corresponding to at least 0.200–0.400 volt was necessary to balance the circuit.[15]

Experimental

A large number of organic arsenicals was analyzed by the method herein described; the results of a few of these analyses are given in Table I.

TABLE I

TESTS OF THE METHOD

Compound	Arsenic trioxide		Arsanilic acid		*n*-Butylarsonic acid		Diphenylamine-*o*-arsonic acid	
Sample, g.	0.1002	0.1013	0.2022	0.2009	0.1986	0.1987	0.2095	0.2199
As found, %	75.76	75.78	34.59	34.58	41.26	41.24	25.62	25.54
As calcd., %	75.75	75.75	34.56	34.56	41.21	41.21	25.57	25.57
Deviation, %	+0.01	+0.03	+0.03	+0.02	+0.05	+0.03	+0.05	−0.03

Summary

The arsenic content of organic compounds can be determined readily and accurately by digesting the compound with hot sulfuric acid in the presence of potassium acid sulfate, diluting the solution thus obtained and titrating electrometrically with potassium bromate.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE CATALYTIC "COUPLING" OF MANGANESE DIOXIDE WITH PHOSPHORIC OR SULFURIC ACID AS AN OXIDIZING AGENT. THE EFFECT OF ACIDITY ON THE OXIDATION OF BUTYRIC ACID WITH HYDROGEN PEROXIDE

BY EDGAR J. WITZEMANN

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The results given in this paper constitute a part of a study of the influence of a few chemical variables upon the oxidation of butyric acid.[1] This report concerns the influence of the amount and nature of the acids present on the oxidation of butyric acid by hydrogen peroxide.

The Influence of Phosphoric Acid.—Since previous work had brought out the catalytic properties of dialkali phosphate in the oxidation of butyric acid, attention was first given to phosphoric acid, in studying the effect of acidity upon this oxidation, especially in view of the fact that it is possible that the catalytic effects of dialkali phosphates may be due to the intermediate formation of a perphosphate.

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[15] When this 0.200–0.400 volt increase in e.m.f. caused by a single drop of the bromate solution is compared to the increase of 0.01–0.03 volt caused by one cubic centimeter of the solution, it is obvious that the end-point is extremely easy to recognize.

[1] (a) Witzemann, *J. Biol. Chem.*, **35**, 83 (1918); **49**, 123 (1921); (b) THIS JOURNAL, **48**, 202, 208, 211 (1926); **49**, 987 (1927).

Experiments were, therefore, set up with free phosphoric acid: 100 cc. of solution contained 50 cc. of 3% hydrogen peroxide, 0.25 g. of butyric acid as the potassium salt and phosphoric acid as indicated below. These experiments were allowed to stand at room temperature for forty-two to forty-five hours before analysis for acetone. The methods of analysis used were those previously described.[2]

	1	2	3	4	5	6	7
H_3PO_4 (85%), g.	0.0	0.066	0.198	0.33	0.66	1.32	3.3
Molarity, *M*	....	0.0057	0.0171	0.0285	0.057	0.014	0.285
Acetone, g.	0.0011	0.0010	0.0022	0.0034	0.0020	0.0128	0.0588

Calculated acetone yield, 0.164.

In the above experiments, the results of which are typical, an increasing yield of acetone was associated with increasing acidity.

The use of manganese dioxide during distillation had been adopted as a routine procedure in oxidations with hydrogen peroxide in order to obtain distillates free from hydrogen peroxide. It had become customary to add about 3 to 4 g. of manganese dioxide for this purpose. Such high yields of acetone as those indicated in (6) and (7) were obtained when no more than this was used. Under these conditions the mixture in the distilling flask becomes gray in (6) and (7) before distillation is complete and the mixture foams freely throughout the distillation. If a large excess of manganese dioxide is added the mixture remains black, tends to bump during distillation and no more acetone is obtained than in (4) and (5).

Data Concerning the Phosphoric Acid–Manganese Dioxide Catalysis.—The facts that the manganese dioxide was reduced with the formation of manganese phosphate and that the addition of large excess of manganese dioxide led to a striking decrease in the yield of acetone, suggested that manganese dioxide is vitally concerned in this process. Special test experiments brought out the following facts. When phosphoric acid and manganese dioxide but no hydrogen peroxide were allowed to act upon potassium butyrate as usual, no acetone whatever was obtained. Although it is generally stated that dilute sulfuric acid does not liberate oxygen from manganese dioxide, a suitably arranged test experiment was made with this acid as well as with phosphoric acid. No oxygen was evolved in the course of a week. When phosphoric acid and hydrogen peroxide were used with potassium butyrate and the peroxide was decomposed by making the solution alkaline and adding precipitated calcium carbonate, very little acetone was obtained. Moreover, the hydrogen peroxide concentration remained unchanged in the experiments containing phosphoric acid, butyric acid and peroxide, for as long as three weeks, as was shown by permanganate titrations.

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[2] Witzemann, *J. Biol. Chem.*, **49**, 123 (1921).

These and other test experiments developed the fact that this catalysis is dependent upon the presence of two components and that both the hydrogen peroxide and the manganese dioxide are reduced when the best results are obtained.

The only well-known reaction in which an acid interacting with manganese dioxide causes the decomposition of hydrogen peroxide with the reduction of the manganese dioxide is the following

$$H_2SO_4 + MnO_2 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$$

Nothing could be found in the literature concerning oxidations brought about by this system.

Test experiments showed that sulfuric acid may be replaced with phosphoric acid. Small concentrations of phosphoric acid were used (comparable with those in Nos. 5, 6 and 7 above) with a considerable excess of manganese dioxide. It was noted that the presence of the phosphoric acid very materially retarded the time rate of oxygen evolution upon addition of manganese dioxide. The volume of oxygen evolved was measured in each case. The results showed that at the lower concentrations all of the phosphoric acid reacted apparently as follows

$$2H_3PO_4 + 3MnO_2 + 3H_2O_2 \longrightarrow Mn_3(PO_4)_2 + 6H_2O + 3O_2 \qquad (1)$$

The excess hydrogen peroxide not required for this reaction was decomposed thus

$$MnO_2 + 2H_2O_2 \longrightarrow MnO_2 + 2H_2O + O_2 \qquad (2)$$

In any case the observed volume of oxygen corresponded closely with the volume calculated on this assumption. With higher concentrations of phosphoric acid not all of the phosphoric acid entered reaction according to (1) and so the observed volume of oxygen was less than that calculated on this assumption. This suggests that at the lower concentrations all of the phosphoric acid enters into some complex relation with hydrogen peroxide before the reaction is over.

These experiments furnish a clew for the interpretation of the catalytic oxidations of butyric acid described below.

The Influence of Sulfuric and Boric Acids on Butyric Acid Oxidation.—Having learned that phosphoric acid interacts like sulfuric acid with manganese dioxide and hydrogen peroxide, it was of interest to learn how sulfuric acid influences the oxidation of butyric acid. Flasks containing 100 cc. of solution of which 50 cc. was 3% hydrogen peroxide and 0.25 g. butyric acid, containing also sulfuric acid as indicated below, were otherwise treated as in the phosphoric acid experiments and upon analysis the contents gave the results shown

Sulfuric acid, g.	0.28	0.56	1.12	2.80
Molarity of acid, *M*	0.03	0.06	0.11	0.28
Acetone yield, g.	0.0036	0.0053	0.0052	0.0053

Such negative results were obtained several times until suddenly data similar to those given below were obtained by changing the conditions slightly in some way.

An experiment like the last of this group was set up containing 500 cc. of 0.28 *M* sulfuric acid, 500 cc. of 3% hydrogen peroxide, 2.50 g. of butyric acid in 50 cc. of water and 1.59 g. of potassium hydroxide in 50 cc. of water. After standing for forty-five hours the mixture was distilled in portions of 110 cc. with 50 cc. of distilled water using various catalysts for the decomposition of the peroxide.

(a) and (b) Added 3 to 4 g. of manganese dioxide (Baker's analyzed) and distilled slowly. Acetone found, 0.0514 g. (31.3% of the possible yield) and 0.0552 g., respectively.

(c) Repeated (a) with a much less dense form of manganese dioxide and found 0.0464 g. of acetone.

(d) Repeated (a) with three times as much managnese dioxide. The evolution of oxygen was more rapid and only 0.0036 g. of acetone was found.

(e) Added a teasponful of unglazed porcelain chips and distilled as slowly as possible. Hydrogen peroxide was not present in the distillate and 0.0335 g. of acetone was found.

(f) Added a teaspoonful of 60-mesh quartz sand and distilled slowly as in (e). Acetone found, 0.0340 g.

These results show that the influence of sulfuric acid on this oxidation is at least roughly similar to that of phosphoric acid.

Boric Acid.—Boric acid was selected for some additional experiments because in some respects it is so different from either of the two acids previously used. The reaction mixture was made up as follows: 250 cc. of 0.28 *M* boric acid, 250 cc. of 3% hydrogen peroxide, 1.25 g. of butyric acid in 25 cc. of water and 0.80 g. of potassium hydroxide in 25 cc. of water.

(a) After standing for two days at room temperature, 110 cc. of the above with 50 cc. of water was distilled slowly with about 2 g. of manganese dioxide. The manganese dioxide was not visibly changed and no peroxide distilled over. The acetone obtained was 0.0029 g. or 1.7% of the possible yield.

(b) The preceding distillation was repeated with 1 g. of manganese dioxide with slow heating in the beginning. The results were the same—0.0031 g. of acetone.

(c) When (a) was repeated using a teaspoonful of unglazed porcelain chips and no manganese dioxide, 0.0823 g. of acetone or a 50.2% yield was obtained. A repetition gave 0.01023 g. of acetone or a 62.3% yield.

The hydrogen peroxide content of the solution was practically unchanged after standing for a month in the laboratory.

It seemed that manganese dioxide must necessarily catalyze this oxidation as well as porcelain chips, but a good many trials failed to give the desired result.

The Fate of the Butyric Acid Used in These Oxidations.—The preceding data suggest that a considerable portion of the butyric acid is oxidized in these experiments. Some more definite data were desired.

The oxidation mixture with phosphoric acid was set up as follows:

250 cc. of 0.285 *M* phosphoric acid, 250 cc. of 3% hydrogen peroxide, 1.25 g. of butyric acid in 25 cc. of water and 0.8 g. of potassium hydroxide in 25 cc. of water. The hydrogen peroxide content of this solution was 1.36%, as determined by titration with potassium permanganate; after standing at room temperature for about three weeks it was unchanged.

Two hundred and twenty cc. of the mixture with 50 cc. of water and 3 to 4 g. of manganese dioxide were distilled slowly. The distillate was made up to 300 cc.; 125 cc. of this analyzed for acetone gave 0.147 g. of acetone for the entire distillate, a yield of 44.8%.

A portion of 110 cc. with 50 cc. of water and 2 g. of manganese dioxide was treated similarly. The distillate was made up to 225 cc. and fractionated in four 50-cc. portions, which neutralized 0.1 *N* alkali as follows: (1) 10 cc., (2) 6.4 cc., (3) 5.07 cc., (4) 3.13 cc., (residue) 1.87 cc., total 26.47 cc. This result indicated that considerable unchanged butyric acid was present.[3] These solutions were united, acidified with phosphoric acid and again distilled. The distillate was made up to 240 cc.; 120 cc. was then distilled off. This neutralized 16.53 cc. of 0.1 *N* alkali. The residue in the flask required 8.8 cc. of alkali.

In order to determine approximately how much butyric and acetic acid was present, it was desired to use the method of Wiegner and Magasanik[4] as applied by Virtanen.[5] In order to do this effectively the distillation constants for very dilute solutions of these acids were determined in our own apparatus. It was found that when 240 cc. of dilute acid (equivalent to 15 to 25 cc. of 0.1 *N* sodium hydroxide) was distilled, the first 120 cc. of distillate when acetic acid was used required 36.0% of the total alkali, while with butyric acid it required 71.6%. These figures are slightly lower than those given by Virtanen for the apparatus used by him.

Using the above data we have the following simultaneous equations

$$\begin{array}{r} A + B = 25.33 \\ 0.360\,A + 0.716\,B = 16.53 \end{array} \quad \left\{ \begin{array}{l} A \text{ and } B \text{ are the alkali equivalents of acetic} \\ \text{and butyric acids, respectively.} \end{array} \right.$$

Solving for A and B we obtain $A = 4.49$ cc., $B = 20.84$ cc.; *i. e.*, 74.4% of the butyric acid was recovered unchanged in this experiment.

Virtanen reports that this method serves also as a criterion of the purity of the substances used. In order to check the qualitative nature of the mixture being analyzed, a synthetic mixture of pure acetic and butyric acids was prepared in 240 cc. of water having the supposed composition of the unknown. The half distillate neutralized 16.80 cc. of 0.1 *N* alkali, while the residue required 8.85 cc. The total acidity, therefore, corresponded to 25.65 cc. of 0.1 *N* alkali. When these data were calculated

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[3] Witzemann, This Journal, **41**, 1946 (1919).

[4] Magasanik, *Chem.-Ztg.*, **43**, 656 (1919); *Analyst*, **45**, 24 (1920); *C. A.* **14**, 1947 (1920).

[5] Virtanen, *Soc. Scient. Fennicae, Comm. Phys. Math.*, **1**, No. 36 (1923); see also This Journal, **50**, 3138 (1928).

by the above equations, the acetic acid found neutralized 4.38 cc. of 0.1 *N* alkali, while the butyric acid neutralized 21.27 cc. This corresponds very nearly to the amounts added and gives good agreement with the data for the unknown mixture.

A simultaneous determination of acetone and carbon dioxide was made using a method previously described;[2] 110 cc. of the original mixture with 50 cc. of water and 1 g. of manganese dioxide and a few porcelain chips were heated slowly in the apparatus: 0.0657 g. of acetone or 40.1% and 0.155 g. of carbon dioxide or 31.0% were obtained. One-fifth of the distillate diluted to 100 cc. was treated with silver oxide (from 5 g. of silver nitrate) and 4 cc. of concentrated ammonium hydroxide in a sealed magnesium citrate bottle in a warm water-bath for about four hours.[6] On filtering off the silver residues, acidifying with hydrochloric acid and distilling, 0.0456 g. or 27.8% of acetone was obtained. Quite a little silver chloride was precipitated, indicating that a corresponding amount of acid formation had occurred.

When the above and other results not given are summarized, a fairly good account can be rendered of the butyric acid used in spite of the general variations in the results of the oxidation. Forty per cent. or more of the butyric acid used was recovered unchanged; as much as 28% was oxidized to acetone and carbon dioxide; enough more carbon dioxide was formed to account completely for 23% of the butyric acid; quite a little acetic acid was also found.

With Sulfuric Acid.—The oxidation mixture was set up as follows: 500 cc. of 0.28 *M* sulfuric acid, 500 cc. of hydrogen peroxide, 2.5 g. of butyric acid in 50 cc. of water and 1.59 g. of potassium hydroxide in 50 cc. of water. The peroxide titer remained unchanged three days later.

Aliquot portions of this solution were analyzed by the methods used above. On the basis of the butyric acid originally present, this solution yielded 0.139 to 0.20 g. of acetone, *i. e.*, a minimum of 42.1%. Fractionation and analysis of the volatile acids present showed that about 23.7% of the butyric acid was recovered unchanged, while the remainder of the volatile acid was apparently pure acetic acid, as shown by fractionation of controls having the same acid titer and presumably the same composition. In some analyses smaller amounts of volatile acids were obtained, but unchanged butyric acid was always present.

The acetone as determined in the crude distillate varied from 35 to 60%, but in the former case dropped to 23.8% after treatment with silver oxide and ammonia.

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[6] Portions of a solution containing about 0.05 g. of pure acetone in 50 cc. were treated with silver oxide, etc., at the same time. These solutions showed 0.045 g. of acetone upon analysis, whereas the untreated solution gave 0.046 g. of acetone. This showed that acetone is not materially influenced by this treatment.

From 28.8 to 44.3% of the carbon in the butyric acid was converted into carbon dioxide, which was recovered as barium carbonate.

The results obtained with sulfuric acid correspond to those obtained with phosphoric acid, except that very small amounts of unchanged butyric acid are recovered. The transformation is much more profound in this case. More undetermined products are formed, and the results do not so adequately account for the butyric acid used as was the case with phosphoric acid.

Summary

The influence of the presence of considerable amounts of free acids (phosphoric, sulfuric and boric) upon the oxidation of butyric acid with hydrogen peroxide was studied. Under these conditions the concentration of hydrogen peroxide remains unchanged indefinitely and no oxidation occurs unless or until a suitable catalyst is added. The catalyst most frequently used was manganese dioxide. It is thought that the oxidation observed arose from the action of this compound upon the peroxide compound of the acid, although this point was not proved. Under these conditions the butyric acid present is often largely oxidized, with the formation of much acetone, carbon dioxide and acetic acid. The volatile acid products consisted of acetic acid and unchanged butyric acid.

No adequate interpretation of this unexpected catalytic system was developed.

This catalytic oxidation of butyric acid, unlike that brought about by ammonia and sodium phosphate, is a very rapid reaction.[1b,2]

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTION OF BROMINE ON PHENOLPHTHALEIN. FURTHER EVIDENCE OF THE TAUTOMERIC CHARACTER OF PHENOLPHTHALEIN

BY ALLAN R. DAY

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It was noted during the course of previous work[1] that the action of bromine (as generated by acidifying a bromate–bromide mixture) on phenolphthalein varied greatly with conditions. In the presence of a solvent such as chloroform tetrabromophenolphthalein was always formed. This, of course, is the usual and well-known reaction. The lack of color of this derivative indicates its lactoid structure. An attempt was made to make this bromination the basis of a quantitative determination but the results obtained varied from the theoretical by 1 to 2%.

[1] Day and Taggart, *Ind. Eng. Chem.*, 20, 545 (1928).