

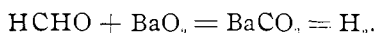
The use of the figure 200 instead of 228 as the iodine figure of rosin by his method will result in giving the true percentage of rosin with a little greater accuracy in most cases; we believe, however, that in order to guard against the rather remote possibility that the use of the figure 200 might give a percentage of rosin slightly too high, it is better policy to use the figure 228.

THE ACTION OF BARIUM PEROXIDE AND HYDROGEN PEROXIDE UPON FORMALDEHYDE.

By C. ALLAN LYFORD.

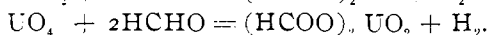
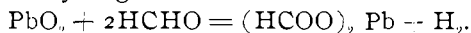
Received June 13, 1907.

The problem of the action of peroxides upon solutions of formaldehyde has been left in a rather unsettled condition. The present research has for its purpose the clearing up of this question. While experimenting upon the oxidation of formaldehyde it was believed that by using barium peroxide there might result mutual oxidation and reduction with the production of barium formate. Upon looking up the literature of the subject the writer found that Geisow¹ believes to have obtained only barium carbonate and hydrogen from the interaction of these two substances. He says he was unable to detect formic acid as an intermediate product either in neutral or acid solution. Geisow gives the following reaction:

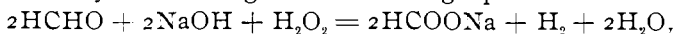


So far as the writer can ascertain, this work has neither been confirmed nor disproved by other writers.

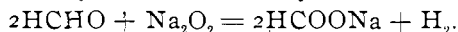
For a number of reasons this reaction does not seem probable. In the first place, acetaldehyde forms a hard resin with barium peroxide, no methane being evolved. If there were such an easy direct removal of the carbonyl group one would not expect a resin to be formed. Geisow states that the dioxides of lead and manganese acting upon formaldehyde in neutral solution produce formates and hydrogen. It is known that uranium peroxide acting upon formaldehyde in neutral solution produces uranyl formate and hydrogen.



In alkaline solutions it has been shown that hydrogen peroxide acts upon formaldehyde according to the following equation²:



(in cold), from which it would follow that the reaction with sodium peroxide and sufficiently dilute formaldehyde would be:

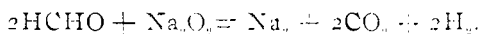


If 30 per cent. formalin be dropped upon sodium peroxide, there is,

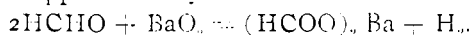
¹ Geisow, Ber., 37, 515.

² Blank and Finkenbeiner, Ber., 31, 2979.

evidently, a reduction to metallic sodium with explosive violence, and the sodium then burns with the characteristic flame.

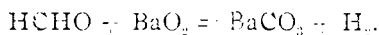


It is seen that in alkaline solution formic acid after being produced, is fixed by the excess of base, and is apparently not further attacked in the primary reaction. It should follow that if barium peroxide were used the reaction should be approximately as follows:



This does not agree with Geisow's statement of the case. In acid solutions peroxides invariably give carbon dioxide and hydrogen, or water as oxidation products.

Since, strictly speaking, it is impossible to work with barium peroxide in neutral solutions, because of its slow decomposition, even in cold water, the case reduces itself to the action of a peroxide upon formaldehyde in alkaline solution. The only way it seems possible that carbon dioxide can result is by using free acid, which of course would change the case to that of the action of a peroxide in acid solution. The fact that the writer finds barium formate is produced by the action of barium peroxide upon formaldehyde makes it certain that the reaction is not so simple as Geisow believes it to be. The writer cannot see how Geisow obtained hydrogen to the extent of 98.15 per cent. of the theoretical amount demanded by the equation:



There is at the most only a very small amount of barium carbonate produced, and that seems to be chiefly due to the action of atmospheric carbon dioxide upon the mixture. Any evidence as to a difference between barium peroxide as a true "peroxide" and manganese dioxide as a true "dioxide," which Geisow seeks to bring forward is unsound, as it is based upon evidently false results. Barium peroxide produces formate just as do the dioxides of lead and manganese, and so far as its action upon formaldehyde is concerned, may possess a structure identical with that of manganese dioxide.

In the experimental work the writer has used pure barium peroxide prepared from hydrogen peroxide and recrystallized barium hydroxide. The formaldehyde was in some cases prepared from paraformaldehyde, and was in others the best commercial formalin carefully standardized by the Haywood-Smith modification of the Blank-Finkenbeiner method¹.

The strength of aldehyde is given in per cent. by volume.

EXPERIMENTAL PART.

A few cubic centimeters of 35 per cent. formaldehyde were put upon a large mass of barium peroxide and allowed to act. The peroxide was in excess. The hard cake finally produced after violent effervescence, was

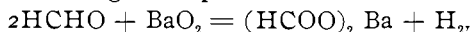
¹ Haywood-Smith, *This Journal*, 27, 1183.

taken up with water and nearly all went in solution. The solution was treated with carbon dioxide, boiled, filtered, and evaporated to a small volume. A few drops of silver nitrate solution then produced a white crystalline precipitate of silver formate which soon turned dark in the light, depositing black, amorphous silver. This is characteristic of silver formate.

20 g. of barium peroxide were treated gradually with 40 cc. of neutral 35 per cent. formaldehyde. After the action had ceased there was an excess of aldehyde. The mixture was allowed to stand half an hour with occasional shaking, so as to use up all the peroxide. Water was added, and nearly all the original mass went into solution. The solution was alkaline, owing to the reduction of some peroxide to barium oxide by the action of water and the nascent hydrogen evolved. The barium hydroxide was removed by treating the hot solution with carbon dioxide and filtering. Upon evaporation, over 20 g. of barium formate were recovered in excellent white crystals, with a very slight odor of formaldehyde, which was removed by again dissolving and evaporating down with frequent additions of alcohol.

Barium Formate and Hydrogen produced.—10.88 gr. barium peroxide and 30 cc. water were treated in a flask with gradual additions, during three minutes, of 30 cc. of 35 per cent. formaldehyde solution (excess). The temperature was kept at 20°-25° by cooling in water. 1202 cc. (reduced) of hydrogen, corresponding to 0.1077 g., were collected. From the solution after filtering off a very small precipitate of barium carbonate, little carbonate could be thrown down with carbon dioxide, showing that not much reduction by the action of water and of hydrogen had taken place. 14.3 g. barium formate were recovered from the solution. The salt was perfectly crystalline. Analysis showed it to be nearly pure barium formate (Ba = 60.1 per cent.). Solutions of the salt gave the characteristic test with silver nitrate solution; also, treated with dilute sulphuric acid and warmed, it gave a strong odor of formic acid.

By Geisow's reaction, $\text{HCHO} + \text{BaO}_2 = \text{BaCO}_3 + \text{H}_2$, or by the following one, $2\text{HCHO} + \text{BaO}_2 = (\text{HCOO})_2\text{Ba} + \text{H}_2$, 10.88 g. barium peroxide would set free about 0.1284 g. of hydrogen. It is evident that about 200 cc. of the gas disappeared in some way. This may be due either to oxidation of some hydrogen while in the nascent condition, or to other reactions taking place which do not liberate hydrogen. However, the rough agreement of the yields 14.3 g. barium formate and 0.1077 g. hydrogen with the theoretical figures 14.6 g. and 0.1284 g. respectively, makes it certain that the greater portion of the reaction takes the form of



and that under the conditions, only a small amount of barium is converted into any other form than formate. The amounts of formate and

hydrogen obtained are respectively 97.9 and 83.9 per cent. of the theoretical demanded by the above equation, while Geisow's equation demands twice as much hydrogen.

3.017 g. barium peroxide were treated with 10 cc. of water, and a slight excess of 20 per cent. formaldehyde. 3.7262 g. of formate were obtained by direct weighing of the crystals left upon evaporating the mother liquor after removing all other barium. Here 91.97 per cent. of the barium was changed to formate.

2.3582 g. barium peroxide and 10 cc. of water were treated with a slight excess of 3.78 per cent. (volume) formaldehyde. After removing all barium other than formate, there were obtained from the solution 2.9417 g. barium sulphate. Here 90.7 per cent. of the barium was converted to formate in the reaction with the aldehyde. It is evident that barium formate is produced either with dilute or strong formaldehyde.

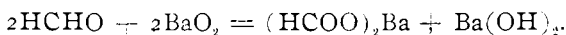
Since in one of the earlier experiments it was evident that there was considerable loss of hydrogen, it was attempted to see if by altering the conditions a more quantitative yield might be obtained. Occasion was also taken to study the effect of time upon the reaction.

Ten g. barium formate, and 25 cc. water were treated with 5 cc. 37.8 per cent. formaldehyde (not excess). The aldehyde was added instantaneously. Most of the gas came off in two minutes. The temperature was kept down by cooling with a water-bath. 593 cc. (reduced) of hydrogen were collected. The reading was taken after a quarter of an hour.

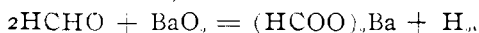
The above experiment was repeated except that the aldehyde was added slowly, in small amounts during one-half hour. The gas was evolved very gradually during three-quarters of an hour. One hour after the beginning of the experiment the reading was taken. 601 cc. (reduced) of hydrogen were collected.

According to the experiments no appreciable quantity of hydrogen which would be evolved upon instantaneous action, is fixed as water during prolonged action. The insolubility of the peroxide would not allow of much reduction in one hour at low temperatures. The increased volume of gas actually obtained in the second experiment is doubtless due to the increased time the peroxide was in contact with the water, thus liberating some oxygen. The amount of oxygen was so small, however, that it could not be directly measured with certainty, though there was a slight contraction with pyrogallic acid, using a 30 cc. fraction of the gas.

It is evident that the deficiency of hydrogen below the theoretical is due, not so much to the fixing of some hydrogen as water, as to reactions not producing hydrogen taking place along with the primary reaction. Possibly the following takes place:



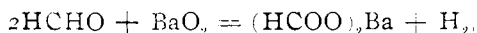
601 cc. of hydrogen is equivalent to 0.5385 g., which is 85.4 per cent. of that which would theoretically be generated from the amount of aldehyde used according to the reaction,



and only 42.7 per cent. of the amount demanded by Geisow's reaction.

By the use of more dilute formaldehyde solution, more quantitative yields of hydrogen result.

Two g. barium peroxide and 10 cc. water were treated in a special apparatus with an instantaneous addition of 5 cc. of 3.78 per cent. formaldehyde solution, and the mixture shaken from time to time. At intervals, readings of the gas evolved were taken as shown in the table. For the reaction,



there were taken the equivalent of 0.0063 g. of hydrogen.

Time.	Vol. H ₂ .	Grams H ₂ .	Available H ₂ .	Per cent. evolved.
10 min.	67.8 cc.	0.00607	0.0063 gr.	96.4
20 min.	68.0 "	0.00609	"	96.7
1 hr.	69.0 "	0.00618	"	98.1
1½ hrs.	69.8 "	0.00625	"	99.2
2 hrs.	70.5 "	0.00632	"	100.2
15 hrs.	75.3 "	0.00675	"	107.1
24 hrs.	77.3 "	0.00693	"	109.9

Under the conditions employed it is seen that in from 1½ to 2 hours, a fairly accurate estimation of the formaldehyde may be made from the volume of hydrogen liberated. Geisow claims, however, that from a solution of 3.7 per cent. by weight he obtained 27.8 cc. of hydrogen per cc. of the aldehyde solution. Taking the above two hour determination as closely approaching the theoretical for the reaction producing barium formate, it is seen that for one cubic centimeter 14.1 cc. of gas result. The solution worked with, being 3.53 per cent. by weight, is closely comparable to Geisow's 3.7 per cent. solution. Geisow gets, or claims to get, twice as much gas as seems possible to obtain. Other experiments have never failed to give only half as much gas as was to be expected from Geisow's reaction. Geisow's hydrogen may have contained appreciable amounts of oxygen, derived from the slow decomposition of the peroxide with water.

The Action of Hydrogen Peroxide upon Formaldehyde.— Because of Geisow's conclusions as to the action of hydrogen peroxide upon formaldehyde it was somewhat surprising to find that much free formic acid can be detected. This suggested that his idea of the mechanism of the reaction is not correct. His equation to show the reaction is $\text{HCHO} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{CO}_2 + \text{H}_2$, no formic acid being produced in any stage of the reaction. It will be shown that this cannot satisfy the requirements.

Five cc. of a 3.78 per cent. formaldehyde solution were treated with

50 cc. 3 per cent. hydrogen peroxide of neutral reaction. The solution was warmed fifteen minutes under a reflux condenser. After all effervescence had ceased the temperature was allowed to rise to the boiling point for fifteen minutes longer. At the end of this time all odor of formaldehyde was gone, and the odor of formic acid was very strong in the hot solution, which was also of a strong sour taste. The solution was then titrated against 0.525 normal solution of sodium hydroxide, with phenolphthalein.

85.7 cc. sodium hydroxide were required, or 2.0696 g. formic acid were present in the solution. Five cc. of 37.8 per cent. formaldehyde would give 2.89 g. of acid. 71.6 per cent. of the aldehyde was changed to acid. Only a small portion of the gas evolved from this reaction was carbon dioxide, for very little precipitate was given with barium hydroxide when the gas was passed through it. Later, carbon dioxide appeared to come off in greater abundance.

Formaldehyde Changed to Formic Acid by 3 Per cent. Hydrogen Peroxide.—5 cc. of 37.8 per cent. formaldehyde and 50 cc. of 3 per cent. hydrogen peroxide (10 cc. at a time) were boiled under a reflux condenser until no odor of aldehyde was detected. The free acid was then neutralized with sodium hydroxide. 3.4 g. of sodium formate were recovered. This is equivalent to 1.5 grams of aldehyde. 1.89 g. of the aldehyde were taken, consequently 79.36 per cent. of it was oxidized to free acid. That the residue was sodium formate is proven by the fact that the solution gave colorless crystals of silver formate, which quickly decomposed to silver on exposure to light. Also when the residue was heated for a time at 300°, and then dissolved in water, barium hydroxide gave a white precipitate of barium oxalate insoluble in excess of dilute hydrochloric acid.

Since formic acid is produced in large quantities by the action of hydrogen peroxide upon formaldehyde, it was thought that this should be borne out by analysis of different fractions of the gas given off. An apparatus was fitted up for collecting the gases in fractions, so that they could be transferred to a Hempel gas burette for analysis.

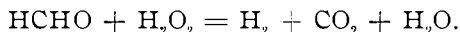
Five cc. of 3.15 per cent. formaldehyde were treated in the special apparatus with 35 cc. of 3 per cent. hydrogen peroxide solution, the temperature being kept at 80°. The gases were collected in consecutive fractions and analyzed.

Fraction.	Time collecting.	Total cc.	Per cent. by volume.					
			CO ₂ .	O ₂ .	H ₂ .	CO.	O ₂ .	H ₂ .
1	20 min.	30.0	3.8	9.6	16.6	12.65	31.97	55.38
2	35 "	31.2	11.2	10.5	9.5	35.84	33.60	50.56
3	50 "	24.4	11.2	8.9	4.3	45.81	36.40	17.59
4	1½ hrs.	29.6	14.1	12.5	3.0	47.66	42.25	10.14
5	2¾ "	36.6	11.6	23.8	1.2	31.67	64.97	5.28
6	5 "	35.9	9.5	25.5	0.9	26.11	70.89	2.50
Totals,		187.7	61.4	90.8	35.5	32.71	48.57	18.91

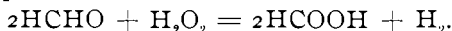
After the experiment 25 cc. more hydrogen peroxide were added to the aldehyde, and a subsequent fraction collected inside of one-half hour contained 2.8 cc. of carbon dioxide, showing that the formic acid was still not all oxidized. The increase in the percentage of oxygen in successive fractions is due to the increased time during which the peroxide is undergoing decomposition, while the hydrogen soon falls off, as the aldehyde disappears.

0.1575 g. of the aldehyde should give 0.231 g. carbon dioxide, or 117.2 cc. Only 58 cc. (reduced) were collected, showing that only 50 per cent. of the formic acid had been oxidized. In dilute solutions formic acid is only slowly affected by weak hydrogen peroxide. The sudden stop in the evolution of hydrogen after the fourth fraction shows that the aldehyde had practically all been converted into some other product by that time.

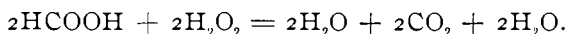
Geisow claims to have obtained a quantitative yield of hydrogen according to the equation :



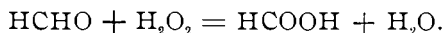
In this experiment, using 30 per cent. peroxide and 3.7 per cent. (by weight) aldehyde, he was unable to detect the presence of formic acid. The above equation calls for equal volumes of hydrogen and of carbon dioxide. The fact that the evolution of hydrogen ceases before half the carbon is oxidized, and that the quantity is so small, shows that Geisow's idea of the reaction is incorrect. The experiments bear out the writer's opinion that several reactions are proceeding simultaneously. If formic acid is produced as an intermediate product, the following equations explain well the phenomena observed :



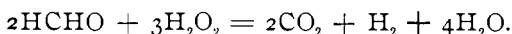
The above reaction predominating in the first part of the process, is later followed by—



Carbon dioxide is evolved only as formic acid is produced and oxidized, not immediately, as by Geisow's reaction. There seems also to be a reaction as follows :

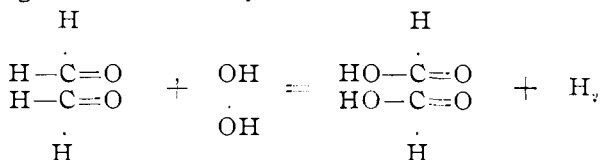


Also it is probable that considerable of the peroxide is reduced by the nascent hydrogen, for the yield of this gas is much too low for the amount of carbon dioxide coming off. The above two principal equations may be combined into an empirical one demanding at least twice as much carbon dioxide as hydrogen.



Since formic acid is produced as an intermediate product, the hydrogen

must come from the aldehyde, half the hydrogen from each of two molecules coming off simultaneously.



Since by the action of 30 per cent. hydrogen peroxide upon dilute formaldehyde, Geisow claims to have obtained a theoretical yield of hydrogen for his equation, it was thought desirable to repeat his experiment as near as his meagre description would allow. First, however, it was desirable to see if strong peroxide would produce any formic acid.

Aldehyde Converted to Formic Acid by 30 per cent. Hydrogen Peroxide.
—5 cc. 37.8 per cent. of formaldehyde and 15 cc. of water were treated with 20 cc. of 30 per cent. hydrogen peroxide for fifteen minutes under a reflux condenser at boiling temperature. At the end of this time there was a very strong odor of formic acid and no odor of the aldehyde. Titration with standard alkali showed the presence of 1.7557 g. formic acid. Since the theoretical yield is 2.89 g., it follows that 60.7 per cent. of the aldehyde was changed to acid.

The gases evolved in another experiment with strong peroxide were analyzed in successive fractions. In the experiment it was attempted to adhere to conditions like those described in one of Geisow's experiments.

Five cc. 3.78 per cent. formaldehyde (3.53 per cent. by weight) were added to 15 cc. water, and placed in the apparatus previously used. 20 cc. 30 per cent. hydrogen peroxide were added, and fractions taken as follows, and analyzed. No carbon monoxide was detected.

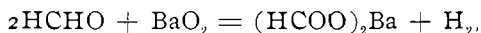
ANALYSIS OF GAS FRACTIONS.						
	Time.	Temperature.	Total cc.	CO ₂ .	O ₂ .	H ₂ .
1	15 min.	70°	55.0	1.8	52.1	1.1
2	15 min.	70°	57.0	3.9	52.1	1.0
3	75 min.	45°	50.9	4.4	45.4	1.1
4	2 hrs.	45°	56.6	5.1	50.5	1.0
5	4 hrs.	40°	58.2	5.3	51.8	1.1
6	5 hrs.	40°	43.6	5.4	36.1	2.1
7	5 hrs.	40°	41.0	6.2	33.0	1.8
8	5 hrs.	40°	51.6	7.8	42.6	1.2
9	15 hrs.	20°	64.6	7.2	53.0	4.4
10	15 hrs.	20°	62.3	7.5	50.8	4.0
11	3 hrs.	45°	68.6	9.6	56.9	2.1
12	4 hrs.	45°	44.4	8.4	35.1	0.9
13	4 hrs.	45°	49.2	7.3	41.4	0.5
14	4 hrs.	45°	45.3	7.0	38.1	0.2
15	4 hrs.	45°	46.8	6.8	40.0	0.0
			795.1	93.7	678.9	22.5

If the carbon in the 0.189 g. formaldehyde used were completely oxidized to carbon dioxide, there should be 140.6 cc. carbon dioxide. It is evident that in seventy-two hours only a little over one-half the carbon has been oxidized; also the yield of hydrogen is not nearly the theoretical amount for Geisow's reaction. There must be much hydrogen oxidized to water by the oxygen constantly evolved in the spontaneous decomposition of the peroxide always taking place.

Here again, with strong hydrogen peroxide, there are unmistakable proofs of the presence of formic acid. It will be observed that increase in temperature of the reaction decreases the amount of hydrogen collected, owing probably to its more complete oxidation to water. Decrease in temperature increases the time necessary to collect fractions. Analysis of the fractions in this case does not show the two separate stages in the reaction as in the case with dilute hydrogen peroxide. This is due all through to the fact that most of the hydrogen is undoubtedly fixed as water by the strong peroxide employed. The increasing amounts of carbon dioxide, however, indicate greater concentration and greater decomposition of formic acid as the reaction proceeds to a certain stage. As formic acid disappears, the carbon dioxide falls off.

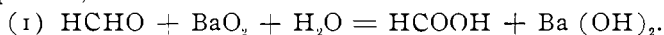
Conclusions.

1. *The Reaction with Barium Peroxide.*—The reaction with barium peroxide proceeds chiefly only as far as the production of barium formate; usually from 90 to 95 per cent. of the barium appearing in that form. The amount of hydrogen probably does not reach such high figures on the average. Though the reaction may be empirically shown by the equation,



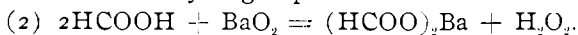
it is most certain that other and intermediate reactions take place. The evolution of hydrogen does not take place until after several seconds have elapsed. After the reaction has taken place, the solution is strongly alkaline to litmus, showing the presence of barium hydroxide. The influence of an alkali upon the oxidation of formaldehyde by a peroxide is always to hasten the process, as happens in the Blank and Finkenbeiner reaction. Also there is some evidence of the presence of small amounts of hydrogen peroxide in the solution. If the above equation solely represents what takes place, there could result no marked quantity of barium hydroxide in the short interval of a couple of minutes, if the temperature is kept at 20° to 25°. The writer feels justified in provisionally explaining the reaction as follows:

First and continually there is a comparatively slow reaction shown by this equation,

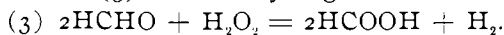


This gives free formic acid, which acts upon any barium monoxide or

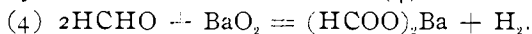
dioxide with which it may come in contact. Coming in contact with peroxide it liberates hydrogen peroxide.



Then reaction (3) liberates hydrogen.

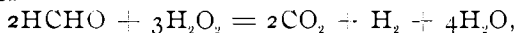


Since the reactions take place at the surface of the peroxide, the hydrogen peroxide acts upon the aldehyde in a very concentrated condition, thus causing reactions (2) and (3) to take place much faster than (1). Reactions (2) and (3), alternating and taking place much faster than (1), may be combined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

Received May 10, 1907.

The antiseptic and preservative properties of formic acid have recently

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