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

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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%.

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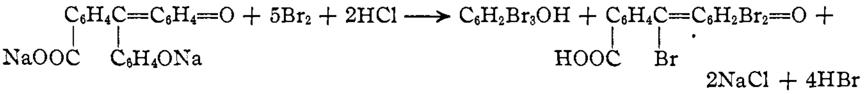
[1] Day and Taggart, *Ind. Eng. Chem.*, **20**, 545 (1928).

When the phenolphthalein was dissolved in sodium hydroxide and the resulting solution acidified with hydrochloric acid, in the presence of an excess of bromate and bromide, a brownish-yellow precipitate was formed. It was found, by adding potassium iodide and titrating the liberated iodine with thiosulfate, that the formation of the brownish-yellow precipitate was accompanied by the loss of five molecules of bromine. The directive groups present in the original molecule seemed to eliminate the possibility that the fifth bromine molecule reacted by substitution. The brownish-yellow color of the precipitate indicated the possible presence of a quinoid structure. It was with the hope that a study of this reaction would furnish more evidence of the chromoisomerism of phenolphthalein that this investigation was undertaken.

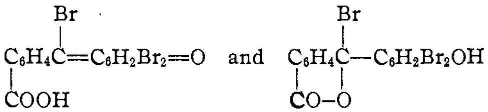
The brownish-yellow material on being carefully heated yielded a sublimate of long, colorless needles and finally a brownish residue remained from which no further sublimate could be obtained. The sublimate consisted entirely of tribromophenol. (Baeyer noted[2] that when dry phenolphthalein was rubbed together with an excess of bromine, tribromophenol was obtained as one of the products. Baeyer, however, did not investigate the reaction.) Further investigation showed that for every molecule of phenolphthalein brominated, one molecule of tribromophenol split off. On the basis of this evidence the following reaction was assumed to take place



$$\underset{\mathrm{NaOOC}}{\mathrm{C_6H_4}}\underset{\mathrm{C_6H_4ONa}}{\mathrm{C}}\mathrm{{=}C_6H_4{=}O} + 5\mathrm{Br_2} + 2\mathrm{HCl} \longrightarrow \mathrm{C_6H_2Br_3OH} + \underset{\mathrm{HOOC}}{\mathrm{C_6H_4}}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{{=}C_6H_2Br_2{=}O} + 2\mathrm{NaCl} + 4\mathrm{HBr}$$

Such a reaction is not an unusual one as many cases are known in which a substituent ortho or para to an OH group is readily replaced by bromine, for example, *o*- and *p*-hydroxybenzoic acids yield tribromophenol.

The quinoid compound, illustrated above, should be capable of existing in two forms



$$\underset{\mathrm{COOH}}{\mathrm{C_6H_4}}\overset{\mathrm{Br}}{\mathrm{C}}\mathrm{{=}C_6H_2Br_2{=}O} \quad \text{and} \quad \underset{\mathrm{CO}}{\mathrm{C_6H_4}}\underset{\mathrm{-O}}{\overset{\mathrm{Br}}{\mathrm{C}}}\mathrm{{-}C_6H_2Br_2OH}$$

Colored Colorless

This was found to be the case. After dissolving the colored form in alcohol, it was recovered, by very slow evaporation, only in the colorless or lactone form. The bromine content of both forms proved to be somewhat less than the theoretical, due to incomplete bromination. An attempt was made to overcome this difficulty by dissolving the yellow form in sodium hydroxide and acidifying the solution with hydrochloric acid in the presence of bromate and bromide. The precipitate obtained,

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[2] Baeyer, *Ann.*, **202**, 78 (1880).

however, was not what was expected. It was reddish-brown in color and its bromine content had increased about 15%. It is hoped, in later work, to be able to prepare these compounds by different methods and conclusively prove the structure of the quinoid and lactone forms.

Tetrabromophenolphthalein when brominated under similar conditions yielded the same products. It is probable that tetrabromophenolphthalein is an intermediate product in the reaction under investigation.

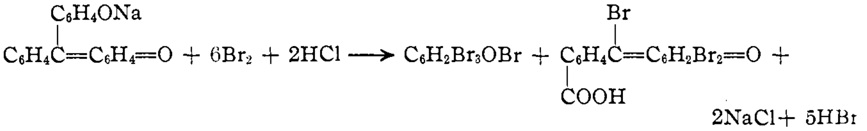
Experimental Part

Bromination of Phenolphthalein.—Five grams of phenolphthalein was dissolved in a little more than the calculated amount of 3 *N* sodium hydroxide. To this was added a solution containing 5 g. of potassium bromate and 18 g. of potassium bromide and the resulting solution was then diluted to one liter. The solution was then vigorously shaken or stirred and 15–20 cc. of 12 *N* hydrochloric acid slowly added. The precipitate at first was very voluminous but after shaking for ten to thirty minutes it settled very nicely and was easily filtered. The brownish-yellow precipitate was dried between filter paper. The precipitate on drying becomes coated with tiny colorless needles of tribromophenol and a small amount of bromine is given off, the latter probably being due to the decomposition of $C_6H_2Br_3OBr$ to $C_6H_2Br_3OH$.

Identification of Sublimate.—The sublimate was obtained, by carefully heating (50–75°) the dried precipitate from above, in the form of long colorless needles. The sublimate melted at 92°. The bromine content determined by a sodium peroxide fusion method was 72.39%. These results check very well the melting point and bromine content of tribromophenol, 92° and 72.48%.

In two other cases the brownish-yellow precipitate, as first obtained, was suspended in water and treated with sulfur dioxide to reduce the $C_6H_2Br_3OBr$ to $C_6H_2Br_3OH$. The dried precipitate from this treatment was subjected to careful sublimation. The sublimate melted at 92° and the bromine content was 72.30%.

Determination of the Total Bromine Consumed in the Reaction.—Half a gram of phenolphthalein was dissolved in a slight excess (1–2 cc. in excess) of 3 *N* sodium hydroxide and the resulting solution diluted to 250 cc. A 25-cc. aliquot was pipetted into a 500-cc. iodine flask, followed by 25 cc. of 0.2 *N* bromine solution (75 g. of potassium bromide and 5.6 g. of potassium bromate per liter). Five cc. of 12 *N* hydrochloric acid was added and the flask stoppered at once. It was vigorously shaken and allowed to stand for one hour with occasional agitation. The flask was then cooled and 5 cc. of 40% potassium iodide solution introduced. After vigorous shaking the liberated iodine was titrated with 0.1 *N* thiosulfate solution. The results from a series of analyses, based on a bromine equivalent of $5Br_2$, varied from 98 to 99.5%. The essential equations for the reaction may be represented as follows



$$C_6H_4\overset{\overset{\displaystyle C_6H_4ONa}{|}}{C}{=}C_6H_4{=}O + 6Br_2 + 2HCl \longrightarrow C_6H_2Br_3OBr + C_6H_4\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}{=}C_6H_2Br_2{=}O + 2NaCl + 5HBr$$

$$C_6H_2Br_3OBr + 2HI \longrightarrow C_6H_2Br_3OH + I_2 + HBr$$

Estimation of Tribromophenol Formed.—The tribromophenol was determined by weighing the sublimate obtained from the bromination of a known amount of phenolphthalein. The results in all cases indicated the formation of one molecule of tribromophenol for one molecule of phenolphthalein. It was found necessary to repeat the bromination in order to complete the reaction. For example, 1.1283 g. of phenolphthalein was brominated as usual. The precipitate was next suspended in water and treated with sulfur dioxide. The dried precipitate was then subjected to careful sublimation. When sublimation had ceased, the residue was again dissolved in sodium hydroxide and the bromination repeated. In this particular case three brominations followed by sublimation were necessary before no more sublimate was formed. The 1.1283 g. of phenolphthalein yielded 1.1629 g. of tribromophenol; theoretical, 1.1736 g.

Analysis of the Quinoid Form.—The brownish-yellow precipitate as first formed was dried, washed with ether and finally heated carefully until sublimation had completely stopped. The bromine content of the residue varied from 48 to 51.08%; theoretical, 51.80%. The low results were undoubtedly due to incomplete bromination. This was demonstrated in the previous paragraph. All attempts to rebrominate the product have failed, as some other reaction (perhaps further substitution or oxidation) resulted. The substance melted at 229–236° with decomposition. It dissolved in sodium hydroxide, forming a greenish-yellow solution which finally became yellow.

Analysis of the Colorless or Lactone Form.—The yellow form, purified as above, was shaken with a large volume of absolute alcohol. It dissolved very slowly, forming a yellow solution which quickly became colorless. When this solution was evaporated almost to dryness, a colorless apparently crystalline material was obtained. This material, after drying, melted at 270–273° with some decomposition. The bromine content checked very well with that of the yellow form. For example, the bromine content of one sample of the yellow was found to be 49.62%. A portion was then changed to the colorless form and the bromine content was now found to be 49.75%. The colorless form dissolved in sodium hydroxide to form a colorless solution. A slight violet color appeared at first but quickly disappeared. Whether this trace of color was due to the lactone form or to the presence of a trace of tetrabromophenolphthalein cannot be answered at present.

Discussion

Friedländer,[3] in 1893, assigned a quinone structure to phenolphthalein salts. About the same time Meyer and Spengler proved it to be a dibasic acid. The tautomeric character of phenolphthalein has been demonstrated since then by various workers, including Stieglitz,[4] Acree and Slagle,[5] Green and King,[6] Hantzsch and Meyer,[7] Meyer and Marx,[8] Orndorff, Gibbs and McNulty,[9] and Gibbs and Shapiro.[10] It was shown by some of these investigators that esters could be prepared from phenolphthalein. They showed that the labile quinoid modifications were yellow or orange, but rearranged in the process of crystallization to give the colorless, stable lactoid form.

According to the views expressed by these papers, the appearance of color during the process of salt formation, with phenolphthalein, would indicate that the color change depends upon changes in constitution rather

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[3] Friedländer, *Ber.*, **26**, 172 (1893).

[4] Stieglitz, This Journal, **25**, 1112 (1903).

[5] Acree and Slagle, *Am. Chem. J.*, **42**, 115 (1909).

[6] Green and King, *Ber.*, **39**, 2365 (1906).

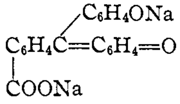
[7] Hantzsch and Meyer, *ibid.*, **40**, 3480 (1907).

[8] Meyer and Marx, *ibid.*, **40**, 1437 (1907).

[9] Orndorff, Gibbs and McNulty, This Journal, **48**, 1994 (1926).

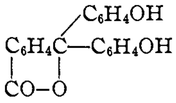
[10] Gibbs and Shapiro, *ibid.*, **50**, 2978 (1928); *Proc. Nat. Acad. Sci.*, **14**, 251 (1928).

than upon the formation of ions. Any ions which may form can possess color only if the non-ionized molecules from which they come are colored. The sodium salt is assumed to have a quinoid structure, while free phenolphthalein has a lactone structure



$$\begin{array}{l} \quad\diagup C_6H_4ONa \\ C_6H_4C{=}C_6H_4{=}O \\ | \\ COONa \end{array}$$

and



$$\begin{array}{l} \quad\diagup C_6H_4OH \\ C_6H_4C{-}C_6H_4OH \\ |\quad\;\, | \\ CO{-}O \end{array}$$

The results presented in this paper can only be explained on the basis of a quinone structure for phenolphthalein in alkaline solution. It is evident that the phenolphthalein must have been brominated before it could change to the lactone structure. If this were not the case, one would naturally expect bromination to proceed as usual with the formation of tetrabromophenolphthalein. That the yellow precipitate first formed is similar to the quinone structure for phenolphthalein is shown by the readiness with which it changes to the colorless or lactone form. The lactone form may be regarded as a derivative of phthalide and the yellow form as the corresponding labile or quinoid structure.

Attempts to prepare these compounds in pure form have not been successful, but it is hoped that later work will overcome some of the difficulties.

Summary

1. It has been shown that the action of bromine (as generated by acidifying bromate–bromide mixtures) upon phenolphthalein varies greatly with conditions. In the absence of a special solvent such as alcohol, chloroform, etc., tetrabromophenolphthalein is not formed. The reaction is accompanied by the loss of five molecules of bromine. Four molecules react by substitution and one by addition.

2. It has been pointed out that the interpretation of the reactions offers further evidence that phenolphthalein possesses a quinoid structure in alkaline solution.

PHILADELPHIA, PENNSYLVANIA