

and support the dish.) Over the plate is inverted a six-inch funnel, with stem cut off, which extends down into the evaporating dish to a sufficient extent to form a trap when a liquid is poured into it. The liquid to be used is selected for the particular purpose at hand, *viz.*, water, a salt solution, an acid such as sulfuric acid or a nonaqueous solvent. Ordinarily the point to be considered is the adjustment of the atmosphere and temperature to suit the purpose of the experiment.

For the determination of ferrous iron in a silicate, a platinum dish is used as the inner container to hold the sample to be analyzed and a platinum rod is extended through the funnel into the dish. This rod is used for stirring and for the addition of hydrofluoric and sulfuric or hydrochloric acids. Phosphoric acid (1 : 2) is used as the solution to form a trap and also to furnish steam. Sufficient solution should be added to cause part of the platinum dish to be immersed. The advantage of phosphoric acid is that it elevates the boiling point of the water to such an extent that the solution contained in the platinum dish is heated much hotter than with water alone, also as more and more steam is evolved the phosphoric acid becomes more and more viscous, still forming a trap and evolving steam which keeps out the air, yet no crystallization occurs as in the case with many salt mixtures. The bath is heated by a direct flame or by an electric hot plate. Hot water, from which any dissolved gases have been removed by boiling, can be easily added to replenish the water lost by evaporation, a steady flow of steam being maintained without difficulty and a uniform heat obtained until the sample is thoroughly decomposed. However, with proper adjustment of volume of solution added at the beginning, and with proper intensity of boiling no addition of water is necessary during a heating period of an hour or even longer. After the sample is completely decomposed it is analyzed according to any reliable method for the determination of ferrous iron.¹ Air-free water should be used to dilute the solution and care should be exercised to avoid oxidation of the iron by the oxygen of the air.

This apparatus is simple, requires no accessories not available in any ordinary laboratory, and is easily adapted to particular temperatures by proper selection of boiling point mixtures. O. L. BARNEBEY.

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[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.
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During the early part of the latter half of the last century, it came to be recognized that the character of the oxidation products of both organic

¹ See Barnebey, *THIS JOURNAL*, 37, 1481, 1829 (1915).

and inorganic substances, with potassium permanganate as the oxidizing agent, was partially dependent upon whether the reaction took place in acid, neutral or alkaline media. Péan de Saint-Gilles¹ was among the first to observe this fact. In working with a number of organic compounds, he obtained varied products, the most common of which were formic, carbonic, acetic acids, etc. A few years later, Chapman and Smith² in their experiments on the action of an aqueous solution of potassium permanganate upon ethyl alcohol, found that small quantities of acetaldehyde, acetic and oxalic acids were formed, together with small quantities of other compounds. They furthermore found that, if the potassium permanganate solution was rendered strongly alkaline with potassium hydroxide, neither acetaldehyde nor acetic acid were produced. "If the solutions were used hot, oxalic acid was the principal product; if cold, various other acids, probably identical with those obtained by Debus in his oxidation of alcohol by nitric acid, were produced." It so happens that the work of these two men is nonreproducible as they incorporated no tangible data into their paper.

Since that time similar experiments with ethyl alcohol have been carried out by different investigators, the results of which are not in complete harmony with each other. With but one exception³ acetic acid has been found in every case. Chapman and Smith obtained oxalic acid as a reaction product when a neutral potassium permanganate solution was employed, while others found it only when using an alkaline solution of the permanganate. Voisenet⁴ detected traces of formaldehyde as another reaction product. According to the results of Fournier⁵ an acetic acid yield of about 50% of the theoretical amount is possible when a strongly alkaline solution of permanganate is employed. He obtained analogous results with propyl, butyl and isobutyl alcohols, when oxidizing them under similar conditions. In the case of ethyl alcohol he did not determine the character and amounts of the remaining 50% of the oxidation products, except to note that if acetaldehyde and ethereal salt were formed, they were in very small amounts. Recently, Denis⁶ carried out two experiments on the behavior of ethyl alcohol towards potassium permanganate, (1) in cold neutral aqueous solution and (2) in cold strongly alkaline aqueous solution. In the first instance she found acetic acid to be the sole reaction product. "When, however, potassium hydroxide was present in excess, acetic acid was still the principal product, but carbonic and oxalic acids were also formed—in larger amount the greater the concentration

¹ *Compt. rend.*, 46, 808-11 (1858).

² *J. Chem. Soc.*, 20, 301-3 (1867).

³ Chapman and Smith, *Loc. cit.*

⁴ *Compt. rend.*, 150, 40-3 (1910).

⁵ *Ibid.*, 144, 331-3 (1907).

⁶ *Am. Chem. J.*, 38, 564 and 569-71 (1910).

of the caustic alkali used." In this connection, the recent observations of Witzemann¹ on the oxidation of glucose, are of great interest. In making a study of the action of neutral potassium permanganate towards ethyl alcohol, Morawsky and Stingl² obtained nothing but acetic acid. From their work on the effect of temperature, they concluded that increase in temperature merely promoted the rate of reaction.

Péan de Saint-Gilles³ believed that the temperature was also an important factor which might influence the character and amounts of the reaction products.

Hemmelmayr,⁴ in his work on the oxidation of sodium ethylate by the oxygen of the air at ordinary temperature, obtained an acid distillate on the distillation of the oxidation mixture with sulfuric acid. But at a temperature of 100°, a small amount of carbon dioxide was formed, and at 200°, traces of oxalic acid were evident as a product additional to the other two acids. The amounts of the two latter substances were considerably increased at 210°. The acid distillate, on analysis, proved to be composed of formic and acetic acids. His results with sodium ethylate have been verified by Nef.⁵

Hitherto, definitely chosen conditions have not been used in much of the experimental work on the oxidation of organic compounds by chemical substances. Among some of the exceptions to the above statement should be included the work of Heimrod and Levene⁶ on "Oxidation of Aldehydes in Alkaline Solution" and that of Kastle and Loevenhart on the "Oxidation of Formaldehyde by Hydrogen Peroxide."⁷ No complete systematic study has been made, from the standpoint of the effect of temperature and the concentration of alkali, on the character and relative amounts of the oxidation products formed when ethyl alcohol is oxidized by means of potassium permanganate in neutral and alkaline media. Nef⁸ records the fact that in the oxidation of many carbohydrates in alkaline solutions, the amount of lactic acid formed varies in a remarkable way, with the concentration of the caustic alkali used. In view of these facts, this work was undertaken with the intention of ascertaining the nature of the above-mentioned relationships. It is the aim, at present, to continue in this laboratory, a study, at given temperatures, of the oxidation of many organic compounds by means of potassium permanganate in the presence of varying concentrations of alkali.

¹ THIS JOURNAL, 38, 151-161 (1916).

² J. prakt. Chem., 18, 82-3 (1878).

³ Ann. chim. phys., [3] 55, 375 (1859).

⁴ Monats. Chem., 12, 155-7 (1891).

⁵ Ann., 318, 177 (1901).

⁶ Biochem. Z., 29, 31-59 (1910).

⁷ THIS JOURNAL, 21, 262 (1899).

⁸ Ann., 357, 215, compare Ann., 357, 258 (1907).

Mr. H. B. Adkins is now engaged in a study of acetaldehyde under known conditions, with a view of correlating his results with these on ethyl alcohol.

Experimental Part.

Methods of Analysis.—Ordinary qualitative methods were employed in the detection of carbonic, acetic and oxalic acids. The presence or absence of formic acid was determined by using a modification of the Jones method on the neutralized acetic acid distillate, by making it alkaline with 1.0 g. of sodium carbonate and adding potassium permanganate solution of known strength until a pink color in moderately warm solution was obtained.¹

The quantitative determination of carbon dioxide was made by means of the Foulk² apparatus. A known portion of the solution under analysis was treated with the proper amount of hydrochloric acid and the carbon dioxide evolved, after having been conducted through a well-cooled condenser and the appropriate drying agents, was absorbed by a caustic potash solution. A correction was applied for the amount of carbon dioxide contained in the potassium hydroxide employed in the oxidations.

An aliquot part of the solution containing the oxidation products was employed in ascertaining the amount of oxalic acid present. The portion was first slightly acidulated with acetic acid, then made slightly alkaline with ammonium hydroxide, after which the soluble oxalate was converted to the insoluble oxalate by means of calcium acetate in hot solution. This precipitate, after being filtered and washed, was titrated against standard potassium permanganate solution in the presence of sulfuric acid in the usual manner.

The acetic acid was determined by the well-known method of Stilwell and Gladding as modified in this laboratory by Withrow and Fritz.³ A portion of the original solution, to which had been added an excess of sirupy phosphoric acid, was distilled in a vacuum apparatus. The distillate was titrated with a potassium hydroxide solution of known value, with phenolphthalein as the indicator. In each case a correction was made for the volatile acids contained in the amount of phosphoric acid used. It was observed in making these distillations, that when the amount of potassium hydroxide present was large, a much larger excess of the phosphoric acid, over that required for the neutralization of the alkali, was necessary in order to distill the last portions of the acetic acid.

Absolute alcohol was employed in this series of oxidations. It was dehydrated by means of calcium oxide and anhydrous copper sulfate in the customary way. Each liter of the standard solution contained 92.096 g. of the water free alcohol (b. p. = 77–77.5° C.), which was a 2 molar

¹ Compare: THIS JOURNAL, 34, 1091 (1912).

² Foulk, "Notes on Quantitative Chemical Analysis," p. 222, 1914 ed.

³ See thesis for M.A. by Howard Fritz, this laboratory.

or 9.21% solution. The specific gravity of the aqueous solution at 20° was 0.9847.

Each oxidation was carried out in the following manner: Thirty grams of crystallized potassium permanganate were placed in a wide-mouth, two liter balloon flask containing 1000 cc. of water which previously had been boiled free from carbon dioxide. In case of alkaline solutions, the desired amount of caustic potash (purified by alcohol) was then added. The flask was immediately closed by a rubber stopper into which was fitted a mechanical stirrer, a 25 cc. pipet and a piece of ordinary size glass tubing. The closed vessel was next clamped in position in a thermostat which was kept at 50°. When the temperature of the contents of the flask and that of the surrounding bath were at the desired value and while the mixture was in complete agitation, the alcohol solution (strength = 9.21%) was slowly admitted, drop by drop, until the reduction of the permanganate was complete. The determination of the end-point was made without difficulty by drawing a portion of the reaction mixture into the pipet, where, after the subsidence of the precipitated hydrated manganese dioxide, the observation could be made. In the majority of cases the end-point was passed to a slight extent, which made it necessary to add solid permanganate until a slight permanent color was attained which was generally discharged within twenty-four hours. The color desired in the case of alkaline solution was a very pale green and in the neutral solution was a delicate pink. The reaction mixture, after being filtered in a specially constructed carbon dioxide free apparatus, was made up to a volume of 2000 cc. and then analyzed.

The results obtained from a series of nine such oxidations can be observed in the tabular data and also as represented in the form of curves shown in Figs. 1 and 2. In Fig. 1 is the curve representing the number

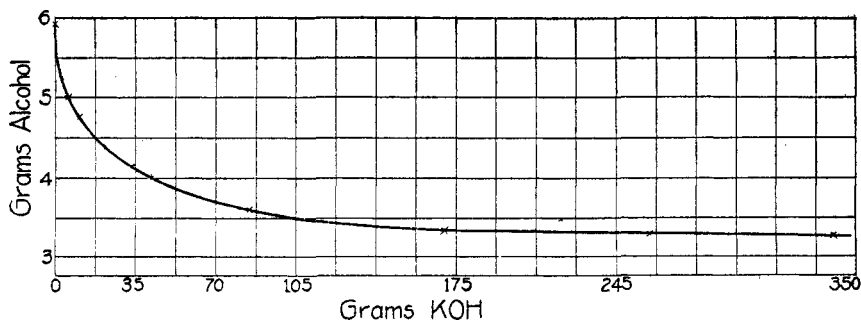


Fig. 1

of grams of absolute alcohol that is required to completely reduce a constant amount of potassium permanganate (30 g.) as the concentration of the alkali was increased. Beyond an alkalinity of about 175 g. per liter

of water, an increased amount of the potassium hydroxide had practically no further effect on the amount of alcohol necessary to bring about complete reduction. It becomes self-evident that the alcohol curve in reversed position would be the curve for variable permanganate with constant alcohol. The curves showing the amounts of the oxidation products in Fig. 2 were plotted on the latter basis, *i. e.*, a constant quantity

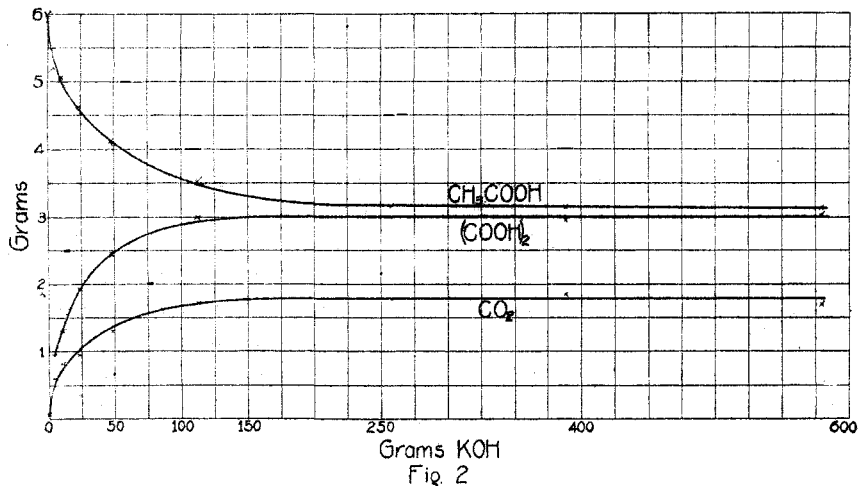


Fig. 2

of alcohol (5 g.). Such a course carried with it the necessity of proportionally increasing or decreasing the amount of potassium hydroxide actually used, depending upon whether the amount of alcohol required was greater or less than 5 g., so that the corresponding concentration of the alkali might be maintained. To be more explicit, take *e. g.*, the case of Expt. 4 where 4.37 g. of alcohol were actually oxidized. In order to oxidize 5 g. of alcohol it would have been necessary to increase the potassium permanganate to 34.3 g., the potassium hydroxide from 21.3 to 24.4 g. and the amount of water from 1000 to 1144 cc.

An error is introduced when the amount of potassium permanganate used is greater than 30 g. If the quantity of alcohol is less than 5 g., then the amount of alkali requisite for 5 g., as computed above, will lie to the left of the curve. This error systematically increases with the excess of the potassium permanganate which is needed to return to the end-point when it has been passed by the addition of a superfluous amount of alcohol. The above is true largely for solutions having values of alkalinity represented by any point in the bend of the curve.

It will be noticed in Fig. 2 that, in the case of the absence of added caustic potash, a small amount of carbonic acid was found. The lowest concentration of potassium hydroxide employed was 0.53% and at this value, oxalic acid was found in addition to the other products. At present we do not know from experiment, in the case of alcohol, the lowest exact

concentration of potassium hydroxide necessary for the formation of the latter named acid. For acetaldehyde, McLeod¹ has found that vinyl alcohol molecules are present in the aqueous solution of the aldehyde as soon as the concentration of the alkali is above 0.1%. In the case of alcohol, as the amount of potassium hydroxide was increased to about 250 g., the oxalic and carbonic acids simultaneously increased, although at different rates. Beyond this concentration of potassium hydroxide, the curves become practically straight lines, parallel to the X-axis. It required two drops of potassium permanganate solution (strength = 0.089 *N*) to give a slight permanent color to the distillate containing acetic acid when it had been previously made alkaline with sodium carbonate. This may be taken as an indication of a mere trace of either formic acid or formaldehyde or both. The total amount of alcohol recovered as oxidation products, in some instances, was slightly higher than that demanded by theory, but this was undoubtedly due to the absorption of slight amounts of carbon dioxide during the process of oxidation.

Series of experiments at 25° and 75° will be completed within a short time and it is hoped that an early report of the same will be made in THIS JOURNAL. We hope to present a discussion of our results at that time.

TABLE I.

Actually used (grams).			C ₂ H ₅ OH calc. for 30 g.	Actually found with proper correction for CO ₂ and CH ₃ COOH (grams).			Calc. for 5 g. alcohol (grams).			
KMnO ₄ .	KOH.	C ₂ H ₅ OH.		CO ₂ .	(COOH) ₂ .	CH ₃ COOH.	KOH.	CO ₂ .	(COOH) ₂ .	CH ₃ COOH.
			KMnO ₄ .	Ave. of two.	Ave. of two.	Ave. of two.				
31.18	None	6.17	5.94	0.088	None	7.400	None	0.071	None	6.000
30.00	5.3	5.02	5.02	0.632	0.975	5.228	5.3	0.629	0.951	5.207
30.41	10.7	4.83	4.76	0.768	1.259	4.873	11.2	0.795	1.303	5.044
30.00	21.3	4.37	4.37	0.828	1.700	4.042	24.4	0.947	1.959	4.624
30.27	42.6	4.07	4.04	1.058	1.996	3.356	52.3	1.300	2.451	4.121
30.30	85.2	3.65	3.61	1.269	2.195	2.564	112.1	1.737	3.000	3.512
30.00	170.4	3.34	3.34	1.184	1.999	2.110	258.1	1.772	2.992	3.519
31.97	255.6	3.51	3.29	1.307	2.077	2.198	388.4	1.863	2.959	3.131
35.38	340.8	3.89	3.28	1.335	2.370	2.440	579.3	1.716	3.049	3.139

COLUMBUS, O.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES. THE FORMATION OF SCHIFF BASES FROM β -PHENYLETHYLAMINE AND THEIR REDUCTION TO ALKYL DERIVATIVES OF THIS AMINE.

[FIFTH PAPER.]

BY NORMAN A. SHEPARD AND ARTHUR A. TICKNOR.

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While working in coöperation with Professor Treat B. Johnson on an investigation dealing with the relationship between chemical constitution

¹ *Am. Chem. J.*, 37, 24 (1907).