, 2657 (1917); Evans and Day, *Ibid.*, 38, 375 (1916); Evans and Day, *Ibid.*, 41, 1267 (1919).

pounds no systematic study has been made of the effect of the added alkali on the nature of the reaction products. The work reported in this paper is a continuation of the experiments begun by Day and one of us on the oxidation of ethyl alcohol. This paper deals with the following phases of the problem:

PART I.—The oxidation of acetaldehyde with potassium permanganate in neutral solutions and in those containing from 200 to 400 g. of potassium hydroxide per liter has been carried out at temperatures of 25, 50 and 75°. The products of oxidation have been determined quantitatively.

PART II.—The oxidation of glycol, glycollic aldehyde, glyoxal, glycollic acid and glyoxalic acid at a temperature of 50° and at various concentrations of potassium hydroxide has been made, and the amounts of oxalic acid and carbon dioxide produced determined.

The data obtained is discussed from three standpoints:

1. The relationship of potassium hydroxide concentration to the products of oxidation.
2. The relationship of temperature to the products of oxidation.
3. Deductions as to the relationship of the compounds during alkaline oxidation.

PART I.—THE OXIDATION OF ACETALDEHYDE.

Historical Discussion.

A search of the literature revealed the fact that very little work has been done in studying the oxidation of this compound. The three more important reports are as follows:

Heimrod and Levene[1] oxidized acetaldehyde in an alkaline solution with hydrogen peroxide. They studied the possible intermediate oxidation products: glycollaldehyde; glyoxal; glycollic and glyoxylic acid; estimating in each case the amounts of carbon dioxide and formic acid formed. They give equations showing the various possible courses of the oxidation. They conclude that acetaldehyde oxidizes through the following stages: acetaldehyde $\longrightarrow$ (vinyl alcohol) $\longrightarrow$ glycol aldehyde $\longrightarrow$ glyoxal $\longrightarrow$ formic acid $\longrightarrow$ carbon dioxide. They claim that there is no evidence of the formation of formaldehyde as an intermediate product.

In view of the fact that acetaldehyde is a good depolarizer, Law[2] oxidized it electrolytically and obtained carbon monoxide and dioxide as well as acetic acid. Formic acid was formed in small amounts. In 0.85 N sulfuric acid acetaldehyde was oxidized almost quantitatively to acetic acid.

Denis[3] conducted two experiments, one in an 8.5 molar alkaline solution, and one in a neutral solution. In the alkaline solution a 75% yield

---

[1] *Biochem. Z.*, **29**, 31–59 (1910).

[2] *Trans. Chem. Soc.*, **87**, 198 (1905).

[3] *Am. Chem. J.*, **38**, 569 (1907).

of acetic acid was obtained together with oxalic acid and carbon dioxide. In the neutral solution after oxidation of the aldehyde only acetic acid was found (96.8% yield). The absence of formic acid was proven.

Experimental Part.

1. **The Preparation of the Aldehyde Solution.**—Acetaldehyde was prepared by the method described by McLeod.[1] Paraldehyde was depolymerized by the use of dil. sulfuric acid (1:4). ·The product of the first distillation after treatment with the acid, was redistilled twice, the fractions coming over below 27° being used in making the standard aldehyde solution. The final distillate contained probably 1–2% of water as shown by the slight coloring of dehydrated copper sulfate. A weighed amount of the aldehyde so prepared was dissolved in water in such a proportion that a two molar solution was obtained.

2. **The Standard Potassium Hydroxide Solution.**—A concentrated potassium hydroxide solution was made and standardized by titrating with 0.5 *N* sulfuric acid. The solution contained 0.445 g. of potassium hydroxide per cc. The carbon dioxide content was ascertained to be 0.0027 g. per cc.

3. **The Oxidation.**—The oxidations were carried on in two-liter balloon flasks. The flasks were supplied with rubber stoppers through which extended a piece of glass tubing, a pipet, and a stirring rod placed in a mercury seal. The stirring rod was attached to a revolving spindle by means of rubber tubing, the glass tubing by the same means to a buret. The oxidizing solution was prepared as follows: A measured amount of the concentrated potassium hydroxide solution was made up to a volume of one liter by the addition of carbon dioxide-free water. Fifteen g. of potassium permanganate were then placed in the alkaline solution.

The flask was placed in the electrically controlled thermostat, and then the motor stirring device and the buret containing the aldehyde solution were attached. When the permanganate had dissolved and the solution had reached the temperature of the thermostat the acetaldehyde was added very slowly until complete decolorization of the permanganate had been accomplished. This point could be determined by drawing the mixture up into the pipet and allowing the precipitated manganese dioxide to settle. The change was from pink to colorless in the neutral and weak alkali (0 to 9 g. of potassium hydroxide per liter) and from green to colorless in the stronger alkali solutions.[2] At 25° on account of the slowness of oxidation it was necessary to allow the mixture to stand several hours between every two additions of 0.1 cc. of the aldehyde solutions when the end-point was almost reached. At 50° the portions added were completely oxidized within less than an hour, even in the case of weak alkali

---

[1] *Am. Chem. J.*, **37**, 27 (1907).

[2] Compare Evans and Day, THIS JOURNAL, **41**, 1271 (1919).

solutions. That the end-point could be ascertained with a fair degree of accuracy is shown by the fact that oxidations carried on two months apart checked with each other within less than 8 mg. of acetaldehyde oxidized, that is, within one drop of the standard solution.

The reaction mixture was filtered in a specially constructed carbon dioxide-free apparatus designed by Evans and Day[1] and the filtrate was made up to a volume of two liters and analyzed.

An aliquot part of this solution was acidified (using a drop on phenolphthalein solution as an indicator) with acetic acid, then ammonium hydroxide added until the reaction was alkaline. The oxalic acid was then precipitated from the hot solution by the use of a 5% solution of calcium acetate. After filtering and washing, the precipitate was dissolved in 15 cc. of sulfuric acid (1:4). 130 cc. of distilled water was added and the hot solution was then titrated with 0.098 *N* potassium permanganate solution.

The carbon dioxide was determined by means of the Foulk apparatus,[2] the carbon dioxide being absorbed in Liebig bulbs, proper correction being made for the carbon dioxide in the standard potassium hydroxide.

The acetic acid was determined by the method of Stillwell and Gladding. Much difficulty has been experienced in the determination of this acid by various analysts. The following procedure when precisely followed gives excellent results, as evidenced by the fact that in 25 determinations of acetic acid it was unnecessary to repeat a single one, two samples from the same solution never varying from each other to a greater extent than 0.2 cc. of 0.1 *N* sodium hydroxide solution and in most cases the determinations were in agreement to within 0.05 cc. Experiments showed that the recovery of acetic acid was 99.8 to 100%.

The apparatus for this determination of acetic acid consisted of a 500 cc. balloon flask fitted with a two-hole stopper through which extended the stem of a dropping funnel, and a Kjeldahl bulb. The Kjeldahl bulb was connected to a Leibig condenser which in turn ended in a cylindrical dropping funnel which was graduated into 25 cc. divisions. The dropping funnel was connected by a two-hole stopper to a 750 cc. Erlenmeyer flask.

The sample (100 cc.) was put into the balloon flask together with bits of porous plate, the flask stoppered and 20 cc. of syrupy phosphoric acid added. Distillation was then begun. When 50 cc. of distillate had collected in the dropping funnel, 25 cc. of hot water was then added and the operations continued, thus maintaining the volume in the distilling flask between 70 and 95 cc. When the distillate had reached a volume of 400 cc. it was found that in all cases the acetic acid had been com-

[1] *Loc. cit.*

[2] Foulk's "Notes on Quantitative Analysis," 1914, p. 222. McGraw-Hill Book Co.

pletely distilled over. In case the alkali present in the sample exceeds 3 g. it is necessary to add considerably more than the 20 cc. of phosphoric acid plus the amount required to neutralize the excess of alkali. If the amount of alkali is as much as 12 g. it is advisable to use 40 cc. of phosphoric acid. If this precaution is not taken the final portions of the acetic acid distil over very slowly. The use of fresh pieces of porous plate shortens the time of distillation about 45 minutes. It reduces the necessary volume of the distillate about 100 cc. and especially with samples high in alkali it is very valuable in preventing the otherwise almost inevitable bumping. The distillate was freed of carbon dioxide by bubbling carbon dioxide-free air through it for 10 minutes, after which it was titrated with 0.1 *N* alkali using phenolphthalein as an indicator. Preliminary experiments showed that results were from one to 3% too high if the precaution was not taken of removing the carbon dioxide.

Explanation of Data Sheet and Curves.

1. Method of Tabulating Results.—All of the 20 oxidations here reported were checked at least once and in several cases checked 3 or more times. The analytical data are the result of at least two analyses of the same solution. The liberty has been taken of discarding a few experiments, the results of which were quite obviously in error due to faulty manipulation, or variation in temperature of the bath during the process of oxidation.

The weight of potassium hydroxide placed in the oxidizing flask is given the first column, the larger figure in parenthesis is the volume in cc. of the solution at the end of the oxidation. The weights of acetic and oxalic acids and carbon dioxide which were found in the solution upon analysis are given Cols. 2, 3 and 4. The aldehyde equivalent of these products is given Col. 5. The weights of acetic and oxalic acid and carbon dioxide which would be produced if 4.4 g. (0.1 mol. wt.) of acetaldehyde were oxidized under the conditions of the experiment are given in Cols. 6, 7 and 8. The figures in Col. 9 give in g. the amount of oxalic acid which would be produced if 4.4 g. of the acetaldehyde equivalent of some intermediate compound were oxidized to oxalic acid and carbon dioxide in the ratio in which they are produced at the given concentration of potassium hydroxide; for example, if in a given experiment one g. of oxalic acid and one g. of carbon dioxide were produced, the acetaldehyde equivalent would be 0.49 and 0.5 g., respectively, or a total of 0.99 g. acetaldehyde. Thus if 0.99 g. of acetaldehyde gave one g. of oxalic acid, then 4.4 g. of acetaldehyde would give 4.44 g. of oxalic acid. Similar values for carbon dioxide production are given in Col. 12. The figures in Col. 10 give in grams the average concentration of potassium hydroxide during the oxidation. Col. 11 contains the weights of aldehyde which were added to reduce the permanganate solution. These

TABLE I.

The Oxidation of Acetaldehyde at Various Temperatures and Concentrations of Potassium Hydroxide.

G. KOK.	CH_3COOH.	$(COOH)_2$.	CO_2.	G. $CH_3.CHO$ recovered as oxidation products.	CH_3COOH 4.4 gr. CH_3CHO.	$(COOH)_2$ 4.4 gr. CH_3CHO.	CO_2 4.4 gr. CH_3CHO.	$\frac{4.4\ (COOH)_2}{CO_2+(COOH)_2}$. 0.50. 0.49.	KOH. Av. g. per L.	CH_3CHO added.	$\frac{4.4\ CO_2}{CO_2+(COOH)_2}$. 0.50. 0.49.
1	2	3	4	5	6	7	8	9	10	11	12
Oxidation at 25°.											
4.45 (1058)	6.17	0.306	0.46	4.89	5.53	0.275	0.414	3.57	3.60	5.00	5.31
8.9 (1049)	4.82	0.62	0.68	4.16	5.09	0.655	0.70	4.18	8.25	4.22	4.72
13.35 (1043)	3.92	0.70	0.70	3.565	4.84	0.87	0.87	4.43	13.0	3.74	4.47
44.45 (1036)	2.95	1.128	0.76	3.07	4.20	1.61	1.09	5.31	43.65	3.13	3.61
175	2.46	1.37	0.68	2.814	3.84	2.14	1.06	....	173.0	2.89	....
200	2.50	1.38	0.70	2.86	3.85	2.13	1.08	....	197.0	2.92	....
Oxidation at 50°.											
4.45 (1037)	3.32	0.67	0.90	3.22	4.52	0.915	1.23	3.80	4.5	3.26	5.09
8.9 (1033)	2.41	0.925	0.98	2.71	3.91	1.51	1.60	4.30	9.05	2.77	4.57

13.35 (1028)	1.90	1.02	0.94	2.34	3.56	1.92	1.77	4.63	13.7	2.42	4.28
22.25 (1025)	1.58	1.18	0.90	2.19	3.18	2.37	1.82	5.06	22.6	2.26	3.86
44.5 (1025)	1.42	1.306	0.90	2.13	2.93	2.69	1.85	....	44.4	2.20	....
89 (1025)	1.44	1.33	0.91	2.16	2.91	2.70	1.85	....	88.7	2.20	....

Oxidation at 75°.

4.45 (1028)	1.90	0.95	1.24	2.49	3.37	1.68	2.19	3.86	4.7	2.53	5.02
8.9 (1025)	1.266	1.225	1.185	2.113	2.64	2.55	2.45	4.49	9.3	2.16	4.41
13.35 (1023)	1.05	1.35	1.15	2.00	2.31	2.97	2.53	4.82	13.8	2.04	4.09
44.45 (1022)	0.90	1.353	1.12	1.89	2.09	3.15	2.60	....	44.5	1.94	....
89.0 (1022)	0.91	1.36	1.14	1.91	2.09	3.14	2.62	....	88.8	1.95	....

"Neutral Solution" at Various Temperatures.

....	7.93	...	...	5.82	6.0	....	....	....	acid	5.94	....
....	7.98	...	...	5.96	6.0	....	....	....	acid	5.96	....
....	7.91	...	...	5.80	6.0	....	....	....	acid	5.91	....

weights are based on the weights of the prepared aldehyde used in making the reducing solution.

That the substance weighed out as aldehyde was not free from water is shown by the slight coloring of dehydrated copper sulfate noted above and by the fact that there is a constancy of yield of 97–98% when the yield is calculated on the basis of the weighed substance being free from water. The work of Denis[1] showed that acetaldehyde as prepared by McLeod[2] was about 97% pure.

2. **To Determine the Concentration of Alkali.**—At the beginning of the oxidation, the alkali concentration is known through the method for the preparation of the oxidizing mixture. However, as soon as oxidation begins, other factors determine the concentration at any given time. The three factors which are taken into consideration in calculating the "average potassium hydroxide" given in Col. 10 of the table are as follows: (*a*) The 15 g. of potassium hydroxide according to the equation $2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O$; this results in an increase in the amount of potassium hydroxide in the oxidizing solution. (*b*) The acetic, oxalic and carbonic acids produced by oxidation will neutralize a certain amount of the potassium hydroxide. (*c*) As the aldehyde solution is added the volume of the alkali solution is increased and consequently the concentration of the alkali is decreased.

Thus, through factor (*a*) the concentration of alkali is increased and through factors (*b*) and (*c*) it is decreased. In plotting the curves the alkali ordinate is found as follows: The amount of hydroxide necessary to give potassium oxalate, potassium hydrogen carbonate and potassium acetate is found. This amount taken from the total amount of potassium hydroxide introduced (*i. e.*, the weight originally put in plus 5.3 g.) gives the number of grams of potassium hydroxide present at the end of the oxidation. This amount divided by the volume of the solution in cc. and the quotient multiplied by 1000 gives the concentration per liter of alkali at the end of the oxidation. The mean between this concentration and the concentration at the beginning of the oxidation is taken as the average concentration during the course of the experiment. Under some conditions the factors almost balance each other, while in others (first expt. at 25° for example) the correction is about 0.85 of a g. of potassium hydroxide, almost $^1/_5$ of the amount of potassium hydroxide originally added. In any event, these corrections can only be approximate.

Another factor which has not been considered in the calculations which probably does effect the alkali concentration is that the precipitated manganese compound or compounds holds some potassium in chemical

---

[1] *Am. Chem. J.*, **38**, 567 (1907).

[2] *Ibid.*, **37**, 27 (1907).

union. Morawski and Stingl,[1] and Smolka[2] and Gmehlin-Kraut-Friedman[3] point out that the compound $KH_8Mn_4O_{10}$ is formed. There is uncertainty as to the exact composition of this substance. Furthermore, there is no data as to the effect of the alkali concentration upon its formation. For these reasons the potassium which may be withdrawn from the solution due to the formation of this compound is not considered in the calculations.

3. **Plotting the Graphs.**—In Fig. 1 the weights of acetic acid which would be produced by 4.4 g. acetaldehyde at the given concentration of alkali are plotted against the grams of potassium hydroxide per liter, present during the oxidation. In Figs. 2 and 3 the weights of oxalic and carbon dioxide are so plotted. In Fig. 4 the acetic acid-alkali relationship is plotted on logarithmic paper.

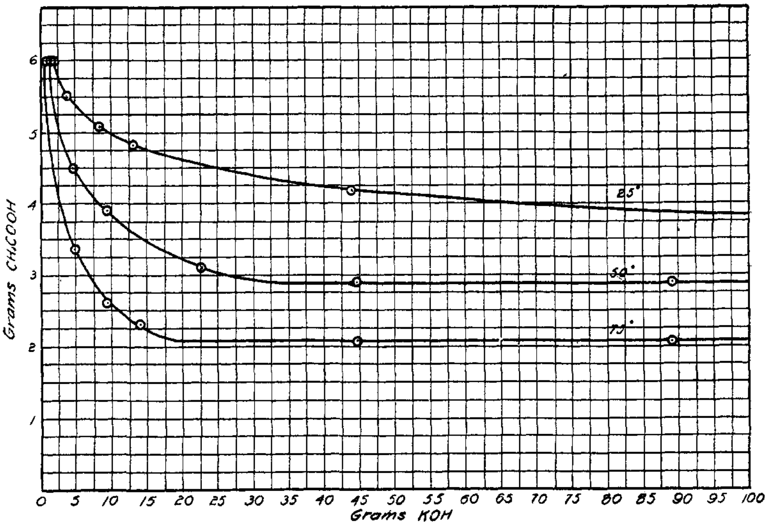


Fig. 1.—Acetic acid produced by 4.4 g. acetaldehyde.

The weight of oxalic acid (Col. 9 of Table I) which would be produced if 4.4 g. of acetaldehyde (or its equivalent) were oxidized to oxalic acid and carbon dioxide in the ratio in which they are produced in the given experiment is plotted against potassium hydroxide concentration in Fig. 5.

Three results (Table I) are given of oxidations carried out in "neutral solution," that is, no potassium hydroxide was added to the oxidizing solution. Since the potassium hydroxide produced by hydrolysis was insuffi-

---

[1] *J. prakt. Chem.*, [2] **18**, 86 (1878); *Jahresb.*, **5**, 275 (1878).

[2] *Sitzungber. Math. Naturwissensch. Klasse Kais Akad. Wissensch. Wein*, 95, II, 5–30 (1887).

[3] *Handb. Anorg. Chem.*, **3**, II, 254.

cient to neutralize the acetic acid produced by oxidation, the oxidation in reality took place in a weakly acid solution. These oxidations took

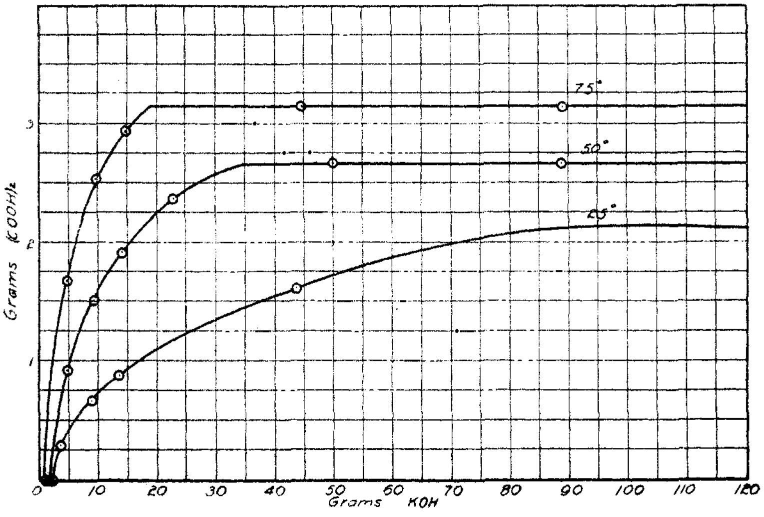


Fig. 2.—Oxalic acid produced by 4.4 g. acetaldehyde.

place at different temperatures from 25 to 75°. It is necessary to filter and analyze these solutions immediately, for the weakly acid solution is

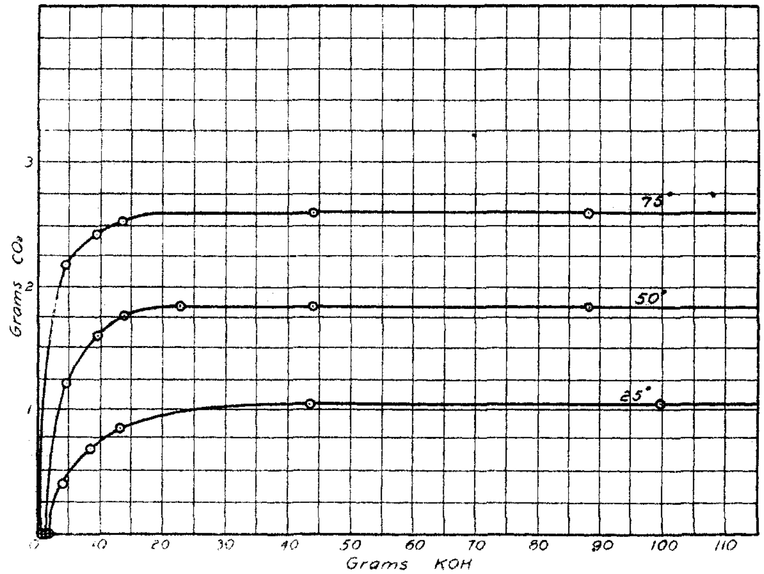


Fig. 3.—Carbon dioxide produced by 4.4 g. acetaldehyde.

apparently an ideal media for the growth of certain organisms. Large masses of these develop in a few days.

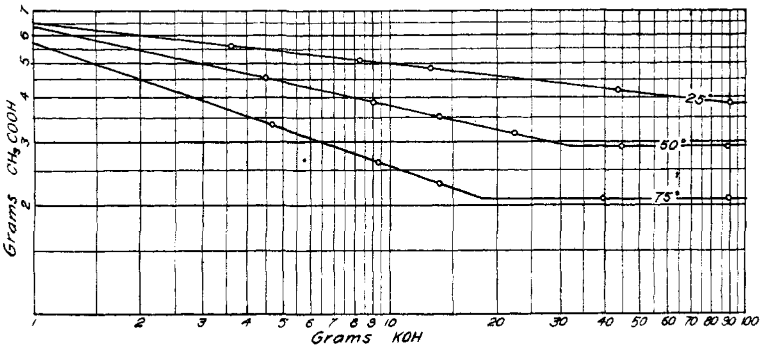


Fig. 4.—Acetic acid alkali relationship.

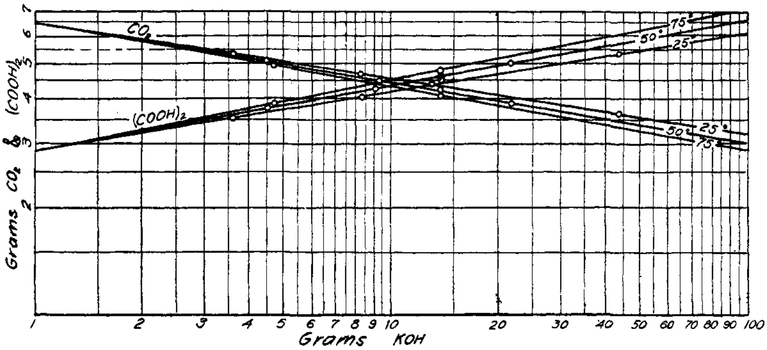


Fig. 5.—Oxalic acid and carbon dioxide produced by 4.4 g. acetaldehyde.

Discussion.

Acetic Acid.—The formation of acetic acid from acetaldehyde is to be expected. The mathematical relationship of the amounts of acetic acid produced to the average alkali concentration may be derived as follows: The fact that the acetic acid-alkali concentration relation gives a straight line when plotted on logarithmic paper means that the relation connecting these two quantities is expressed by the following equation:

$$Y = \frac{B}{X^a}$$

where Y equals the number of g. of acetic acid produced by the oxidation of 0.1 M g. of acetaldehyde at a concentration of X g. of potassium hydroxide per liter, and a is the tangent of the angle which the line makes with the X axis. This equation may be written as follows:

$$\log Y = \log B - a \log X$$

When $X = 1$, the second term on the right side of the equation disappears. The value of B is then found to be equal to the ordinate when the abscissa is one. The values for B and a at the temperatures employed in these experiments are shown in the following equations:

$$Y = 6.49\ X^{-0.114} \text{ at } 25^\circ \qquad (1)$$

$$Y = 6.38\ X^{-0.226} \text{ at } 50^\circ \qquad (2)$$

$$Y = 5.70\ X^{-0.342} \text{ at } 75^\circ \qquad (3)$$

It is of much interest in this connection to note that the above equation is the same one found for the amount of acetic acid formed when ethyl alcohol is oxidized with alkaline potassium permanganate.[1]

It will be observed that the value of the tangent of the angle decreases about 0.114 for each lowering of 25° in the temperature. This indicates that at about 0° the tangent of the angle would be zero, or in other words, at that temperature the line would be parallel to the X axis. That is, at 0° acetaldehyde would be oxidized quantitatively to acetic acid no matter what was the alkalinity of the oxidizing solution. (See Fig. 13.) The weight of acetic acid which would be produced by the oxidation of 4.4 g. of acetaldehyde would be 6 g.

From a study of the logarithmic graph (Fig. 4), it will be seen that the acetic acid-potassium hydroxide line reaches the ordinate 6 at = 1.95, 1.3 and 0.85 for 25°, 50° and 75°, respectively, *i. e.*, those concentrations are the highest concentrations at those temperatures at which acetaldehyde is oxidized quantitatively to acetic acid. Or, stated in terms of Nef's dissociation theory, those are the concentrations of alkali at which the acetaldehyde begins to dissociate with the production of vinyl alcohol. These values are in accord with McLeod's statement noted below. As he does not report the temperature, an exact comparison is impossible.

The minimum amounts of acetic acid obtained are 3.84, 2.91, 2.09 at 25°, 50° and 75°, respectively. By reference to the logarithmic lines it will be seen that these values for the ordinate correspond to 90, 32.5 and 18.5 g., respectively. That is at those concentrations of potassium hydroxide per liter the minimum amount of acetic acid for those temperatures would be produced. Hence, the logarithm of the amount of acetic acid produced by the alkaline permanganate oxidation of acetaldehyde is a linear function of the logarithm of the potassium hydroxide concentration employed between the following limits: 1.95 g. to 90 g. at 25°; 1.3 to 3.25 g. at 50°; and 0.85 g. to 18.5 g. at 75°. At concentrations above the larger value, increase in potassium hydroxide affects no change in the amount of acetic acid, and at concentrations less than the smaller number the oxidation of acetaldehyde to acetic acid is quantitative. Hence, the equations derived, give correct values for Y only between certain limiting values of X.

---

[1] Cf. Evans and Day, This Journal, 41, 1282 (1911).

Oxalic Acid and Carbon Dioxide.—Evans and Day[1] in their paper on ethyl alcohol have shown that there is no good evidence for believing that oxalic acid is produced by the alkaline oxidation of acetates or that carbon dioxide is produced by the alkaline oxidation of oxalates or acetates.

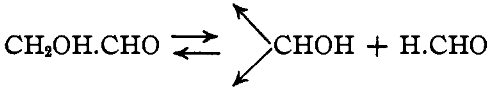
Denis[2] held that the formation of an olefin derivative (in this case vinyl alcohol) was *conditio sine qua non* of the oxidation of acetaldehyde to compounds other than the corresponding fatty acid. McLeod[3] showed that vinyl alcohol molecules did exist in an aqueous solution as soon as sodium hydroxide was present to the extent of 0.1%. The oxidation would then go through the following states:

$$CH_3 = CHO \text{ (in alkaline solution)} \rightleftarrows CH_2 = CHOH \qquad (1)$$

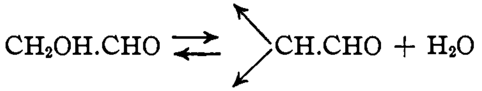
$$CH_2 = CHOH + 2OH \longrightarrow CH_2OH.CH(OH)_2 \qquad (2)$$

That glycollic aldehyde is one of the intermediate compounds in the oxidation of acetaldehyde is convincingly shown in Part II of this paper

Nef[4] postulated that glycollic aldehyde could dissociate as follows:



$$CH_2OH.CHO \rightleftarrows {>}CHOH + H.CHO \qquad (3)$$



$$CH_2OH.CHO \rightleftarrows {>}CH.CHO + H_2O \qquad (4)$$

The oxidation of the reaction products in (3) would yield carbon dioxide. If the reaction product in (4) is oxidized to glyoxal, then glycollic acid would be one of our intermediate compounds in these reactions since glyoxal and diketo compounds of the same type undergo simultaneous oxidation and reduction, *i. e.*, the benzilic acid rearrangement. It is shown in Part II that glycollic acid is ultimately oxidized to oxalic acid and carbon dioxide.

The alkali concentration might then be supposed to affect the production of vinyl alcohol molecules (cf. Part II). It also undoubtedly affects the reactions whereby oxalic acid and carbon dioxide are produced from the intermediate compounds, since it is evident from a study of the curves that the production of oxalic acid and carbon dioxide is affected by the variation in the concentration of the alkali.

It is important to consider the oxalic acid-alkali concentration relationship as given in Col. 9, Table I, and as plotted in Fig. 5. It is seen that this relationship as expressed on logarithmic paper is also a straight line. As noted above, the acetic acid-alkali concentration relationship plotted

---

[1] *Loc. cit.*

[2] *Am. Chem. J.*, **38**, 568 (1907).

[3] *Ibid.*, **37**, 23 (1907); cf. Nef, *Ann.*, **298**, 316 (1897).

[4] *Ibid.*, **335**, 274, 282 (1904).

on logarithmic paper gives a straight line, showing that the logarithms of the amounts of acetic acid produced from acetaldehyde by the alkaline oxidation with potassium permanganate is also a linear function of the logarithm of the potassium hydroxide concentration. The fact that the relative production of oxalic acid and carbon dioxide may be expressed in a mathematical expression of the same type indicates that the alkali acts in the same general way upon the compound which is the source of these acids as it does upon the acetaldehyde which is a source of the acetic acid.

The equations expressing the oxalic acid-alkali concentration and the carbon dioxide-alkali concentration involved in the oxidation of the acetaldehyde equivalent of the intermediate compound may be derived in the same manner as were those for the acetic acid-alkali concentration. If we let Z_o = grams of oxalic acid so produced; Z_c the grams of carbon dioxide; and X the grams of potassium hydroxide per liter, then the equations will be as follows:

$$\text{For } 25^\circ\ Z_o = 2.87\,X^{0.167} \quad (4) \qquad Z_c = 6.5\,X^{-0.155} \quad (7)$$
$$\text{For } 50^\circ\ Z_o = 2.87\,X^{0.184} \quad (5) \qquad Z_c = 6.5\,X^{-0.165} \quad (8)$$
$$\text{For } 75^\circ\ Z_o = 2.88\,X^{0.200} \quad (6) \qquad Z_c = 6.5\,X^{-0.176} \quad (9)$$

If the amount of acetic acid produced (Equations 1, 2 and 3) is multiplied by the factor 0.733, the product will be the weight in grams of the acetaldehyde equivalent to the actic acid produced. It is evident that if this product is subtracted from 4.4 g. (the total amount of the aldehyde), the remainder will be the acetaldehyde equivalent (W) of the intermediate compound formed in these reactions which is oxidized to oxalic acid and carbon dioxide.

These amounts are found to be as follows:

$$\text{For } 25^\circ\ [4.4 - (0.733)(6.49\,X^{-0.114})] \qquad (10)$$
$$\text{For } 50^\circ\ [4.4 - (0.733)(6.38\,X^{-0.226})] \qquad (11)$$
$$\text{For } 75^\circ\ [4.4 - (0.733)(5.70\,X^{-0.342})] \qquad (12)$$

Equations 4 to 9 inclusive were calculated on the basis that 4.4 g. of acetaldehyde was oxidized to oxalic acid and carbon dioxide in the same ratio as that in which these two compounds were found as reaction products at the concentration of the alkali used. The actual amount of the intermediate compound which is the source of the oxalic acid and carbon dioxide in these reactions is not constant in amount for the same temperature but it depends upon the concentration of the alkali used. Furthermore, the ratio of the oxalic acid and carbon dioxide production from the oxidation of the intermediate compounds is also dependent upon the concentration of the alkali used. The aldehyde equivalent of the intermediate compounds is easily obtained by solving the equations in the preceding paragraph.

Thus we have at hand the data necessary for calculating the oxalic acid and carbon dioxide produced in the oxidation of acetaldehyde as well as the acetic acid production as noted above. For it Y_o = g. of oxalic acid produced by the oxidation of 4.4 g. of acetaldehyde at a concentration of X g. of potassium hydroxide per liter, then Y_o will bear the same relationship to the actual amount of the intermediate compound oxidized to oxalic acid and carbon dioxide as the values of Z_o (Equations 4 to 6 inclusive) bear to 4.4, *i. e.*,

$$Y_o : 4.4 - (0.733)(6.49\,X^{-0.114})] = 2.87\,X^{0.167} : 4.4. \qquad (13)$$

By solving the easily formed equations of this type the oxalic acid production from aldehyde can be readily calculated for any concentration of the alkali at the temperature represented by the equation. The following are the values of Y_o and Y_c (carbon dioxide production):

$$\text{At } 25^\circ\ Y_o = 2.87\,X^{0.167} - 2.090\,X^{0.058} \qquad (14)$$

$$Y_c = 6.5\,X^{-0.155} - 7.03\,X^{-0.269} \qquad (15)$$

$$\text{At } 50^\circ\ Y_o = 2.87\,X^{0.184} - 3.03\,X^{-0.042} \qquad (16)$$

$$Y_c = 6.5\,X^{-0.165} - 6.91\,X^{-0.391} \qquad (17)$$

$$\text{At } 75^\circ\ Y_o = 2.88\,X^{0.200} - 2.724\,X^{-0.518} \qquad (18)$$

$$Y_c = 6.5\,X^{-0.176} - 6.17\,X^{-0.518} \qquad (19)$$

The correlation of the values determined by experiment with the values found by solving the equations is shown in the following table:

TABLE II.—COMPARISON OF VALUES FOUND AND CALCULATED.

Temperature.	Value of X.	CH_3COOH.		$(COOH)_2$.		CO_2.	
		Experiment.	Equation.	Experiment.	Equation.	Experiment.	Equation.
25°	3.6	5.53	5.57	0.275	0.255	0.41	0.39
25°	8.25	5.09	5.08	0.655	0.63	0.70	0.70
25°	13.0	4.84	4.83	0.87	0.87	0.87	0.89
25°	43.65	4.20	4.24	1.61	1.62	1.09	1.08
50°	4.5	4.52	4.54	0.92	0.93	1.23	1.23
50°	9.05	3.91	3.89	1.51	1.53	1.60	1.60
50°	13.7	3.56	3.56	1.92	1.92	1.77	1.74
50°	22.6	3.18	3.18	2.37	2.42	1.82	1.84
75°	4.7	3.37	3.36	1.68	1.73	2.19	2.19
75°	9.3	2.64	2.65	2.55	2.51	2.45	2.45
75°	13.8	2.31	2.32	2.97	2.99	2.53	2.51

Summary.

1. Acetaldehyde is oxidized in alkaline solution to acetic acid, oxalic acid and carbon dioxide.
2. The logarithm of the amount of acetic acid produced is a linear function of the logarithm of the alkali concentration between definite limits. Acetic acid production decreases as alkali concentration increases and as temperature increases.
3. These limits are a function of the temperature.

4. There is a minimum production of acetic acid at a concentration of alkali which is a function of the temperature. Increases in potassium hydroxide beyond this concentration has no appreciable effect upon acetic acid production.

5. The amounts of oxalic acid and carbon dioxide produced by the oxidation of acetaldehyde at a constant temperature are expressed as a mathematical function of the potassium hydroxide concentration between certain limits.

6. Since the production of these compounds is dependent upon those factors which decrease the amount of substance going to acetic acid, the same limits apply to the production of them as does to the production of acetic acid.

7. The ratio of oxalic acid to carbon dioxide increases with rise in temperature, and increase in alkali concentration. The amount of substance going to oxalic (or carbon dioxide) as compared to the total amount going to oxalic acid and carbon dioxide is a simple algebraic function of the alkali concentration.

8. The effect of the alkali on the yield of acetic acid should disappear at a temperature below 0°.

PART II.—THE OXIDATION OF ETHYLENE GLYCOL, GLYCOLLIC ALDEHYDE, GLYOXAL, GLYCOLLIC ACID AND GLYOXALIC ACID.

Historical Discussion.

The compounds ethylene glycol,[1] glycollic aldehyde,[2] glyoxal,[3] glycollic acid,[4] and glyoxalic acid,[5] and acetic acid are more or less readily transformed into each other by acid oxidizing or reducing agents.

As to the conduct of these compounds in the presence of bases the following reports are in the literature. Hydrogen is evolved and formic acid is formed when glycol is heated with lead peroxide and potassium hydroxide.[6]

Meyer and Jacobson in their text book[7] state that upon boiling, a solution of glyoxal is changed over into a solution of glycollic acid. Debus showed that upon boiling the solution of the calcium salt of glyoxalic acid, the salts of oxalic and glycollic acids were formed. Böttinger[8] showed that boiling the salt of the acid in the presence of potassium hydroxide caused the same reaction to take place. A basic barium glyoxalate is formed as an intermediate product during the action of

---

[1] Debus, *Ann.*, **110**, 316 (1859); Renard, *Ann. Chim.*, [5] **17**, 313 (1879).

[2] Neuberg and Schwenk, *Z. ver. Zuch.*, **1916**, I, 430.

[3] Debus, *Ann.*, **102**, 20 (1857).

[4] Würtz, *Ibid.*, **103**, 366 (1857); Claus, *Ibid.*, **145**, 256 (1868).

[5] Debus, *Ibid.*, **100**, 1 (1856); **110**, 316 (1859).

[6] Glaser and Morawski, *Monats.*, **10**, 582 (1890).

[7] 2nd Ed., **1**, 815 (1913).

[8] *Ber.*, **13**, 1832 (1880).

barium hydroxide on glyoxalic acid. More prolonged action causes the evolution of hydrogen and the formation of oxalic acid.[1] Traube says that the quantity of hydrogen evolved is less in the experiments in which only small amounts of barium hydroxide were used.

To summarize these transformations in the presence of alkali it may be said that by the action of bases an intermolecular oxidation-reduction may be accomplished in the case of glyoxal and glyoxalic acid. It has also been shown that in two cases (glycol and glyoxalic acid) an alkali causes the evolution of hydrogen and the consequent oxidation of the compound to the alkali salt of oxalic acid.

Heimrod and Levene[2] have done considerable work upon the alkaline oxidation of glycol, glycollic aldehyde, glyoxal, glycollic acid and glyoxalic acid. Their method of experimentation was as follows:

A solution of the compound was made; to this was added varying amounts of a 4 *N* potassium hydroxide solution. A 30% hydrogen peroxide solution was added as an oxidizing agent. They analyzed the solution containing the oxidation products for total volatile acids (formic acid and carbon dioxide). They also tested for oxalic acid in the residue after the expulsion of the volatile acids. Large yields of formic acid and some carbon dioxide were obtained by the oxidation of glycol, glycollic aldehyde and glyoxal. Glycollic acid gave some glyoxalic acid, a larger amount of formic acid and over 50% yield of carbon dioxide.

The glyoxalic acid gave on oxidation large amounts of carbon dioxide and some oxalic and formic acids. Heimrod and Levene believe that the oxalic acid was produced by the action of the alkali on glyoxalic acid. They detected oxalic acid in a control experiment in which they used no hydrogen peroxide. In some of their experiments an excess of the oxidizing agent was used and in all others all of the hydrogen peroxide entered into reaction with the compound being oxidized. The temperature factor was not regulated and the yields were not quantitative.

Experimental Part.

Oxidations of glycol, glycollic aldehyde, glyoxal, glycollic acid and glyoxalic acid were conducted at a temperature of 50° in the same manner as described for acetaldehyde. The method of preparation of the compounds and the results of the oxidation of them are here given.

Ethylene Glycol.

Preparation of Ethylene Glycol.—The ethylene glycol was prepared from ethyl alcohol, through the intermediate formation of ethylene, ethylene dibromide, and glycol diacetate.

---

[1] Traube, *Ber.*, **42**, 3295 (1909).

[2] *Biochem. Z.*, **29**, 31 (1910).

The Oxidation of Ethylene Glycol.—The oxidation of the ethylene glycol was carried out at an initial volume of 500 cc. The volume at the end of the oxidation was 525 cc.

The data obtained are given in the following table:

Table III.

G. $KMnO_4$.	G. KOH per l.	G. $(CH_2OH)_2$.	G. $(COOH)_2$.	G. CO_2.	G. (CH_2OH) recovered as $(COOH)_2$ and CO_2.	$(COOH)_2$ from 6.2 g. $(CH_2OH)_2$.	CO_2 from 6.2 g. (CH_2OH_2).	Av. g. KOH per l.
7.75	None	0.97	0.215	1.15	0.96	1.37	7.35	1.02
7.00	0.96	0.96	0.47	0.90	0.957	3.04	5.81	1.66
7.00	1.98	0.98	0.906	0.50	0.977	5.73	3.16	2.64
7.00	4.86	0.99	1.05	0.37	0.985	6.57	2.32	5.5
7.00	14.6	1.00	1.05	0.38	0.99	6.51	2.35	15.0
7.00	24.1	0.99	1.05	0.37	0.985	6.57	2.32	24.3
7.00	48.6	0.99	1.05	0.37	0.985	6.57	2.32	48.3

The amounts of oxalic acid and carbon dioxide which would be produced by the oxidation of 6.2 g. (0.1 Mol. wt.) of glycol under the conditions of the experiment are given in Cols. 6 and 7. These values plotted against the potassium hydroxide concentration are shown in Fig. 6.

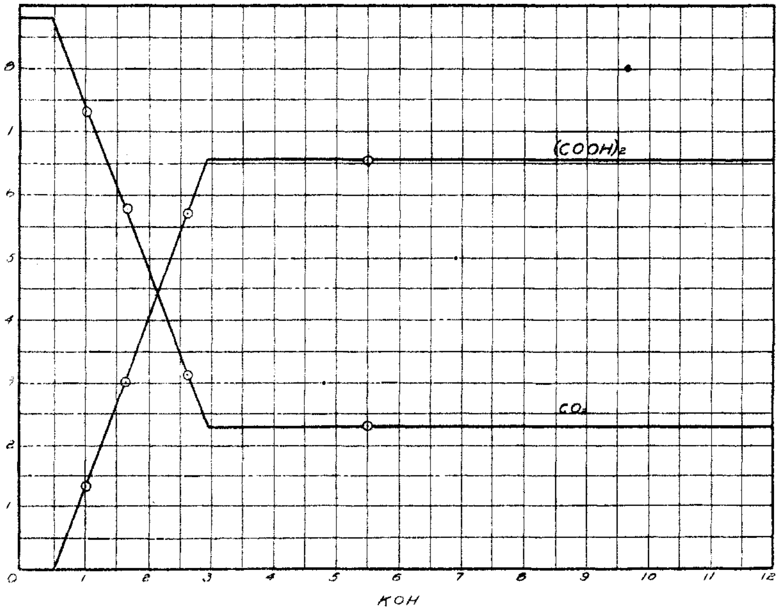


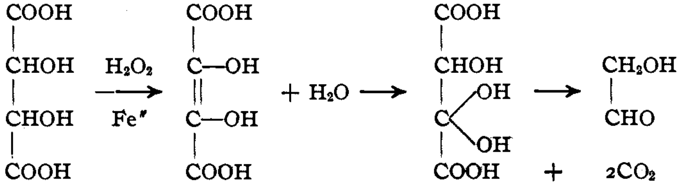
Fig. 6.—Glycol oxidations.

It may be seen that the amounts of these acids produced by the oxidation of a fixed amount of glycol constitute a linear function of the potassium hydroxide concentration between concentration of 0.5 g. and 3.0 g.

per liter. The equations showing these relationships are $Y_o = 2.73\,X - 1.46$ and $Y_c = 10.13 - 2.64\,X$, where Y_o equals the grams of oxalic acid, and Y_c the grams of carbon dioxide produced by the oxidation of a tenth molecular weight of glycol at a concentration of X g. of potassium hydroxide per liter. At concentrations below 0.5 g. of potassium hydroxide per liter it appears that glycol is oxidized quantitatively to carbon dioxide; at concentrations above the 3 g. per liter the ratio of the acids produced is not affected by changes in the concentration of potassium hydroxide. At concentrations above 3 g. per liter 73% of the glycol is oxidized to oxalic acid, and 27% to carbon dioxide.

Glycollic Aldehyde.

1. **Preparation.**—Three syntheses of glycollic aldehyde are reported in the literature. Fisher and Landsteiner[1] prepared a dilute solution from acetal. Marchwald and Ellenger[2] prepared a concentrated solution from α,β-dichloro-ethyl ether. Fenton[3] by the oxidation of a concentrated solution of tartaric acid with hydrogen peroxide in the presence of a small amount of ferrous iron prepared an acid which he showed to be dihydroxy maleic acid, $C_4H_4O_6.2H_2O$. This acid in cold aqueous solution slowly, and in warm solutions rapidly loses carbon dioxide and glycollic aldehyde is formed.



$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ COOH\end{array} \xrightarrow[Fe^{\prime\prime}]{H_2O_2} \begin{array}{l}COOH\\ |\\ C-OH\\ \|\\ C-OH\\ |\\ COOH\end{array} + H_2O \longrightarrow \begin{array}{l}COOH\\ |\\ CHOH\\ |\diagup OH\\ C\\ |\diagdown OH\\ COOH\end{array} \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHO\\ \\ \\ \\ \end{array} + 2CO_2$$

Dihydroxy-maleic acid was prepared by the Fenton method. From this a solution of glycollic aldehyde was prepared by dissolving a weighed amount of the crystallized dihydroxy maleic acid in water, which had been freed of oxygen. The decomposition of the acid was effected in an atmosphere of hydrogen at a temperature of about 70°. Carbon dioxide is rapidly evolved at this temperature. After expelling the carbon dioxide, the solution had a negligible acidity, gave the aldehyde reaction with Schiff's reagent, a silver mirror with ammoniacal silver nitrate, and a phenyl-osazone which melted at 169°. The phenyl-osazone of glyoxal melts at 169.5°.[4]

2. **The Oxidation of Glycollic Aldehyde.**—The oxidation was conducted in the usual manner. The data are given in the following table:

---

[1] *Ber.*, **25**, 2549 (1892).

[2] *Ibid.*, **25**, 2984 (1892).

[3] *J. Chem. Soc.*, **65**, 899 (1894).

[4] Pickel, *Ann.*, **232**, 231 (1885).

TABLE IV.

G. $KMnO_4$	G. KOH per l.	G. $C_2H_4O_2$.	G. $(COOH)_2$.	G. CO_2.	G. $C_2H_4O_2$ recovered as $(COOH)_2$ and CO_2.	$(COOH)_2$ from 6 g. $C_2H_4O_2$.	CO_2 from 6 g. $C_2H_4O_2$.	Av. g. KOH per l.
5.5	1.0	0.92	0.46	0.95	0.95	3.00	6.19	1.2
5.3	2.4	0.94	0.54	0.87	0.95	3.45	5.55	2.5
5.2	4.8	0.98	0.637	0.82	0.98	3.90	5.00	4.8
5.0	13.4	0.94	0.715	0.67	0.93	4.57	4.30	13.0

The amounts of oxalic acid and carbon dioxide produced by the oxidation of 6 g. (0.1 mol. wt.) of glycollic aldehyde are given in Cols. 6 and 7 and are plotted against the potassium hydroxide concentration in Fig. 7. The curve so obtained is a logarithmic one, for when the points are plotted on log paper a straight line is produced. This relationship is plotted on logarithmic paper in Fig. 8. The circled dots are the points experimentally determined.

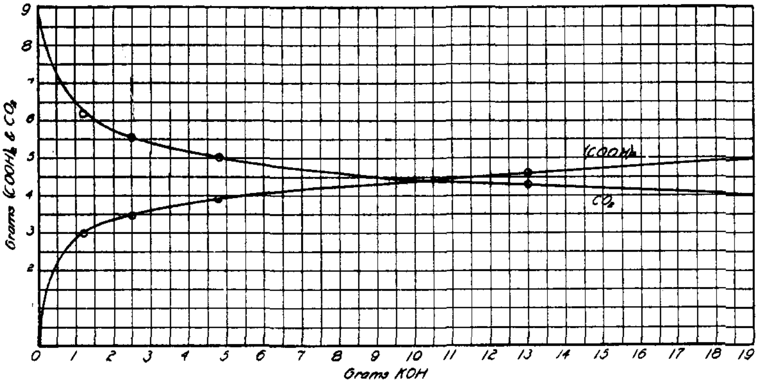


Fig. 7.—Oxidation of glycollic aldehyde.

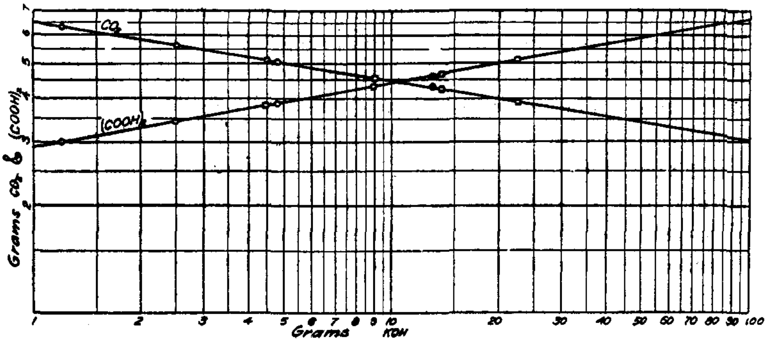


Fig. 8.—Oxidation of glycollic aldehyde.

Glyoxal.

1. The sodium acid sulfite derivative of glyoxal was used in this series of oxidations. Due to the comparative insolubility of the glyoxal bisulfite a standard solution was not prepared.

2. **The Oxidation of Glyoxal.**—The oxidation was carried out at a constant volume of one liter, the powdered bisulfite derivative being slowly added until the oxidizing solution was decolorized. The alkalinity at the end of the reaction was determined by titration, the average concentration of the potassium hydroxide being then calculated. The experimental results are given in Table V.

TABLE V.—OXIDATION OF GLYOXAL.

G. $KMnO_4$.	G. KOH per l.	G. $(CHO)_2$.	G. $(COOH)_2$	G. CO_2	G. $(CHO)_2$ recovered as $(COOH)_2$ and CO_2.	$(COOH)_2$ from 5.8 g. $(CHO)_2$.	CO_2 from 5.8 g. $(CHO)_2$.	Av. g. KOH per l.
10.00	None	1.09	None	1.66	...	None	8.80	Acid
11.00	4.45	1.30	0.156	1.84	1.307	0.69	8.21	4.39
10.40	8.9	1.25	0.265	1.64	1.253	1.24	7.61	8.4
10.24	13.35	1.24	0.402	1.50	1.249	1.88	7.01	12.5
10.00	22.25	1.23	0.686	1.20	1.234	3.23	5.65	21.5
10.15	44.5	1.28	1.45	0.53	1.284	6.58	2.40	43.4
10.50	72.0	1.36	1.617	0.49	1.36	6.90	2.09	71.0
10.50	96.0	1.36	1.617	0.50	1.365	6.90	2.13	95.0

The amounts of oxalic acid and carbon dioxide which would be produced by 5.8 g. (0.1 mol. wt.) of glyoxal under the conditions of the experiment are given in Cols. 7 and 8. These values plotted against the concentration of potassium hydroxide per liter are shown in Fig. 9.

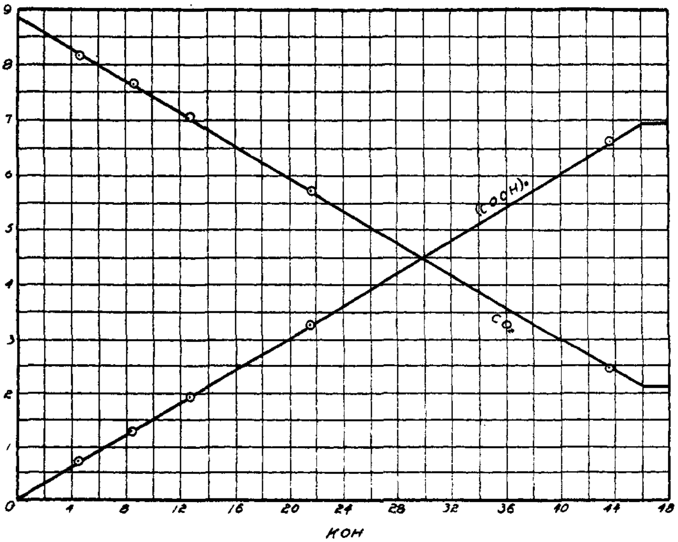
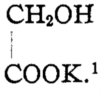


Fig. 9.—Oxidation of glyoxal.

It may be seen that the amounts of these acids produced by the oxidation of a constant amount of glyoxal is a linear function of the potassium hydroxide concentration between the concentration of zero g. and 45.5 g. per liter. At concentrations above the latter figure changes in concentration of the potassium hydroxide produce no changes in the ratio of oxalic acid and carbon dioxide produced. Between these limits $Y_o = 0.151\ X$ and $Y_c = 8.8 - 0.145\ X$ where Y_o and Y_c represent the grams of oxalic acid, Y_c the grams of carbon dioxide produced by the oxidation of 5.8 g. of glyoxal at a concentration of X g. of potassium hydroxide per liter. At concentrations above 45.5 g. potassium hydroxide per liter 76.7% of the glyoxal is oxidized to oxalic acid.

Glycollic Acid.



$$\begin{array}{l}CH_2OH\\ \quad|\\ COOK.{}^1/_2H_2O\end{array}$$

Preparation of Potassium Glycollate, $COOK.{}^1/_2H_2O$.—Glycollic acid was prepared as by Witzemann.[1] The crystals of glycollic acid were washed and dried, dissolved in water, and neutralized with potassium hydroxide solution. After concentration of the solution on the water bath, the potassium glycollate crystallized out. The salt was recrystallized once.

The Oxidation of Glycollic Acid.—The oxidation of glycollic acid was carried out in the usual manner. The results are given in Table VI. The amounts of carbon dioxide and oxalic acid produced by the oxidation of 12.3 g. potassium glycollate are plotted against potassium hydroxide concentrations in Fig. 10.

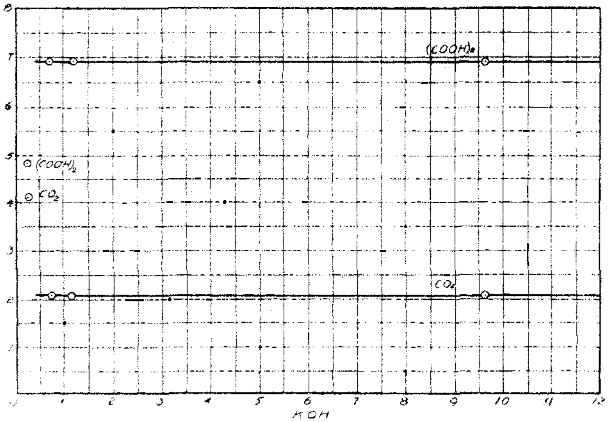


Fig. 10.—Oxidation of glyoxalic acid.

---

[1] This Journal, 39, 109 (1917).

TABLE VI.—OXIDATION OF GLYCOLLIC ACID.

G. $KMnO_4$.	G. KOH.	$(C_2H_3O_3K)$ $^1/_2H_2O$.	G. $(COOH)_2$.	G. CO_2.	G. $C_2H_3O_3K.^1/_2H_2O$ recovered as $(COOH)_2$ and CO_2.	$(COOH)_2$ from 12.3 g. of the salt.	CO_2 from 12.3 g. of the salt.	Av. g. KOH per l.
2.00	None	1.05	0.41	0.35	1.057	4.80	4.10	0.23
2.00	0.43	1.05	0.59	0.18	1.053	6.90	2.09	0.68
2.10	0.96	1.18	0.664	0.20	1.182	6.91	2.07	1.11
2.10	9.6	1.23	0.695	0.205	1.233	6.95	2.05	9.6
2.10	48.0	1.23	0.69	0.21	1.232	6.90	2.10	47.0

The same percentage of potassium glycollate is oxidized to oxalic acid regardless of whether the initial concentration of potassium hydroxide is 0.68 g. or 48 g. per liter.

It is only in the solution to which no potassium hydroxide was added that a less percentage of the oxalic acid is produced. The average concentration of potassium hydroxide in the "neutral solution" would be 0.23 g., for the amount of potassium hydroxide produced by the hydrolysis of potassium permanganate and by the potassium glycollate is in excess of the amount needed to neutralize the acids.

Glyoxalic Acid.

Preparation of Potassium Glyoxalate.—Potassium glyoxalate was prepared by the method of Otto Bechurts.[1] The salt was recrystallized from water and alcohol.

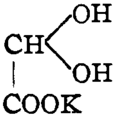
Oxidation of Potassium Glyoxalate.—The results obtained by the oxidation of  $CH(OH)_2-COOK$ are given in Table VII.

TABLE VII.—OXIDATION OF GLYOXALIC ACID.

G. $KMnO_4$.	G. KOH per l.	G. $C_2H_3O_4K$.	G. $(COOH)_2$.	G. CO_2.	G. $C_2H_3O_4K$ recovered as $(COOH)_2$ and CO_2.	$(COOH)_2$ from 13 g. salt.	CO_2 from 13 g. salt.	Av. conc. KOH per l.
1.2	None	0.80	None	..	...	..	8.80	Acid
1.2	0.50	1.24	0.403	0.44	1.231	4.22	4.61	0.47
1.2	0.99	1.24	0.43	0.41	1.227	4.50	4.30	0.93
1.2	2.4	1.20	0.453	0.36	1.185	4.91	3.90	2.1
1.2	4.9	1.20	0.50	0.32	1.193	5.42	3.47	4.6
1.2	4.8	1.30	0.624	0.26	1.293	6.35	2.64	45.0

The amounts of oxalic acid and carbon dioxide which would be produced by the oxidation of 13 g. (0.1 mol. wt.) of potassium glyoxalate are given in Cols. 7 and 8 of the table and are plotted against the average potassium hydroxide concentration in Fig. 11 and on logarithmic paper in Fig. 12. The logarithm of the oxalic acid and carbon dioxide production is a linear function of the logarithm of the potassium hydroxide concentration. The mathematical expression of this is $Y_o = 4.55\ X^{0.1027}$ and

---

[1] *Ber.*, 14, 581 (1881).

$Y_c = 4.28\ X^{-0.1377}$ Y_0 equals g. of oxalic acid and Y_c g. of carbon dioxide produced by the oxidation of 13 g. of potassium glyoxalate at a concentration of X g. of potassium hydroxide per liter.

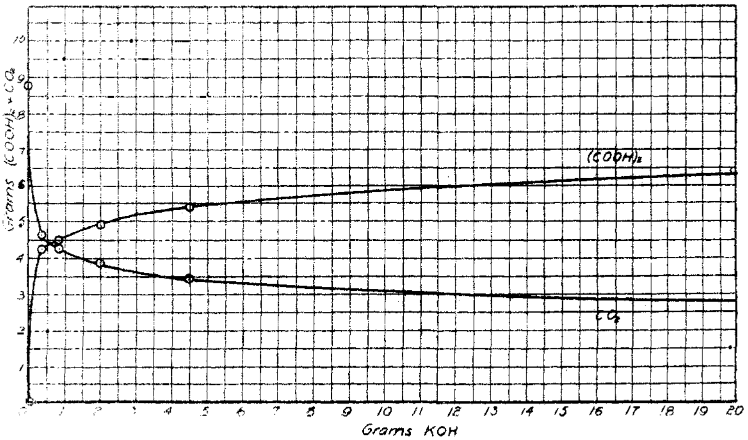


Fig. 11.—Oxidation of glyoxalic acid.

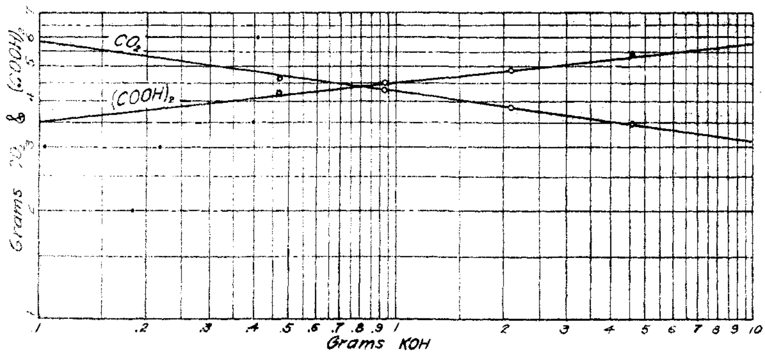


Fig. 12.—Oxidation of glyoxalic acid.

Discussion of Results.

1. The compounds whose oxidation products have here been studied may be classified in a number of ways. One way which is rather suggestive is on the basis of the similarity of the groups in the molecule.

A. Acetaldehyde, glycollic aldehyde, glyoxalic acid, glycollic acid would be classified together on this basis for the groups within the molecule are dissimilar. In the first compound there is a methyl group and an aldehyde group, in the second an alcohol group and an aldehyde group, in the third an aldehyde group and a carboxyl group, in the fourth an alcohol group and a carboxyl group.

B. In glycol and glyoxal, the two carbons in each compound hold the same groups, hence are classified together.

2. The relationship of the potassium hydroxide concentration to the amount of the oxidation products of group A is markedly different from the relationship which it bears to the oxidation products of the compounds of group B. The logarithms of the weights of the oxidation products of group A are (with the *possible* exception of glycollic acid) linear functions of the logarithms of the potassium hydroxide concentration employed. The amounts of the oxidation products of group B are linear functions of the potassium hydroxide concentration. Ethyl alcohol would be in group A for in this compound dissimilar groups are attached to the two carbon atoms.

3. In Fig. 8 the amounts of oxalic acid and carbon dioxide which are obtained by the oxidation of $^1/_{10}$ the molecular weight of glycollic aldehyde at various concentrations of potassium hydroxide are plotted. The experimental points on this line are circled. In this same graph the points within the squares represent the figures given in Col. 9 of acetaldehyde Table I for 50°. It may be seen by reference to the description of the method for deriving these figures that they represent the weights of oxalic acid which are produced by the oxidation of $^1/_{10}$ of the molecular weight of the substance which is oxidized to oxalic acid and carbon dioxide during the alkaline oxidation of acetaldehyde. As may be seen the points within the squares lie on the same straight line as the points within the circles. This means that the potassium hydroxide has the same effect on the intermediate compound formed in the alkaline oxidation of

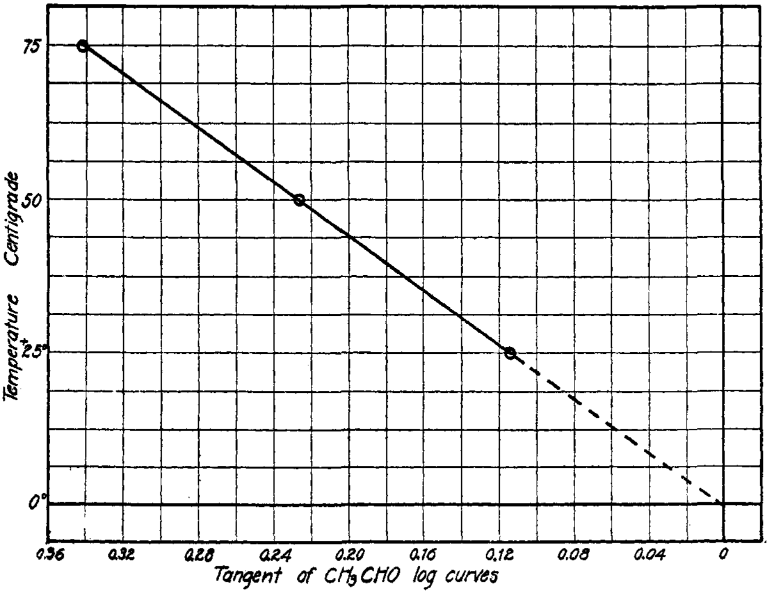


Fig. 13.

acetaldehyde as it does upon glycollic aldehyde when the latter compound is oxidized in alkaline solution with potassium permanganate. This identity of effect may be shown in another way. If glycollic aldehyde is the intermediate product in the oxidation of acetaldehyde then the equations which were derived for the production of oxalic acid and carbon dioxide from the intermediate product should hold true for the production of these compounds from glycollic aldehyde. The equations derived for 50° were as follows:

$$Z_o = 2.87\, X^{0.184} \qquad (1)$$

$$Z_c = 6.5\, X^{-0.165} \qquad (2)$$

where Z_o is the weight of the oxalic acid; Z_c, the weight of the carbon dioxide; and X, the weight of the potassium hydroxide per liter.

The correlation of the weights of the oxidation products obtained from glycollic aldehyde experimentally and those calculated by means of the two above equations is shown in the following table:

TABLE VIII.—GLYCOLLIC ALDEHYDE OXIDATION. RESULTS CALCULATED AND OBSERVED.

Value of X G. per l.	G. of oxalic acid.		G. of carbon dioxide.	
	By expt.	By calculation.	By expt.	By calculation.
1.2	3.00	2.97	6.19	6.30
2.5	3.45	3.40	5.55	5.60
4.8	3.90	3.83	5.00	5.02
13.0	4.57	4.60	4.30	4.25

This shows that these equations do express within the limits of experimental error the relationship of the alkali concentration to the amounts of oxidation products.

This, then, is strong evidence in favor of the theory of Nef and Denis that glycollic aldehyde is an intermediate compound formed in the alkaline oxidation of acetaldehyde with potassium permanganate.

McLeod[1] has shown that vinyl alcohol molecules are present in a solution of acetaldehyde as soon as a concentration of 0.1% of alkali is attained. It is shown in Part I that the oxidation of acetaldehyde to acetic acid is not quantitative when the potassium hydroxide concentration is greater than about 0.1%. That is, oxalic acid and carbon dioxide begin to be formed by the alkaline oxidation of acetaldehyde as soon as the alkali concentration reaches a point which is approximately the same as that which McLeod has shown to be the concentration at which the formation of vinyl alcohol molecules first occurs. The present paper also shows that potassium hydroxide concentration has the same effect upon the intermediate compound in the oxidation of acetaldehyde as it does upon glycollic aldehyde, and that it behaves in an entirely different

---

[1] *Loc. cit.*

manner upon the other two carbon atom compounds which have been studied.

4. It may be seen by reference to the tables that the maximum amount of oxalic acid produced by the oxidation of $^1/_{10}$ the molecular weight of glyoxal is the same as the maximum amount produced by the oxidation of $^1/_{10}$ the molecular weight of potassium glycollate. A concentration of 45.5 g. of potassium hydroxide per liter is required in the case of glyoxal while in the case of potassium glycollate less than one gram is required.

Glyoxal on being boiled in aqueous solution is converted into glycollic acid. Benzoyl formaldehyde does not undergo the benzilic acid rearrangement in hot water, but in cold alkaline solutions this change takes place with such remarkable speed to form mandelic acid that Fehling's solution is unaffected by this keto-aldehyde. The effect of the alkali on glyoxal is to cause this compound to undergo the benzilic acid rearrangement to glycollic acid. Consequently, the amount of oxalic acid produced by the oxidation of glyoxal should be the same as the maximum amount produced by the oxidation of glycollic acid.

5. The effect of the alkali concentration on the production of oxalic acid and carbon dioxide from glycol, glycollic aldehyde, glyoxal, glycollic acid and glyoxalic acid under the conditions of these experiments is seen to be widely different within certain limits in the compounds studied. Considerable light is shed on the course of the oxidation of these compounds when the relationships of the graphs are studied.

A. Glycol.—The production of oxalic acid and carbon dioxide from glycol reaches a constant value when the concentration of the alkali is 3 g. per liter; from glycollic acid at a concentration lower than that for glycol; from glyoxal at a concentration of 46 g. per liter.

Nef,[1] made a study of the behavior of certain glycols and glycerol towards alkalies alone and towards alkaline oxidizing agents. He found that hydrogen, ethyl alcohol, carbon dioxide, formic acid, acetic acid and glycollic acid were obtained by heating a mixture of ethylene glycol and sodium hydroxide for 2.5 hours at 230° to 285°.[2] As noted above glycol reacts with aqueous solutions of alkalies containing lead peroxide giving hydrogen as one of the products. This result in aqueous solution is in harmony with the pyrogenic decomposition of glycol.[3]

The presence of carbon dioxide in our experiments with glycol and also those of Glaser and Morawski[3] can be readily explained on the assumption

---

[1] *Ann.*, **335**, 279 (1904).

[2] Cf. Wurtz, *Ann. chim. phys.*, [3] **55**, 417, 477 (1859).

[3] *Loc. cit.*

of the intermediate formation of glycollic aldehyde which is immediately dissociated into two molecules of formaldehyde,[1] *i. e.*,

$$(a)\ CH_2OH.CH_2OH \longrightarrow CH_2OH.CHO \longrightarrow 2CH_2O.$$

In harmony with Nef's views to the effect that the metallic salts of the alcohols dissociate at lower temperatures than the alcohol itself, it is evident that as the concentration of the alkali increases in these oxidations, the tendency of the glycol would be towards the formation of glyoxal, *i. e.*,

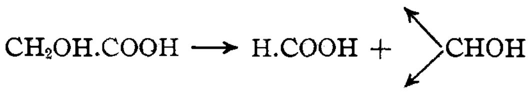
$$CH_2OH.CH_2OH \longrightarrow CHO.CHO + 2HOH.$$

As we have repeatedly pointed out, glyoxal is converted to glycollic acid even in the cold in aqueous alkalies. This reaction is so rapid in Fehling's solution that no reduction whatsoever takes place.[2]

If glycol reacts to give compounds which yield carbon dioxide on oxidation, and furthermore if glycol reacts to give glycollic acid as an intermediate compound, then it follows since glycol and glycollic acid are both oxidized to carbon dioxide and oxalic acid under the same conditions, the yield of carbon dioxide should be greater and that of the oxalic acid should be less than the yield of these two compounds would be from glycollic acid. That this explanation of the oxidation of glycol is the correct one is very evident from Figs. 6 and 10.

The only glyoxal which we had at our disposal was that obtained from the sodium acid sulfite compound obtained from Kahlbaum. Harries and Temme[3] have pointed out the existence of several polymerized forms of glyoxal which reduce Fehling's solution while the monomolecular variety does not. From our general knowledge of the behavior of monomolecular glyoxal and like compounds towards alkalies, it is evident that Fig. 10 would also be that for monomolecular glyoxal. From these facts it is obvious that Fig. 9 must be that of one of the polymeric varieties of glyoxal.

B. Glycollic Acid.—That glycollic acid is the intermediate compound in the oxidation of glycol which in turn is oxidized to carbon dioxide and oxalic acid follows from a consideration of Figs. 10 and 12. If glyoxalic acid were such an intermediate compound then the amounts of oxalic acid and carbon dioxide produced would not become constant at concentrations of alkali as low as one gram per liter. Glycollic acid may be supposed to react as follows:

(a) 

$$CH_2OH.COOH \longrightarrow H.COOH + \rangle CHOH$$

which would yield carbon dioxide, and

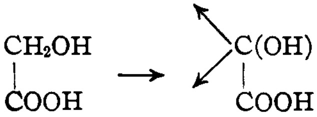
---

[1] Cf. Nef, *Ann.*, **335**, 312 (1904).

[2] Debus, *Ibid.*, **100**, 5 (1856); *Ibid.*, **102**, 20 (1857).

[3] *Ber.*, **40**, 165 (1907).

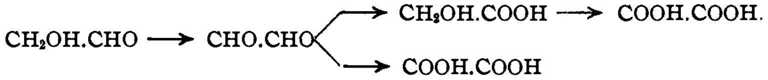
(b)



$$\begin{array}{c}\mathrm{CH_2OH}\\ | \\ \mathrm{COOH}\end{array} \longrightarrow \begin{array}{c}\nwarrow\!\!\!\swarrow\mathrm{C(OH)}\\ | \\ \mathrm{COOH}\end{array}$$

which on oxidation would give oxalic acid.

Glycollic Aldehyde.—Since it has been firmly established by the above work that glycollic aldehyde is an intermediate product in oxidation of acetaldehyde to oxalic acid and carbon dioxide it is of the greatest interest to trace the course of this oxidation if possible to the intermediate compound just preceding the formation of oxalic acid and carbon dioxide. Heimrod and Levene,[1] Witzemann[2] and Denis[3] explain the oxidation of glycollic aldehyde on the basis that this compound is oxidized to glyoxal and this in turn to oxalic acid, i. e.,



$$\begin{tikzcd} & & \mathrm{CH_2OH.COOH} \arrow[r] & \mathrm{COOH.COOH.} \\ \mathrm{CH_2OH.CHO} \arrow[r] & \mathrm{CHO.CHO} \arrow[ur] \arrow[dr] & & \\ & & \mathrm{COOH.COOH} & \end{tikzcd}$$

If glyoxal is formed in the alkaline oxidation of glycollic aldehyde, then the intermediate formation of glycollic acid is to be expected by the reaction of glyoxal with alkalies.

A second possibility is that the alcohol and the aldehyde group of glycollic aldehyde undergo simultaneous oxidation with the formation of glyoxalic acid. A third possibility is that the aldehyde group of glycollic aldehyde is oxidized to a carboxyl group with the formation of glycollic acid. The experimental evidence presented in this paper does not offer conclusive evidence as to the exact course of the reaction in the alkaline oxidation of glycollic aldehyde.

Summary.

1. The production of oxalic acid and carbon dioxide from glycol and polymeric glyoxal in the alkaline oxidation with potassium permanganate is a linear function between certain definite limits of the potassium hydroxide concentration in the oxidizing media.

2. The logarithm of the production of oxalic acid and carbon dioxide from glycollic aldehyde and glyoxalic acid (and probably from glycollic acid) is a linear function between certain limits of the logarithm of the potassium hydroxide concentration in the oxidizing media.

3. Very strong experimental evidence is given to show that glycollic aldehyde is formed as an intermediate product in the alkaline oxidation of acetaldehyde with potassium permanganate.

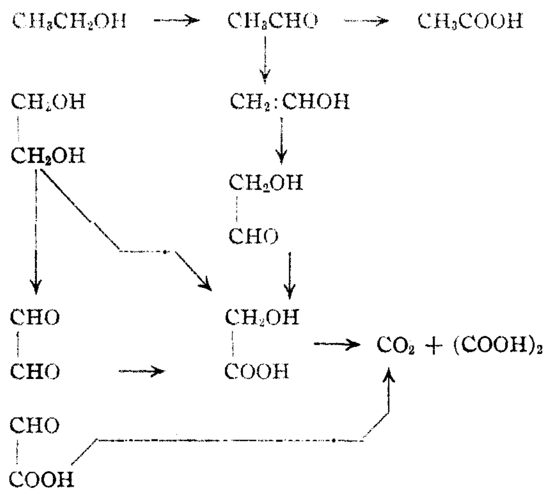
4. Evidence is presented to show that potassium permanganate in alkaline solution oxidizes the two carbon alcohols, aldehydes and acids according to the following scheme:

---

[1] *Biochem. Z.*, **29**, 31 (1910).

[2] THIS JOURNAL, **39**, 2657 (1917).

[3] *Am. Chem. J.*, **38**, 568 (1907).



Columbus, Ohio.

ETHYLENE CHLOROHYDRIN AND β,β-DICHLOROETHYLSULFIDE.[1]

By M. Gomberg.

Received June 21, 1919.

Within a few days after the so-called "mustard gas" was introduced as a means of offence in warfare (July 12–13, 1917), it was definitely identified as β,β-dichloroethylsulfide. There was reason to believe that it had been manufactured from ethylene chlorohydrin, according to the method described some 30 years previously by V. Meyer.[2] A second possible method,—the reaction between ethylene and the mono- or dichloride of sulfur,—was also given some consideration, but on the basis of preliminary experiments in several laboratories, was not looked upon at that time as promising.[3]

The directions in the literature for the preparation of dichloroethylsul-

---

[1] This article has been approved for publication by the Director of the Chemical Warfare Service. The experimental work was done at the Chemical Laboratory, University of Michigan, under the auspices of the Bureau of Mines, War Gas Investigations. The results were reported to the Bureau of Mines in three reports—March 9, April 8, and June 28, 1918.

[2] *Ber.*, **19**, 3260 (1886).

[3] In the light of subsequent and the more recent events, it seems almost certain that Guthrie actually did have in his hands some dichloroethylsulfide, as a result of his experiments with this reaction. He says: "Its smell is pungent and not unpleasant, resembling that of oil of mustard; its taste is astringent and similar to that of horse-radish. The small quantities of vapor which it diffuses attack the thin parts of the skin, as between the fingers and around the eyes, destroying the epidermis. If allowed to remain in the liquid form on the skin, it raises a blister." (*Quart J. Chem. Soc.*, **12**, 117 (1860).)