p-amino-benzhydrol. They are very much alike in properties, but vary in color from yellow to crimson.

The first 3 compounds listed in this table constitute examples of alkali-insoluble phenols (naphthols). The insolubility of these dyes lends support to the theory of Torrey and Kipper,[1] *viz.*, that phenols are generally insoluble if in each molecule there is a long side chain *ortho* to the hydroxyl group and at least one other substituent in the ring. In this case the C_4H_4 residue of the naphthalene constitutes the auxiliary substituent. The behavior of these dyes in dilute alkalies is in harmony also with Adams'[2] more recent theory concerning the solubility of phenols.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE OXIDATION OF ETHYL ALCOHOL BY MEANS OF POTASSIUM PERMANGANATE.

BY WILLIAM LLOYD EVANS AND JESSE E. DAY.

Received May 22, 1919.

A preliminary report of a portion of the work included in this paper has already been made.[3] The influence of the alkali on the oxidation of organic and inorganic compounds by means of potassium permanganate has been studied by other early investigators (Margueritte, Pelouze, Bussey, Hempel and Berthelot) in addition to those mentioned in the preliminary article.

Among the objects of this investigation were the following: (1) to ascertain what are the reaction products when ethyl alcohol is oxidized both in neutral and in alkaline potassium permanganate solutions under known conditions of temperature; (2) to study the effect of temperature, of change in the initial concentration of the alkali present, and their combined effect on the character of the reaction products; (3) to study the mechanism of the oxidation of ethyl alcohol under these variable conditions.[4]

It has been definitely established that acetic acid is the only product obtained when ethyl alcohol is oxidized by an aqueous solution of potassium permanganate, but that acetic acid, oxalic and carbonic acids are also formed when the oxidation is conducted in the presence of potassium hydroxide the concentration being above certain minimum values (p. 1282), Hepter,[5] studying the action of potassium permanganate on organic compounds in acid and alkaline solution, found that substances

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[1] Torrey and Kipper, THIS JOURNAL, 30, 840 (1908).

[2] Adams, *Ibid.*, 41, 247 (1919).

[3] THIS JOURNAL, 38, 375 (1916).

[4] *Ibid.*, 38, 377 (1916).

[5] *Z. anal. Chem.*, 51, 409–29 (1912).

having an alkyl group were always oxidized by alkaline permanganate to the corresponding aliphatic acid, carbon dioxide and oxalic acid, and the results were dependent upon the temperature of the reaction mixture and upon the position which the intermediate oxidation substance occupied in its own homologous series.

Barendrecht[1] determined alcohol in rather dilute solution by adding the alcohol to a boiling mixture of potassium permanganate and potassium hydroxide solutions, in which it is oxidized to carbon dioxide: $C_2H_5OH + 12KMnO_4 + 12KOH \longrightarrow 12K_2MnO_4 + 9H_2O + 2CO_2$. He noticed that the temperature was an essential factor in the complete conversion of the alcohol to carbon dioxide.

Cochenhausen,[2] on treating acetone with potassium permanganate in solution with potassium hydroxide found that it was oxidized to acetic, oxalic and carbonic acids. Greifenhagen, Koenig and Scholl[3] estimated carbohydrates, polyhydric alcohols, the corresponding aldehydes, ketones, and polysaccharides by oxidizing them to oxalic and carbonic acid with alkaline potassium permanganate. Greifenhagen found that the formation of oxalic acid and carbon dioxide was quantitative, and was dependent upon the alcohol, aldehyde and ketone groups.

Witzemann[4] has investigated the character of the reaction products obtained by oxidizing acetone with potassium permanganate with varying initial concentrations of alkali. His experimental results were similar to those reported by us in our previous paper.

Experimental Part.

(*a*) **Methods of Analysis.**—The methods of analysis were the same as those described in our first paper, together with the following addenda.

Oxalic Acid.—The acid was first precipitated as the calcium salt by the method previously described for its quantitative determination. The salt was then filtered, washed and finally dissolved in slightly more than its equivalent of dil. sulfuric acid. On the addition of an equal volume of absolute alcohol the calcium sulfate was precipitated and removed. On spontaneous evaporation the free oxalic acid crystallized out in the well defined needle form. This procedure cannot be quantitative because of the presence of the slight excess of sulfuric acid. The purity of the product was checked by a melting-point determination. Another qualitative test for oxalic acid was that contained in our preliminary paper.[5]

An aliquot part of the solution containing the oxidation products was used to determine the oxalic acid present as potassium oxalate. With

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[1] *Z. anal. Chem.*, **52**, 167–72 (1913).

[2] *J. prakt. Chem.*, [2] **58**, 451 (1898).

[3] *Biochem. Z.*, **30**, 151 (1910); **35**, 169–193 (1911).

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

[5] *Ibid.*, **38**, 378 (1916).

phenolphthalein as the indicator the sample was first slightly acidulated with 20% acetic acid boiled for a few minutes to drive off carbon dioxide, then made barely alkaline with ammonium hydroxide after which the oxalate was precipitated by 5% calcium acetate solution. The removal of the carbon dioxide was unnecessary but insured the absence of carbonate in the calcium precipitate. After filtering and washing the calcium oxalate on purified asbestos in a Caldwell crucible, it was titrated against standard potassium permanganate solution in the presence of 5% sulfuric acid in the usual manner. The filtration, washing and titration of the insoluble oxalate, when carried out as described, were found to be more rapid and satisfactory than when the precipitate was collected and washed on a filter paper, dissolved by means of sulfuric acid and then titrated.

Acetic Acid.—Methods were examined for the determination of this acid by the use of (1) hydrochloric acid, (2) sulfuric acid, (3) potassium hydrogen sulfate, (4) sirupy phosphoric acid, (*a*) distillation to approximately complete dehydration under reduced pressure, (*b*) distillation at ordinary pressure and maintaining the volume being distilled at 75 cc.

Some of these methods are discussed by Stilwell and Gladding,[1] particularly (4*a*). Withrow and Fritz[2] have modified the method of Stilwell and Gladding according to (4*b*).

The following additional facts were observed relative to these methods and their bearing on this problem: When proceeding according to (1) it was found necessary to add an excess of hydrochloric acid in order to sweep over the last portions of the acetic acid. By (2) and (3), sulfur dioxide was found present in the distillate, which introduced an appreciable error when the amount of oxalic acid in the oxidation solution was large. Carbon dioxide was present in the acetic acid distillate regardless of the method employed. When distilled with sirupy phosphoric acid under reduced pressure as in (4*a*), the solution of carbon dioxide in the condensate was avoided. Evans and Witzemann[3] have found that the loss of acetic acid by use of suction, was negligible when the acetic acid solution was very dilute. This was also the case in the experiments recorded in this paper. The distillation was much expedited by placing a second fractionating flask and a Kjeldahl connecting bulb between the distillation flask and the condenser, making it unnecessary to cool the contents of the distilling flask in order to prevent spattering on the addition of water to the hot mixture, as it was then extremely difficult for the phosphoric acid to reach the receiving vessel. The addition of water was made at the ordinary pressure in order to avoid the foaming, which otherwise occurred when the amount of alkali on the original sample was large.

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[1] THIS JOURNAL, 4, 105 (1882).

[2] Thesis by Howard Fritz of this laboratory.

[3] THIS JOURNAL, 34, 1091 (1912).

In (4*b*) the total volume of the distillate was not constant in quantity, as it was dependent upon the amount of acetic acid present in the sample. Inasmuch as the distillation was carried out at ordinary pressure, the carbon dioxide liberated was present in the condensate. Dr. Homer B. Adkins (this laboratory) found that bubbling carbon dioxide-free air through the distillate removed the undesirable gas without seriously affecting the quantity of acetic acid contained in these solutions of considerable dilution. In the following experiments on alcohol the same method was employed in eliminating the carbon dioxide. The distillate from methods (4*a*) and (4*b*) was titrated with a standardized potassium hydroxide solution with phenolphthalein as the indicator. In each experiment a correction was made for the volatile acids contained in the amounts of phosphoric acid used. It was observed in making these distillations that when the amount of potassium hydroxide present was large, a much greater excess of phosphoric acid over that required for the neutralization of the alkali, was necessary in order to completely expel the acetic acid, and also that the time required for the operation was decreased thereby.

(*b*) **Chemicals Used in the Oxidation.**—Absolute alcohol[1] was employed in these series of oxidations. Additional tests with phenyl-hydrazine and sodium hydroxide gave no turbidity, proving the absence of aldehydes. To obtain a pure product, commercial absolute alcohol was treated with calcium oxide in the customary way and then was stored with anhydrous copper sulfate in air-tight glass-stoppered bottles. In making up a standard solution sufficient alcohol (b. p. = 77.7° and 77.8°, at 739 and 749 mm.; $[d]_4^{20} = 0.7897$; $[d]_4^{25} = 0.7854$) was distilled from the copper sulfate to give a 2 *M* or 9.21% solution (92.096 g. anhydrous alcohol per liter of solution), having $[d]_4^{20} = 0.9830$ and $[d]_4^{25} = 0.9817$. These density values were referred to "Circular of the Bureau of Standards" No. 19, pp. 6 and 7, in order to get the per cent. by weight of alcohol present. An ordinary pyknometer (capacity about 60 cc.) was used in making these density determinations. All alcohol distillations were made in glassware, with cork connections.

Distilled water was aerated with carbon dioxide-free air for 5 to 6 hours. Carbon dioxide blanks were then run. One drop of 0.1017 *N* potassium hydroxide solution gave a permanent pink color to 100 cc. of the water containing one drop of phenolphthalein.

The oxidizing power of the potassium permanganate was established by titrating samples of about 0.13 g. each in solution against standard potassium tetroxalate solution. It was found to have a value of 98.67% of that required by theory.

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[1] Satisfying the requirements given in Merck, "Chemical Reagents, their Purity and Tests," 1914 edition.

A potassium hydroxide solution containing 340.8 g. per liter (1 cc. = 0.004 g. carbon dioxide) was prepared and kept in a stock bottle.

(*c*) **Apparatus and Manipulation.**—Each oxidation which involved the addition of alkali was carried out as follows: The required amount potassium hydroxide solution was measured into a wide-mouth, 2-liter balloon flask, and made up to 1000 cc. with carbon dioxide-free water. When the alkalinity was less than 5.32 g. per liter (*v.* Table IV) about 1100 cc. of solution was prepared and small portions were titrated against standard sulfuric acid, to avoid any error due to the extensive dilution of a small volume (0.14 to 8.5 cc.) of the potassium hydroxide stock solution. 30.404 g. of crystallized potassium permanganate, equivalent to 30 g. of 100% salt, was next introduced, and the flask immediately closed by a rubber stopper into which was fitted a mercury sealed glass stirrer, a 25 cc. pipet and a piece of ordinary glass tubing, for the oxidations carried out at 25° and 50°. For the series at 75° and 100°, in addition to the above, an ordinary condenser provided with a soda-lime guard-tube was attached through the stopper by means of two adapter tubes. The closed vessel was next clamped in position in a bath which was kept at the desired temperature

The thermostat bath was water for the 25° and 50° oxidations and paraffin for the 75° and 100° series. Heat was supplied by a large size "El Boilo" immersion heater. The amount of current flowing through the heater was automatically controlled by means of a mercury-toluene regulator and a lamp rheostat of considerable range. The temperature was held constant to within 0.15°.

When the desired temperatures of the flask and bath were reached and with the reaction mixture constantly stirred, 9.21% alcohol solution was slowly added drop by drop from a buret, loosely stoppered at the upper end, attached to the small glass tubing, until the reduction of the permanganate was complete. The end-point was determined by drawing a portion of the reaction mixture into the pipet, where, after the precipitated hydrated oxide or oxides of manganese had settled, the observations could be made. The color desired before discontinuing the addition of the alcohol in the case of the alkaline solutions was a very pale green, and in the neutral solutions was a delicate pink. This faint color was generally discharged within 24 hours through decomposition of the oxidizing agent.

Approximately the same color changes were observed by Chapman and Smith[1] in both their alkaline and neutral solutions. They stated "that the alkaline solution rapidly becomes green, and for a considerable time no binoxide of manganese is deposited," while it came down at once from the neutral solution. They made no reference to the weak alkaline

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[1] *Loc. cit.*

solution. In solutions of high alkali concentration we found a light coat of the brown oxide of manganese on the surface almost immediately following the addition of the reducing agent.

The reaction mixture after being filtered in a carbon dioxide-free apparatus was made up to 2000 cc. and analyzed.

The 2-liter flask A containing the oxidation mixture was removed from the thermostat, placed on the rubber covered ring C and connected up as shown in Fig. 1. On the application of suction, and with the pinch-clamp F and screw-clamp H closed, the mixture was drawn from A into the glass jar E. The oxide of manganese was retained on the outside of the Pukal filter G while the filtrate passed on into the 2-liter suction flask. After a sufficient amount of material had been transferred to E, the clamp F was opened to stop transference. When the filtration and washing were complete, clamp H was opened and water sucked into the cell to wash the inside of it. The plate glass cover D and the vessel were ground and coated with vaseline so as to prevent leakage of air into the apparatus. Several

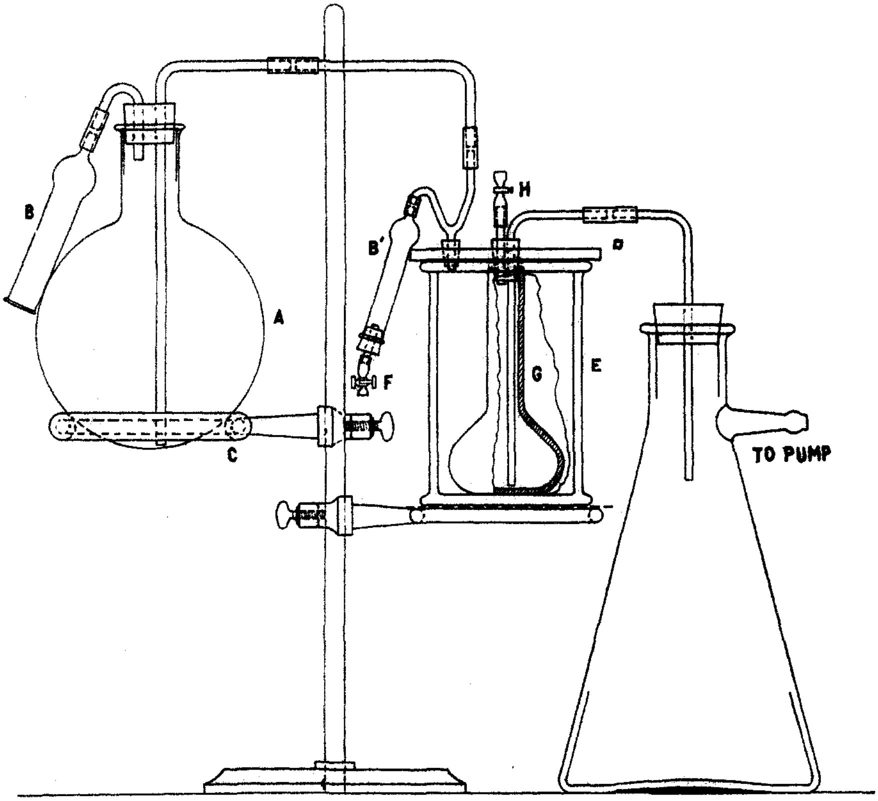

Fig. 1.

types of filters were tried, but the unglazed cell was found to be highly satisfactorv. as a clean filtration and three washings were usually completed within 10 to 15 minutes. The cell was cleaned by first removing the main portion of the precipitate with a steel spatula, then was sponged off and finally treated with hydrochloric acid after which water was sucked through it until the washings were free from chlorides. To assure ourselves that no appreciable error was introduced due to absorption or possible adsorption by the Pukal filter, determinations were made on a filtrate containing the maximum amount of oxidation products obtained in the experiment.

(*d*) **Data.**—The results obtained from 4 series carried out at 25, 50, 75 and 100° are given in Tables I, II, III and IV, respectively. They are also represented in the form of curves as found in Figs. 2, *et. seq*. 30.404 g. of potassium permanganate was used in each experiment.

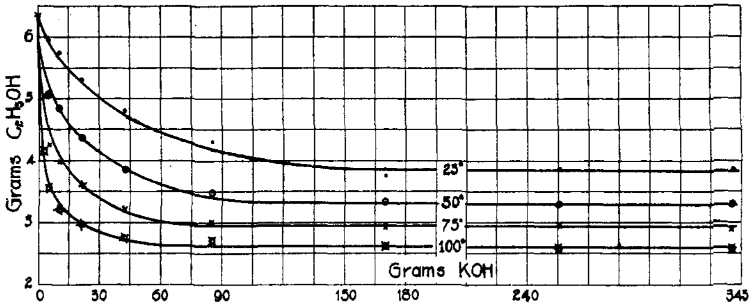

Fig. 2.

OXIDATION RESULTS.

TABLE I.

Temperature = 25°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Expt. No.	KOH.	C_2H_5OH.	CO_2.	$(COOH)_2$.		CH_3COOH.	CO_2.	$(COOH)_2$.	CH_3COOH.	% yield.
1	0.00	6.37	0.00	0.000	0.00	8.17	0.00	0.000	5.91	98.43
2	5.32	5.95	0.581	0.401	59.80	7.03	0.450	0.310	5.44	99.16
3	10.65	5.72	0.845	0.869	49.30	6.21	0.680	0.700	5.00	98.78
4	21.30	5.30	1.02	0.912	46.94	5.17	0.890	1.05	4.49	96.58
5	42.60	4.82	1.08	1.60	40.69	4.44	1.03	1.53	4.24	99.33
6	85.20	4.30	1.22	2.09	37.35	3.60	1.14	1.95	3.86	98.90
7	170.4	3.74	0.942	1.71	35.96	3.04	1.16	2.11	3.75	99.09
8	255.6	3.85	0.866	1.81	34.00	3.18	1.06	2.17	3.80	99.43
9	340.8	3.86	0.964	1.75	36.09	3.16	1.15	2.09	3.77	99.06

TABLE II.

Temperature = 50°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1.	2.	3.	4	5.	6.	7	8.	9.	10.	11.
Expt. No.	KOH.	C_2H_5OH.	CO_2.	$(COOH)_2$.		CH_3COOH.	CO_2.	$(COOH)_2$.	CH_3COOH.	% yield.
								0.00	5.87	97.76
10	0.00	6.40	0.00	0.00	0.00	8.17	0.05	0.98	4.55	97.48
11	5.32	5.05	1.04	1.07	50.00	4.99	0.9	1.58	3.88	97.42
12	10.65	4.77	1.39	1.64	46.30	4.02	1.34	2.06	3.51	98.74
13	21.30	4.37	1.45	1.96	43.22	3.33	1.53	53	2.99	98.13
14	42.60	3.85	1.49	2.12	41.71	2.50	1.78	2.	2.77	97.68
15	85.20	3.48	1.33	2.15	38.78	2.09	1.76	2.84	2.70	98.89
16	170.4	3.35	1.32	2.18	38.13	1.96	1.81	3.00	.57	98.82
17	255.6	3.30	1.35	2.24	38.12	1.84	1.88	3.12	2 7	99.61
18	340.8	3.30	1.32	2.10	38.90	1.98	1.84	2.93	2.7,	

TABLE III.

Temperature = 75°.

	Materials used. G		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Expt. No.	KOH.	C_2H_5OH.	CO_2.	$(COOH)_2$.		CH_3COOH.	CO_2.	$(COOH)_2$.	CH_3COOH.	% yield.
19	0.00	6.38	0.00	0.00	0.00	8.24	0.00	0.00	5.95	99.11
20	5.32	4.25	1.38	2.19	43.21	3.22	1.50	2.02	3.49	97.61
21	10.65	3.97	1.58	2.10	43.30	2.60	1.83	2.44	3.02	98.20
22	21.30	3.62	1.65	2.33	42.01	2.00	2.10	2.96	2.54	99.04
23	42.60	3.20	1.65	2.40	41.35	1.46	2.38	3.45	2.10	100.34
24	85.20	3.03	1.63	2.41	40.84	1.19	2.47	3.66	1.81	98.89
25	170.4	2.93	1.65	2.34	41.80	1.09	2.59	3.68	1.71	98.80
26	255.6	2.95	1.57	2.38	40.20	1.17	2.45	3.71	1.83	99.46
27	340.8	2.88	1.58	2.28	41.39	1.11	2.52	3.64	1.78	98.72

TABLE IV.

Temperature = 100°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Expt. No.	KOH.	C_2H_5OH.	CO_2.	$(COOH_2)$.		CH_3COOH.	CO_2.	$(COOH)_2$.	CH_3COOH.	% yield.
28	0.00	6.22	0.00	0.000	0.00	8.12	0.00	0.000	6.00	99.91
29	0.415	6.18	0.00	0.000	0.00	8.02	0.00	0.000	5.98	99.59
30	0.461	6.09	0.172	0.034	83.95	7.79	0.130	0.026	5.89	99.87
31	0.530	6.00	Undetd.	0.052	...	7.43	...	0.040	5.70	..
32	0.662	5.81	0.504	0.341	60.23	6.96	0.400	0.270	5.52	99.46
33	0.863	5.65	0.981	0.767	56.65	6.14	0.800	0.625	5.00	99.30
34	2.66	4.14	1.20	1.99	38.00	3.20	1.33	2.21	3.56	98.96
35	5.32	3.54	1.33	2.21	38.13	2.19	1.73	2.87	2.85	99.02
36	10.65	3.22	1.52	2.32	40.00	1.63	2.17	3.32	2.33	100.37
37	21.30	2.97	1.64	2.39	41.30	1.17	2.55	3.71	1.81	100.34
38	42.60	2.75	1.69	2.36	42.20	0.86	2.83	3.96	1.44	100.14
39	85.20	2.72	1.78	2.47	42.30	0.685	3.01	4.19	1.16	100.08
40	170.4	2.64	1.81	2.45	43.02	0.539	3.16	4.28	0.940	99.13
41	255.6	2.57	1.77	2.39	43.04	0.508	3.17	4.29	0.910	98.85
42	340.8	2.58	1.98	2.23	47.53	0.515	3.54	3.99	0.920	99.89

Discussion.

Fig. 2 shows the number of grams of absolute alcohol required to reduce a constant weight of potassium permanganate at the 4 different temperatures and with increasing initial concentrations of the alkali. Beyond an alkalinity of about 100 g. (cf. Fig. 10) per liter of water, an increase in the initial concentration of the potassium hydroxide had little further effect on the amount of alcohol necessary to reduce the potassium permanganate completely. The curves showing the amounts of the oxidation products in Figs. 3, 4, 5 and 6 are plotted on the basis of a constant quantity of alcohol (4.605 g. or 0.1 molecule). Figs. 7, 8 and 9 show the acetic, oxalic and carbonic acid curves for the 4 temperatures, respectively, and are represented on the same basis.

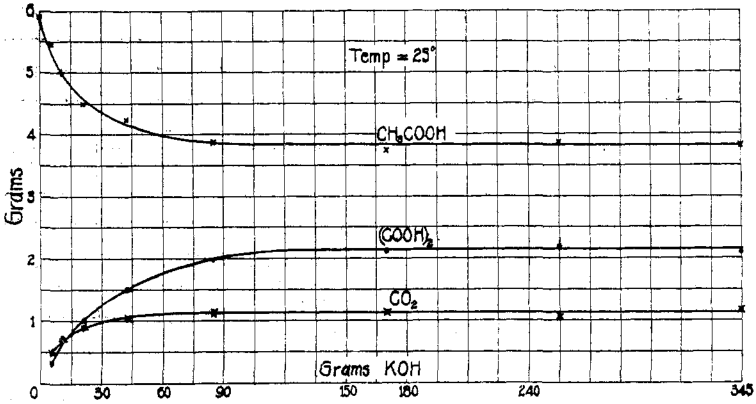

Fig. 3.

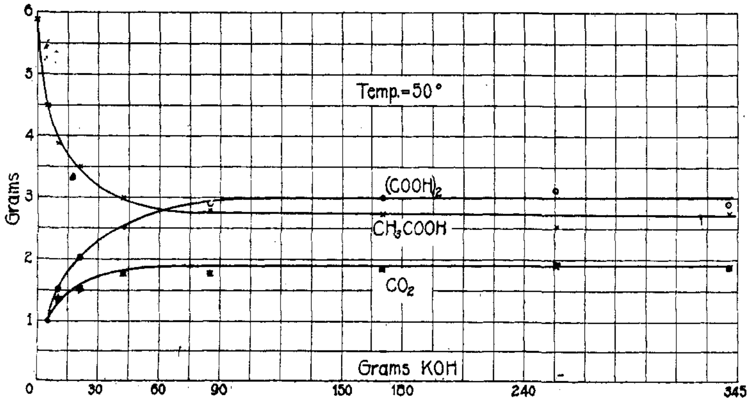

Fig. 4.

(*a*) **Oxidation Products.**—In the neutral reactions, acetic acid was the only substance found in quantities estimable by the common analytical methods. Chapman and Smith[1] oxidized alcohol with alkaline potassium permanganate and obtained acetic aldehyde, acetic acid, "together with various other bodies and oxalic acid." The difference in our experiments between the yields of alcohol as accounted for in the form of oxidation products and 100% might, in some cases, be construed as "various other bodies." The Jones test did not indicate any formic acid or formaldehyde. For a number of years the purity of alcohol has been determined by its oxidation to acetic acid by means of a chromic acid mixture.[2]

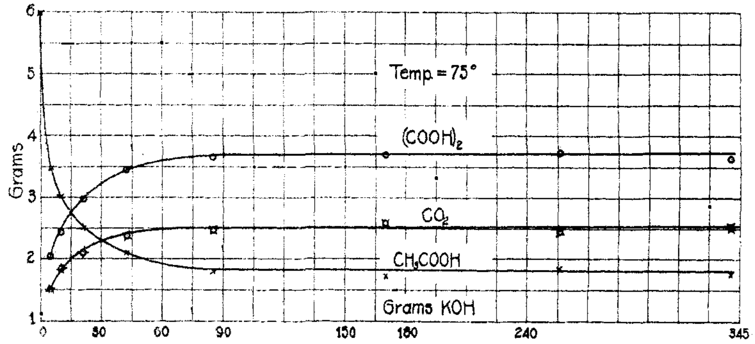

Fig. 5.

Dr. Homer B. Adkins and one of us have shown that acetaldehyde is readily oxidized under the conditions used in this research. Hence, the amount of acetaldehyde, if present, must have been small. If other substances than acetic acid were present, the amounts were too small to allow detection. Denis[3] obtained only acetic acid in her experiments.

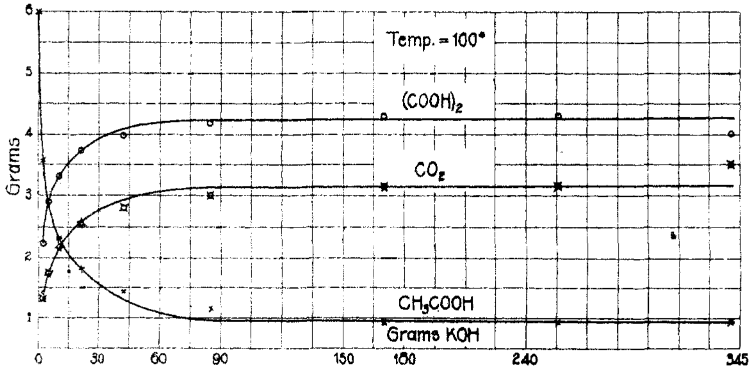

Fig. 6.

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[1] *Loc. cit.*

[2] Chapman and Thorp, *J. Chem. Soc.*, 19, 482–3 (1866).

[3] *Am. Chem. J.*, 38, 564, 569–571 (1910).

It is interesting to note that when Voisenet[1] oxidized alcohol with the oxides of nitrogen, he obtained formaldehyde as a product of the reaction.

The yields of alcohol accounted for as oxidation products (Col. 11, Tables I, II, III and IV) are between 97.42 and 100.37%. In general, the yields of the 100° experiments came nearer totalling 100% than any of the others. This does not necessarily mean that the 100° results should be accorded greater weight than the others. The low yield may have been due to incomplete oxidation or loss of the alcohol itself by evaporation from our reagent bottle. The latter is hardly possible because specific-gravity determinations of the alcoholic solution were made about every 5 days and at no time was there a difference of more than one or two in the fourth place. At the temperature of 75° and 100°, it was thought that there might be a slow but appreciable evaporation of alcohol while the drops were travelling from the end of the dropping tube to the oxidation mixture (a distance of 8–10 cm.). To check up this possibility, the dropping tube was extended below the surface of the mix-

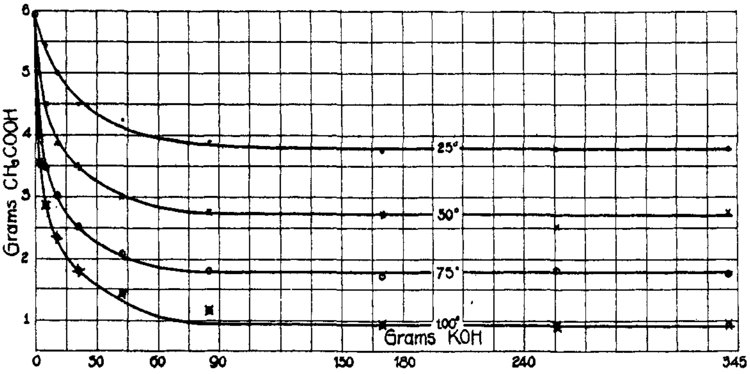

Fig. 7.

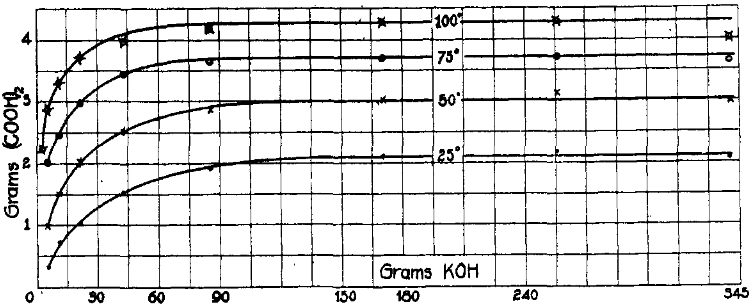

Fig. 8.

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[1] *Compt. rend.*, **150**, 40–43 (1910).

ture in the flask after which the repetition of all of the 75° series, and the last 5 of the 100° series, showed little or no difference in the amount of alcohol required for complete reaction from that used when the tube was of the shorter length.

Carbon Dioxide.—Only a trace was found in all our neutral experiments, and this was undoubtedly due to the unavoidable absorption of atmospheric carbon dioxide.[1] A correction for the carbon dioxide content of the reagents was always made. Test experiments showed that the mercury seals on the stirrers were effective in preventing the circulation of the air.

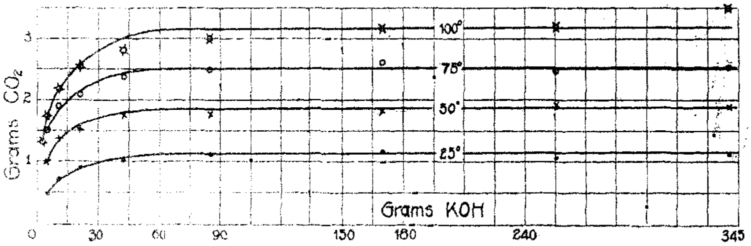

Fig. 9.

The formation of carbon dioxide in the alkaline experiments might be attributed to the following causes: (1) oxidation of acetates or (2) formates formed in the reaction; (3) decomposition of the oxalates formed and subsequent oxidation; (4) oxidation of the intermediate compounds arising from the dissociation of the oxidation products of alcohol. That the presence of carbon dioxide cannot be due to the decomposition of the acetates is abundantly borne out by the many instances in the literature of the stability of acetates in alkaline potassium permanganate solutions. Chapman and Smith found that oxalates were also totally unaffected in boiling solutions of potassium hydroxide and potassium permanganate. Hence, the presence of the carbon dioxide cannot be due to any action between the acetates and oxalates and the alkaline potassium permanganate. Therefore, possibilities (1) and (3) are rigidly excluded.[2] The presence of carbon dioxide might be due to the intermediate formation of formates, as indicated by the work of Truchot,[3] who showed that formic acid is converted quantitatively into carbon dioxide in alkaline potassium permanganate solutions. Heimrod and Levene[4] explained the oxidation of acetaldehyde in alkaline solutions on the ground that formic acid is one of the reaction products. In view of the above facts, if formic acid is considered as an intermediate reaction product, it must be the decom-

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[1] Cf. Denis, *Am. Chem. J.*, 38, 564, 571 (1907).

[2] Evans and Witzemann, THIS JOURNAL, 34, 1096 (1912).

[3] *Compt. rend.*, 63, 274 (1866).

[4] *Biochem. Z.*, 29, 49 (1910).

position product of a substance obtained from the acetaldehyde formed in the reaction. It will be shown below that it is not absolutely essential to postulate the formation of formic acid in order to account for the presence of carbon dioxide.

Oxalic Acid.—When the oxidations, with the exception of Expt. 30, were carried on in the presence of various initial concentrations of potassium hydroxide, oxalic and carbonic acids were formed with the acetic. Similar observations were made by Evans and Witzemann[1] in their experiments on the oxidation of propylene glycol, lactic acid, and pyruvic acid by means of alkaline potassium permanganate. Cochenhausen[2] also made similar observations in his work on the oxidation of acetone. Denis[3] found that acetic, oxalic and carbonic acids were the reaction products when alcohol is oxidized with alkaline potassium permanganate, a type of reaction which, in the present work, we have studied under definitely chosen conditions.[4] The amounts of the oxalic, carbonic and acetic acids obtained in the oxidation of ethyl alcohol at 50° have been expressed in our preliminary report as functions of the initial concentration of the alkali employed. In a recent study of the oxidation of acetone by means of alkaline potassium permanganate, Witzemann[5] has expressed his results in a somewhat similar manner.

The formation of the oxalic acid may be due to the following possible causes: (5) oxidation of any acetates or (6) formates formed in the reaction; (7) oxidation of intermediate compounds formed from acetaldehyde. Denis[6] studied the effect of an excess of potassium permanganate on acetic acid in the presence of potassium hydroxide at 100°, and found that no reduction took place. Wanklyn and Cooper,[7] on heating acetates with a considerable excess of alkaline potassium permanganate at a temperature of 160–180° in the presence of manganese dioxide, obtained potassium carbonate. When manganese dioxide was not added, oxygen was evolved. Barendrecht[3] did not detect any reaction between boiling strongly alkaline permanganate and acetic acid. Sodium acetate, according to Lossen,[8] was partially converted into sodium oxalate when heated with sodium hydroxide, potassium permanganate and a small amount of water. Truchot[3] made the observation that potassium permanganate had no effect on acetic acid in the presence of potassium

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[1] This Journal, 34, 1086 (1912).

[2] *J. prakt. Chem.*, [2] 58, 454 (1898).

[3] *Loc. cit.*

[4] See This Journal, 38, 377 (1916).

[5] *Ibid.*, 39, 2663 (1917).

[6] *Am. Chem. J.*, 38, 564 (1910).

[7] *Phil. Mag.*, [5] 7, 138–140 (1879).

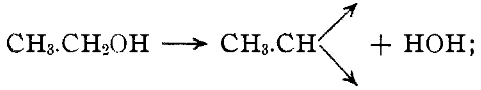
[8] *Ann.*, 148, 174–6 (1869).

hydroxide. These facts indicate that oxalic acid is not formed by the oxidation of acetic acid.

Two drops of 0.089 *N* potassium permanganate solution were required to give a slight permanent color to the acetic acid distillate when it had previously been made alkaline with sodium carbonate, indicating the absence of formic acid. A blank containing the same amounts of acetic acid and sodium carbonate needed but one drop to give a color of the same intensity. Had formic acid been one of the intermediate reaction products, it would have been immediately oxidized to carbon dioxide as shown above. Hence oxalic acid is not formed by the oxidation of formic acid. It is true, however, that formic acid has been oxidized to oxalic acid by means of nitric acid.[1]

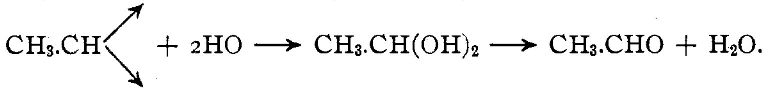
It is apparent, therefore, that the oxalic acid is formed in alkaline solution from the reaction compound of acetaldehyde.[2] On the basis of this research and those of other investigators, this explanation must be accepted as the correct one.

Nef[3] and Denis[4] assume that the course of the reaction is as follows: Alcohol is dissociated into ethylidene and water.



$$CH_3.CH_2OH \longrightarrow CH_3.CH\langle + HOH;$$

the ethylidene is oxidized to ethylidene dihydroxide,



$$CH_3.CH\langle + 2HO \longrightarrow CH_3.CH(OH)_2 \longrightarrow CH_3.CHO + H_2O.$$

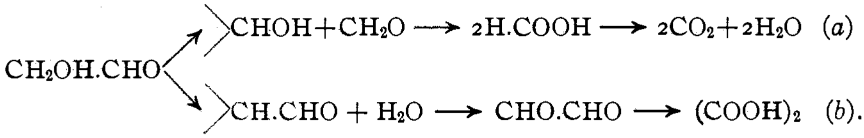
McLeod[5] has shown that acetaldehyde is converted into vinyl alcohol in the presence of alkali of a concentration of 0.10% or more; that is, the carbonyl group is enolized,

$$CH_3.CHO \longrightarrow CH_2 = CHOH;$$

the vinyl alcohol is then converted to glycollic aldehyde,

$$CH_2 = CHOH + 2HO \longrightarrow CH_2OH.CH(OH)_2 \longrightarrow CH_2OH.CHO + H_2O.$$

The glycollic aldehyde then undergoes a dissociation as expressed by the following:



$$CH_2OH.CHO \longrightarrow \rangle CHOH + CH_2O \longrightarrow 2H.COOH \longrightarrow 2CO_2 + 2H_2O \quad (a)$$

$$CH_2OH.CHO \longrightarrow \rangle CH.CHO + H_2O \longrightarrow CHO.CHO \longrightarrow (COOH)_2 \quad (b).$$

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[1] Weyl, *Ber.*, **17**, 9 (1883).

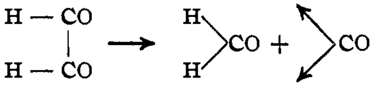
[2] Homer Adkins and one of us have completed work on acetaldehyde which we hope to publish in the near future.

[3] *Ann.*, **298**, 315, 319 (1897).

[4] *Am. Chem. J.*, **38**, 563–7 (1907).

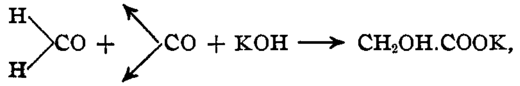
[5] *Ibid.*, **37**, 25 (1907).

Such an interpretation would readily explain the presence of both oxalic and carbonic acids in alkaline solutions. It has been shown by Adkins and one of us that in alkaline solutions of potassium permanganate glyoxal is oxidized to both oxalic acid and carbonic acid, hence possibility (*a*) is not really essential for an understanding of these reactions. As is well known, the 1,2-diketo compounds[1] can readily undergo the benzilic acid rearrangement as follows:



(*c*)

then in the presence of alkali,



(*d*)

which compound, as has been shown by Adkins and one of us, is oxidized to oxalic acid and carbon dioxide by alkaline potassium permanganate. That glyoxal is converted to glycollic acid in cold alkalies is a well known fact. This reaction is analogous to the conversion of pyruvic aldehyde into lactic acid in alkaline solutions. Heimrod and Levene[2] give the following steps for the oxidation of acetaldehyde in alkaline solution: acetaldehyde ⟶ vinyl alcohol ⟶ glycollic aldehyde ⟶ glyoxal ⟶ formic acid and oxalic acid. In view of these facts it is apparent that the presence of formic acid does not necessarily explain the presence of carbon dioxide in these reactions.

In this connection it is interesting to note that in the experiment of Denis[2] on the oxidation of ethyl alcohol in alkaline potassium permanganate solution, the ratio of the alcoholic equivalent of carbon dioxide to that of oxalic acid is as 12.6%: 7.6%, *i. e.*, the alcoholic equivalent of carbon dioxide is 62.5% of the total as carbon dioxide and oxalic acid. In the oxidation of acetaldehyde under approximately the same conditions the ratio of the acetaldehyde equivalent of carbon dioxide to that of oxalic acid is as 17%: 9.2% or the acetaldehyde equivalent of carbon dioxide is 64% of the total as carbon dioxide and oxalic acid. Col. 6 in the "Oxidation Results," gives similar information for our work on alcohol.

(*b*) **Effect of Variation of Initial Concentration of Alkali.**—This effect on the character of the oxidation products at 25, 50, 75 and 100° is shown in Figs, 3, 4, 5 and 6, respectively. In general, an increase in the initial concentration of the alkali causes an increase in the oxalic acid and carbon dioxide production, and a decrease in the acetic acid production. An examination of the curves shows that the yields of these acids reach approximately a constant value for a given temperature when the initial

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[1] Cf. *Am. Chem. J.*, **35**, 116 (1906).

[2] *Loc. cit.*

concentration of the alkali is about 100 g. per liter. The lowest initial concentration of potassium hydroxide employed at 25, 50 and 75° was 5.3 g. per liter. At this concentration oxalic acid and carbon dioxide were found at all 3 temperatures. At 100° the lowest possible initial concentration of alkali necessary for the production of oxalic acid in appreciable amounts was found to lie between 0.415 and 0.461 g. of potassium hydroxide (Expts. 29 and 30).

In Fig. 10 the logarithms of the acetic acid production are plotted against the logarithms of the initial concentration of the potassium hydroxide. The general equation for these lines is

$$y = \frac{B}{x^a}$$

where y is the concentration of the acetic acid obtained, x is the initial concentration of the potassium hydroxide, a is the tangent of the line and B is a constant. The values of a given below were obtained directly from Fig. 10 by measurement. To derive B we may use the equation

$$\log y = \log B - a \log x; \text{ thus,}$$

Temperature.	B.	a.
25°	6.74	0.1227
50°	6.20	0.1839
75°	5.41	0.2459
100°	4.74	0.3084

Knowing the values of B and a, it is easy to calculate the maximum alkali concentration which will still give the theoretical yield of acetic acid. This value was found to be as follows:

Temperature.	Alkali concentration
25°	2.55
50°	1.19
75°	0.655
100°	0.460

As noted above, we found that the value at 100° must lie between 0.415 and 0.461 g., while our calculation shows that the amount of alkali is 0.46 g. These values mean that at any concentration of alkali greater than those given, acetic acid production will diminish and oxalic acid and carbon dioxide will begin to form.[1] It is therefore to be concluded that one of the marked effects of an increase in the alkali concentration must be to increase the concentration of vinyl alcohol.

It is evident that the results of any two oxidations at a given temperature will afford a means of obtaining both the value of a and the maximum alkali concentrations that may be used in obtaining the theoretical yield of acetic acid. If y' and x' are the data obtained in a second oxidation, y the theoretical yield (*i. e.*, 6.003 g. of acetic acid), then x, the alkali concentration, may be calculated from the following equations:

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[1] McLeod, *Am. Chem. J.*, 37, 24 (1907).

$$\log y - \log y' = a\,(\log x' - \log x)$$

or

$$\frac{\log y - \log y' - a \log x'}{a} = -\log x.$$

(*c*) **Effect of Temperature.**—It was found that the temperature also has a twofold effect in these oxidations; namely, to increase the speed of the oxidation, and to modify the character of the reaction products. The general effect of temperature on the production of acetic, oxalic and carbonic acids, is shown in Figs. 7, 8 and 9, which shows that the acetic acid production falls off rapidly with the temperature while that of oxalic and carbonic acids increases with the temperature.

The fact that less alcohol was required for complete reduction at 100° (excluding neutral solution) than at the lower temperatures, means that more permanganate would have been required for the same amount of alcohol. In other words, the quantitative conversion of alcohol into oxalic and carbonic acids becomes more nearly complete at higher temperatures and in the presence of more of the oxidizing agent. Barendrecht employed a temperature of approximately 100° for his work. Kastle and Loevenhart found that an increase in temperature accelerated the reaction between formaldehyde and hydrogen peroxide.

Hetper[1] states that when ethyl alcohol is oxidized with alkaline potassium permanganate, the temperature requisite for a theoretical yield of acetic acid must be below 0°. This conclusion is not warranted, as can be seen from the discussion of Fig. 10, where it is shown that acetic acid is the only product formed with low potassium hydroxide concentrations.

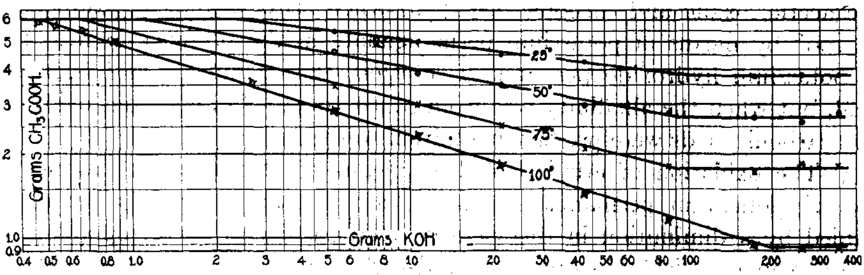

Fig. 10.

In Fig. 11 the tangents of the acetic acid log curves are plotted against temperature. A straight line passed through the 4 points cuts the Y-axis at a point near —25°. At this temperature the slope of the acetic acid curve is *zero*. If, *e. g.*, $x = 300$ when $a = 0$, by substitution in $\log B = \log y + a \log x$, the last term becomes zero, and $B = y = 6.003$, which is the theoretical yield in g. of acetic acid from 4.604 g. ethyl alcohol. This

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[1] *Z. anal. Chem.*, **51**, 415 (1912).

means that at the temperature indicated by the intersection of the line of tangents and the Y-axis the concentration of the alkali does not affect the theoretical yield of acetic acid.

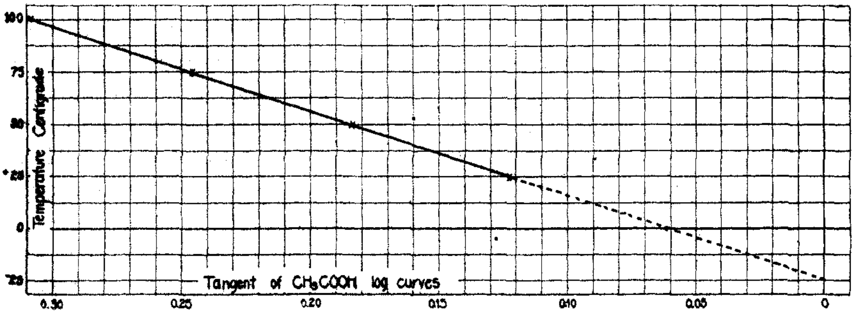

Fig. 11.

It has been repeatedly observed in these experiments that the rate of adding the alcoholic solution had no appreciable influence on the relative quantities of the oxidation products.

Summary.

1. In neutral aqueous solutions of potassium permanganate at temperatures of 25, 50, 75 and 100°, the sole reaction product of the oxidation of ethyl alcohol is acetic acid.

2. (*a*) When ethyl alcohol is oxidized at the temperature of 25, 50 and 75° by means of alkaline potassium permanganate solution containing 5.32 to 340.8 g. potassium hydroxide per liter, the reaction products are acetic, oxalic and carbonic acids; (*b*) when ethyl alcohol is oxidized at 100° by means of potassium permanganate in the presence of 0.415 g. potassium hydroxide per liter of solution, the product is still acetic acid, but when the alkalinity was from 0.461 to 340.8 g. per liter, oxalic and carbonic acids were present in addition to the acetic acid.

3. The oxidation of ethyl alcohol by means of alkaline (*v.* Summary No. 2) potassium permanganate at the above temperatures is accompanied by a diminution in the yield of acetic acid and a corresponding increase in the yield of oxalic acid and carbonic acids as the concentration of the alkali was increased up to the beginning of the maximum effect.

4. (*a*) An increase in the temperature of the alkaline reaction mixture (excluding Expt. 29) diminishes the yield of acetic acid proportionately; (*b*) an increase in the temperature of the alkaline reaction mixture (excluding Expt. 29) increases the yield of oxalic and carbonic acids proportionately.

5. An increase in the temperature of the reaction mixture hastens the rate of oxidation.

6. An increase in the alkalinity of the reaction mixture, up to a certain maximum amount, increases the rate of oxidation.

7. A comparison between the results of two experiments recorded by Denis is given.

8. The rate of the addition of the alcoholic solution has no effect on the relative amounts of the oxidation products so far as could be ascertained.

9. An equation has been developed for the relationship between the acetic acid production and the initial concentration of the alkali used when alcohol is oxidized at a given temperature in the presence of potassium hydroxide.

10. By means of this equation it is easy to establish the upper limit of the alkali concentration permitted and still obtain a theoretical yield of acetic acid, *i. e.*, the lower limit of alkali concentration at which oxalic acid forms.

11. By means of this equation it can be shown that at —25° the magnitude of the initial concentration of the potassium hydroxide used would not affect a quantitative yield of acetic acid.

12. An apparatus has been described for the filtering of sludge precipitates in the absence of the carbon dioxide of the air.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

THE YELLOW COLORING SUBSTANCES OF RAGWEED POLLEN.

BY FREDERICK W. HEYL.

Received May 26, 1919.

These coloring substances belong to the flavonols and are entirely glucosidic. They are extracted with alcohol; and after preparing an aqueous solution from this alcoholic extract a complete precipitation may be secured with basic lead acetate. The yield amounts to about 7.0 g. from 1150 g. pollen or approximately 0.6%.

The least soluble of these was identified as a quercitin glucoside having the composition $C_{21}H_{20}O_{12}$ and melting at 228–9°. The only sugar obtained upon hydrolysis was glucose. It is therefore isomeric with, and differs from, quercimeritrin and isoquercitrin, which were first isolated by A. G. Perkin[1] from the flowers of *Gossypium herbaceum*. These melt, respectively, at 247–249° and 217–219°. One other isomer is known, having been isolated by Rogerson[2] from the flowers of *Trifolium incarnatum*. Incarnatin melts at 242–245°. The most characteristic behavior of pollen quercitin glucoside on melting is the sharp formation of a cherry-

[1] *J. Chem. Soc.*, **95**, 2181 (1909); Viehoever, Chernoff and Johns, *C. A.*, **12**, 1562 (1918).

[2] *J. Chem. Soc.*, **97**, 1008 (1910).