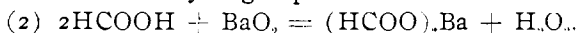
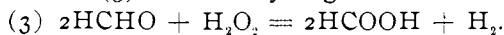


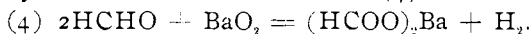
dioxide with which it may come in contact. Coming in contact with peroxide it liberates hydrogen peroxide.



Then reaction (3) liberates hydrogen.

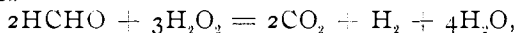


Since the reactions take place at the surface of the peroxide, the hydrogen peroxide acts upon the aldehyde in a very concentrated condition, thus causing reactions (2) and (3) to take place much faster than (1). Reactions (2) and (3), alternating and taking place much faster than (1), may be combined in the form of (4).



This tells the story of the whole reaction almost quantitatively. However, since reaction (1) undoubtedly takes place to some extent, it is evident that the yield of hydrogen, if accurately separated from any oxygen, can never be quite quantitative.

2. *The Reaction with Hydrogen Peroxide.*—The action of hydrogen peroxide upon formaldehyde is not as simple as it has been credited to be. Formic acid is always produced as an intermediate product, along with hydrogen; then the acid may be oxidized to carbon dioxide and water. If all carbon dioxide and all hydrogen could be collected, the volume of carbon dioxide would be about twice that of the hydrogen. The reaction approaches



with the production of formic acid as an intermediate product, according to the following reaction,



Except upon prolonged action, most of the reaction goes no farther than this intermediate stage.

Since the above work was completed, the writer has found that Kastle and Loevenhart¹ worked upon the basis of the fact that formic acid is produced in the action of hydrogen peroxide upon formaldehyde. They did not realize the character of the reaction, however, for there is no mention made of the production of hydrogen, nor of the subsequent oxidation of formic acid to carbon dioxide, which latter fact must appreciably affect their values for the coefficient of velocity of formation of formic acid from the aldehyde.

CHEMICAL LABORATORY, CLARK UNIVERSITY,
May 15, 1907.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY. U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, BOSTON LABORATORY.]

FORMIC ACID AS A PRESERVATIVE.²

By BERNARD H. SMITH.

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The antiseptic and preservative properties of formic acid have recently

¹ Kastle and Loevenhart, *This Journal*, 21, 262.

been referred to in several articles¹, which are of particular interest at this time because of the widespread attention attracted by all matters relating to the purity of foods. Preservatives under trade names are also appearing which contain a formate as their principal antiseptic ingredient. The chemical literature as a whole contains very little concerning the preservative properties of formic acid though it appears that such characteristics have long been recognized². Because of the frequent occurrence of formic acid in nature and of its being an oxidation product of many materials that go to make up foods, complex questions are likely to arise should this substance come into general use as a preservative.

Efficiency as a preservative. Having found a liberal quantity of formic acid in a sample of French cherries, and becoming interested as to the amount required to preserve ordinary perishable food products, some experimental work was undertaken with a view of obtaining additional information as to its relative efficiency as an antiseptic agent, and to determine if possible which of the usual tests would be of the greatest value in detecting formic acid in foods.

In carrying out the former, though other fresh foods were originally included in the tests the work was ultimately confined to stewed tomatoes, it appearing that these when untreated had a tendency to decompose quite uniformly and with rapidity. In interpreting results of this character it is necessary to keep in mind that some preservatives are more efficient for certain food products than for others. This is particularly true of salicylic acid of which considerable quantities are necessary to affect certain putrefactive germs, and the same is true of formic acid though perhaps not in such a marked degree. In all tests blank controls, and samples treated with 1/10 of a per cent. of salicylic acid and benzoic acid were compared with those to which formic acid in varying amounts had been added. Some of the trials were conducted at different temperatures and some with a specific mould in stoppered receptacles, while others were left quite freely exposed to the air, under condition most favorable for decomposition. Though with the latter method samples side by side and treated in the same way may vary somewhat, these results are of perhaps greater value because in them the irregularities of natural conditions are more closely approximated. The following table gives the results of a series of experiments made in this way, which indicate that formic acid is doubtless efficient as a preservative when present in considerable quantities.

¹ Hoffmann. Apoth.-Ztg., 1904, 78. Von Kuttner and Ulrich. Oeffentl. Chem. XII., 201. Lebbin. Chem.-Ztg., 30, 1909.

² Jodin. Compt. rend. 96, 1179. Vogel. Sitzungsber. Akad. Wissensch., Munich, 1882, 345.

MATERIAL.—TOMATOES.

Amount Acid.	Souring or Moulding.
Control (without acid).	Sour after 2 days.
0.1 per cent. Formic (100% sol.)	Mould and sour after 7 days
0.1 " " " " "	" " " " " 7 "
0.3 " " " " "	" " " " " 12 "
0.5 " " " " "	" " " " " 18 "
0.5 " " " " "	" " " " " 25 "
0.5 " " " " "	" " " " " 34 "
0.7 " " " " "	" " " " " 45 "
0.7 " " " " "	Good " " 85 "
1.0 " " " " "	" " " " " 85 "
1.0 " " " " "	Mould " " 45 "
2.0 " " " " "	Good " " 85 "
2.0 " " " " "	" " " " " 85 "
0.1 Benzoic acid	" " " " " 85 "
0.1 " " " " "	" " " " " 85 "
0.1 Salicylic acid	Sour " " 9 "
0.1 " " " " "	" " " " " 9 "

As the table tends to show formic acid ranks lower than benzoic or salicylic acids as an antiseptic agent, which has been noticeable in all trials made.

The relatively low efficiency of salicylic acid as compared with benzoic acid in preserving tomatoes was not expected, but data obtained from manufacturers of tomato products who have used both indicates that benzoic acid is generally recognized as superior for this purpose; but the reverse is apparently true with many other foods.

One-tenth of a per cent. of the sodium salt of benzoic acid is usually regarded as satisfactory in preventing fermentation in goods packed commercially, and to produce similar results using formic acid it would probably be necessary to use from three to five tenths of a per cent.

Separation from food products.—Distillation after acidifying with phosphoric acid appears to be the most practical method of separating formic acid from a food material, but the phosphoric acid should be tested to make sure that it is free from volatile acids. The distillation is preferably done with a current of steam by the same method employed in the determination of the volatile acids in a vinegar. In distilling a food product with a current of steam, more particularly concentrated saccharine solutions, care should be taken not to allow the contents of the distilling flask containing the material to be greatly reduced in volume or small quantities of formic acid will be formed by decomposition. As has been pointed out¹, formic acid does not distil as readily as might be supposed, for during the first part of a distillation it comes over comparatively slowly, and in order that the total amount of the formic acid in the sample be recovered it is necessary to continue the distillation until the bulk of the

¹ Duclaux. Ann. chim. phys. (5) 11, 233.

distillate is from three to five times that of the sample taken. A distillation of a water solution, without the use of a current of steam, continued until ninety per cent. of the liquid had distilled, gave only sixty per cent. of the formic acid added. The distillate will of course contain other volatile acids which are present as well as other volatile substances, such as aldehydes or alcohol. As sulphurous acid and aldehydes are active reducing agents, it is necessary to make sure of their absence before relying upon certain of the reducing tests.

Qualitative tests.—The following are the most important qualitative tests for formic acid as given in the books: Silver nitrate and mercuric chloride are reduced by formic acid or formates of alkali salts, especially in warm solutions. Metallic silver and mercurous chloride are produced. Potassium permanganate is reduced upon which reaction several quantitative methods are based. Ferric chloride or nitrate, when added to a neutral solution of a formate of an alkali metal gives a deep red color. Certain metallic formates are insoluble in alcohol while the corresponding acetates are soluble. Concentrated sulphuric acid evolves carbon monoxide from formic acid or a formate. Sulphuric acid and alcohol when heated with a formate generate ethyl formate, having the odor of peach kernels. Unless a very large quantity of formic acid is present in a sample it is necessary to concentrate the distillate previously referred to by neutralizing and evaporating on the water bath. Ammonia can be used advantageously, any slight excess of which will have disappeared by the time the solution occupies a small bulk, and to this solution the tests may be applied. The silver nitrate test which is one of the most delicate, has the disadvantage of reacting slightly, particularly upon boiling, with most distillates from foods, due largely to traces of aldehyde. The mercuric chloride test is quite satisfactory where some little formate is present and has the advantage of not being interfered with by aldehydes.

Suggested modification of the ferric chloride test.—The ferric chloride test is very sharp, its great drawback being that acetates produce the same color. In an attempt to differentiate between formic and acetic acids in this test it was found that the formate is insoluble in strong alcohol while the acetate is soluble. In fact many of the metallic formates in addition to those usually mentioned, *i. e.* lead, zinc and magnesium, are practically insoluble in alcohol, this being especially true of the mercury, silver, copper, arsenic, tin, barium, and calcium salts.

The following is the procedure used by the author in the ferric test, making use of this difference of solubility in alcohol of the ferric compounds. The distillate from 100 grams of the sample having been neutralized with ammonia, is evaporated to a few cc., say from 3 to 5; this is transferred to a test tube and is treated with from three to six drops of a ten per cent. solution of ferric chloride, when the characteristic red

color will be developed in the solution if ammonium formate or acetate is present. Now add 5 cc. of 95 per cent. alcohol for each cc. of solution in the test tube and shake. A precipitate indicates formic acid. If formic acid alone is present when the precipitate has settled out there will be left a clear supernatant liquid; the precipitate, which can be separated by filtration, or better by means of the centrifuge, may be tested to further demonstrate the presence of formic acid. Should there have been only acetic acid present no precipitate is formed and the red color is not destroyed, though somewhat reduced in intensity because of the dilution.

If benzoic acid is present, a precipitate forms upon the addition of the ferric chloride, but this is dissolved when the alcohol is added. In the presence of sulphites the manipulation must be slightly altered as the bisulphite precipitates with ferric chloride and both the neutral salt and the bisulphite are insoluble in alcohol. By making use of this insolubility, that is, by adding absolute alcohol, boiling and filtering, the separation may be effected and the ferric chloride may then be added to the filtrate.

Under ordinary conditions 1/20 of a gram of formic acid gives a very good test, but the presence of an excess of acetate such as would be formed in a neutralized distillate from a food containing vinegar, seriously impairs its delicacy, if it does not altogether prevent the precipitate from forming. If the acetate is present in equal quantities with the formate, the test is not appreciably interfered with and a heavy precipitate forms immediately or in a minute or two, particularly upon shaking.

When twice as much acetate as formate is present there is no precipitation until after a few minutes, and three times as much acetate as formate prevents the precipitate forming for an hour or more. If the acetate is present in much greater excess, no precipitate is formed even upon standing several hours.

To remove an excess of acetate in order that the test may be applied to foods containing acetic acid is a somewhat difficult matter, but the following adaptation of the partial neutralization and distillation method¹, it is believed, will give satisfactory results. This process depends upon the fact that if a partially neutralized mixture of fatty acids is subjected to distillation, the more chemically active acids, or the lower of the series, tend to remain behind as fixed salts. The separation is quite sharp and the ferric chloride test can be applied to the residue of such a distillation with positive results when 0.2 of a gram of formic acid is present. It is therefore suggested that when acetic acid is present in a food to be tested for formic acid the following method be employed.

¹Wechsler, *Monatsh. Chem.* 1893, 14, 462. Allen; *Commercial Organic Analysis*, Vol. 1, 3rd. Ed., Page 487.

To the distillate obtained by distillation with a current of steam from 100 grams of the sample add from 3 to 8 cc. of normal sodium hydroxide, or such an amount as will probably neutralize the formic acid present, which if added for purposes of preservation will doubtless not be less than 0.20 per cent. The distillate is then subjected to evaporation over a flame, which is continued until the volume has been reduced to about 15 cc.: finish the evaporation on the steam bath, continuing to dryness. Take up with 3 cc. of water and transfer to a test tube: if warm, cool, and then add from 3 to 6 drops of the 10 per cent. solution of ferric chloride followed by 12 to 15 cc. of 95 per cent. alcohol. Sodium formate gives a precipitate but if present in very small quantity or if the amount of added alkali retained a considerable quantity of acetic acid the precipitate will be slow in coming down and it is well for this reason to let the tube stand an hour before discarding as a negative test. Ammonium hydroxide cannot be used in this test, and as sodium acetate is much more insoluble in alcoholic solutions than the ammonium salt it is well to avoid an excess of ferric chloride or an increased alcoholic strength, and better results are obtained when freshly prepared ferric chloride is used.

For the quantitative estimation of formic acid in foods the permanganate or potassium bichromate oxidation methods are not applicable because of the traces of organic matter in the distillate. The method outlined by F. Sparr¹—originally by Portes and Ruyssen²—gives good results, and by it small quantities can be satisfactorily determined. Sulphurous acid however, interferes to some extent when present in appreciable amounts, but when present it may be removed with but a very slight loss of the formic acid by neutralizing the distillate with sodium hydroxide, adding a cc. of concentrated acetic acid, and boiling, when the sulphurous acid will be displaced by the acetic: continue the evaporation until the free acetic acid is removed. The method follows:—

To 25 cc. of the solution to be tested, which should not be more than 1 per cent. in strength, add 5 grams of sodium acetate and 200 cc. of a 4.5 per cent. solution of mercuric chloride. Heat from one to one and one-half hours on the bath and make up to 500 cc. The number of cubic centimeters of the filtered solution required to give the red color with one gram of potassium iodide is then determined and from this is calculated the content of formic acid.

Credit is due Mr. S. H. Ayers of the laboratory of A. D. Little, Boston, Mass., for a large part of the work reported concerning the efficiency of formic acid as a preservative.

¹ Z. anal. Chem. 1900, 39, 105.

² Compt. rend. 82, 1504.