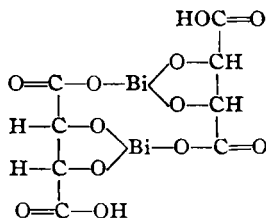


ON THE COMPOSITION OF A SERIES OF BISMUTH SODIUM TARTRATES.

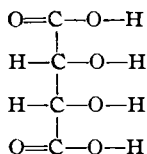
BY W. F. VON OETTINGEN AND Y. ISHIKAWA.*

Warren's review of the commercial bismuth tartrates shows that these vary greatly in composition, the bismuth content ranging from 30 to 75 per cent. The structural formulas suggested for them are not always convincing. We were moved to the attempt to throw some further light on one of these compounds, as prepared by the Fabrègue method, because its chemical and clinical properties differed from those of the citrate prepared by the same method, so as to suggest a different structural relation of the bismuth. We therefore aimed to control and to study, step by step, the reactions of the Fabrègue method for the tartrate, as we had done for the citrate. The preparation of the water soluble bismuth sodium tartrate, as that of the citrate, which is described in a previous paper, involves two phases: first the preparation of the water-insoluble bismuth tartrate and second that of the water-soluble bismuth sodium tartrate.


In the preparation of the bismuth tartrate with the Fabrègue method, 100 Gm. of bismuth nitrate are dissolved in 200 cc. of glacial acid, diluted with 500 cc. of water and mixed with a solution of 97 Gm. of sodium tartrate in 500 cc. of water. A white precipitate is formed which settles slowly on standing. This precipitate is collected on a Buchner funnel and carefully washed with water. The washing is best done by removing the residue from the funnel, re-suspending it in water and filtering it again. During the second washing the precipitate distinctly alters its character to a syrup-like consistency, which changes again on further washing, so that finally a chalky powder remains on the funnel. The washing should be continued until the filtrate is free from acetic acid. The final product is washed with alcohol and ether and dried at 80° C. It represents a fine white powder which is insoluble in water but which is able to absorb considerable amounts of water until it is transformed into a homogeneous magma. The dry powder was analyzed and found to contain 58.3% of bismuth, which corresponds closely to the theoretical value of 58% of a compound $C_4H_6O_{12}Bi_2 = 744$ of the following structural formula:



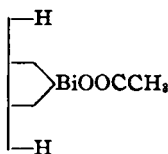
In order to save space the formula of tartaric acid:



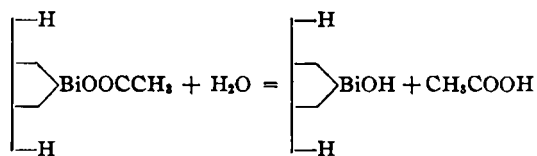
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will be given by the figure  in which the different H atoms will be replaced as needed.

The changes of the original white amorphous precipitate to a syrup and then to a magma, during the washing, suggest chemical changes. It appeared likely that first an aceto bismutho tartaric acid $C_8H_7O_8Bi = 416$

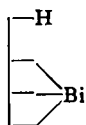
(Formula I)¹

is formed which is decomposed by hydrolysis during the washing. The isolation of this compound was attempted by avoiding the water as much as possible; namely, by mixing a solution of 50 Gm. of bismuth nitrate in 100 cc. of glacial acid with a solution of 48.5 Gm. of sodium tartrate in 100 cc. of water. The white precipitate was collected on the Buchner funnel, washed with 25% acetic acid to remove the excess of the tartrate, and with alcohol to remove the acetic acid; then it was dried and analyzed. It was found to contain 50.7% of bismuth and 15% of acetic acid, values which are very close to the theoretical values of 50.2% of bismuth and 14.4% of acetic acid required by a compound of the assumed formula. The conversion of this aceto bismutho tartaric acid into the bismutho tartaric acid which is assumed to take place by hydrolysis may be illustrated by the following equation (a):



(Formula II.)

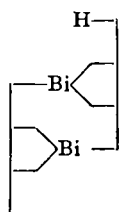
This compound (Formula II) cannot be isolated, because like other bismuth hydroxide compounds, it splits off water during the drying with the formation either of a monomolecular anhydride of the type



(Formula IIIA.)

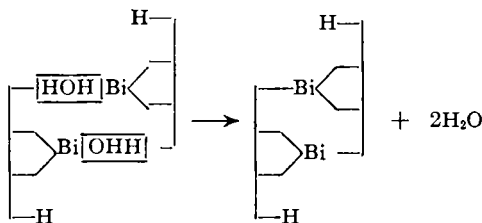
or a bimolecular anhydride of the type

¹ All the formulas are tabulated in the Summary.



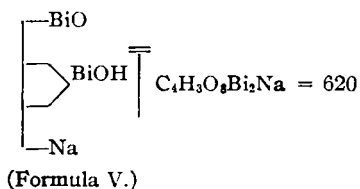
(Formula IIIB.)

Since the two compounds have the same percentual composition, they cannot be identified by analytical means. However, some observations in the second part of the preparation, which will be discussed later, seem to indicate that it is probably IIIB which is formed, and that the reaction takes the course of equation (b):

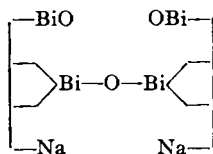


We believe that this compound (IIIB), which might be considered as dibismutho ditartaric acid, represents the final product with the Fabrègue method. It contains 58.3% of bismuth which corresponds closely to 58% of bismuth, the theoretical value of the formula discussed. It represents a white powder, insoluble in water and soluble in alkali. When mixed with water it absorbs considerable quantities before a white magma is formed.

The second part of the preparation of the soluble bismuth sodium tartrate is the solution of the dibismutho ditartaric acid anhydride in sodium hydroxide. For this purpose the dry powder is first transformed into a magma by the addition of water, and then dissolved by the gradual addition of normal sodium hydroxide solution. When just sufficient alkali has been added to secure a solution, a turbidity forms on standing, but clears again on adding a few drops of alkali. When the whole material has been dissolved, the bismuth sodium tartrate is precipitated with alcohol, filtered, washed and dried. Different lots of this compound contained from 67 to 69% of bismuth; but usually about 68.5% of bismuth and 3.8% of sodium. The lower content approaches the 67.4% of bismuth required by Formula V:



but the usual composition corresponds to 68.5% of bismuth and 3.8% of sodium required by Formula VI.

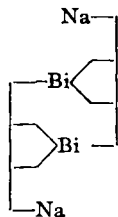


(Formula VI.)

which may be considered as a bimolecular anhydride of Formula V.

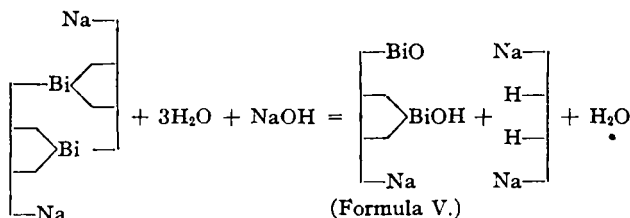
In naming these compounds, the BiO group connected with the carboxyl (end) groups of the tartaric acid will be called "bismuthyl" group, to correspond with the nomenclature of the corresponding bismuth citrates, while the BiO group attached to the (central) hydroxyl groups of the tartaric acid radical will be designed as "bismutho" group.

As it was found that the dibismutho ditartaric acid anhydride dissolves more readily in sodium hydroxide if it was not first suspended in water, this procedure was chosen in a number of experiments, but it was found that the compound precipitated by the addition of alcohol gave always very low analytical values in the range of 60 to 62% of bismuth. As explanation of this finding, it seemed possible that the dibismutho ditartaric acid was not hydrolyzed, but that only the corresponding sodium salt was formed besides a certain amount of bismuthyl bismutho sodium tartrate (Formula V). In an attempt to isolate this unhydrolyzed compound, 30 Gm. of the dibismutho ditartaric acid (Formula III) were very carefully ground in a mortar with 5 cc. 10 *N* sodium hydroxide, until after one and a half hours a homogeneous glassy magma resulted. The addition of alcohol gave a white amorphous precipitate which, after washing with alcohol and drying, was found to contain 54.9% of bismuth and 6.1% of sodium. This corresponds very closely to 55.3% of bismuth and 6.0% of sodium, the theoretical values of a compound $C_8H_4O_{12}Bi_2Na = 756$ of the formula:



(Formula IV.)

This compound might therefore be considered as the intermediate product. It also supports the assumption of the formula of the dibismutho ditartaric acid anhydride Formula IIIB, proposed in the first part. We may assume that by complete hydrolysis by water in the presence of one molecule of sodium hydroxide, the final product, the bismutho monosodium tartrate is formed, corresponding to the equation (c):



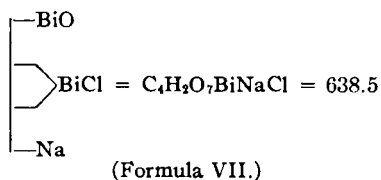
During the drying two molecules of this compound lose one molecule of water, forming a bimolecular anhydride, namely the anhydride of dibismuthyl dibismutho disodium ditartrate with a bismuth content of 68.5% and a sodium content of 3.8%, Formula VI. The final product as obtained conforming to equation (c) is a gelatinous mass which filters only very slowly. After washing with alcohol and ether and after drying, it represents an amorphous mass which can be ground in the mortar to a white slightly yellow powder. This change induces us to believe that the original compound is represented by Formula V, and contains a Bi(OH) group, and therefore may be considered as a bismuthyl bismutho sodium tartrate; and that the change, during the drying, is due to the formation of a bimolecular anhydride of the structure and composition given in Formula VI. The formation of sodium tartrate which is assumed by equation (c) has been demonstrated by the isolation of considerable amounts of this compound by fractional crystallization.

The formulas of the different bismuth tartrates, as we developed them in the course of this investigation, remain somewhat insecure, as we are dealing with amorphous or even gelatinous substances which are difficult to obtain in pure condition, especially as they are all more or less apt to change their character during the washing and drying processes. We found that the correct analytical values for the bismuthyl bismutho sodium tartrate (Formula V) and the anhydride dibismuthyl dibismutho disodium ditartrate depend largely on three factors: (1) these values become too low when inadequate amounts of water are used for the solution of the dibismutho ditartaric acid in sodium hydroxide, which causes, we believe, an incomplete hydrolysis. (2) low values occur also when too much alcohol is added for the precipitation, by which some sodium tartrate is also precipitated; in this case the total weight of the final product is rather high. (3) With the addition of a large excess of sodium hydroxide, the preparation is partly decomposed with the formation of another compound with a higher bismuth content.

The anhydride of dibismuthyl dibismutho disodium tartrate (Formula VI) is easily soluble in water. A 10% solution has a p_{H} of 8.4 and is therefore rather alkaline. When the p_{H} is gradually lowered by the addition of $N/10$ HCl to a p_{H} of 7.6, a slight turbidity may be observed which gradually increases with increasing acidity. When the bismuth tartrate is precipitated with alcohol from such a partly neutralized solution, it is insoluble in water. We may therefore assume that the alkalinity is a property of the anhydride of the dibismuthyl dibismutho disodium ditartrate itself.

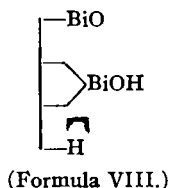
In aqueous solutions this compound probably contains a hydroxyl group as in Formula V, for it forms precipitates with alkali salt, such as sodium chloride,

nitrate and others. The chlorine compound was prepared by mixing equimolecular quantities of solutions of the tartrate (Formula VI) and sodium chloride, and analyzed after washing with alcohol and drying. It was found to contain 65.6% of bismuth, 4.0% of sodium and 5.5% of chlorine. This corresponds to a compound with the formula:



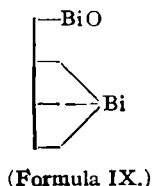
which has the theoretical values of 65.4% of bismuth, 3.6% of sodium and 5.2% of chlorine.

As it was observed that a preparation of the anhydride of the dibismuthyl dibismutho disodium ditartrate (Formula VI), which was completely soluble when freshly precipitated, became less soluble after having been dried on the Buchner funnel by sucking a current of air through the precipitate for many hours, and could then only be brought into complete solution by the addition of a few drops of *N*/10 sodium hydroxide, the influence of carbonic acid on the bismuth sodium tartrate was investigated. By saturating a solution of bismuth sodium tartrate (Formula VI) with carbon dioxide, a white precipitate is formed which is insoluble in water, and which after washing and drying consists of a white powder. This compound does not evolve carbon dioxide with acetic or hydrochloric acid and hence cannot be considered as a carbonate. Samples were found to contain 72.1 to 73% of bismuth and traces of sodium. The fact that the product recovered in this way was found to be free of carbon dioxide, suggested that the sodium was replaced by hydrogen with the formation of a compound $\text{C}_4\text{H}_4\text{O}_8\text{Bi}_2 = 598$ of the type:



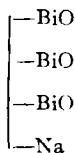
which may be considered as a bismuthyl bismutho tartaric acid.

We believe that by the drying process the compound loses one molecule of water with the formation of an anhydride, bismuthyl bismutho tartaric acid anhydride $\text{C}_4\text{H}_2\text{O}_7\text{Bi}_2 = 580$ of the formula:



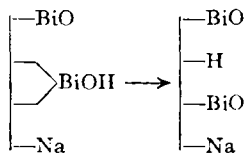
which contains 7.2% of bismuth, which value corresponds to those found by analysis. When this compound is redissolved in the presence of sodium tartrate with sodium hydroxide and reprecipitated with alcohol from its solution, a compound results which contains after drying 68.3 to 68.5% of bismuth and 3.9% of sodium which corresponds to the theoretical values of the anhydride of the dibismuthyl dibismutho disodium ditartrate (Formula VI), namely: 68.5% of bismuth and 3.8% of sodium. When, however, this solution in sodium hydroxide is affected in the absence of sodium tartrate, a compound results which contains 74.3% of bismuth and 2.8% of sodium.

Compounds of the same composition are formed when the anhydride of the dibismuthyl dibismutho disodium ditartrate is dissolved in water and reprecipitated with alcohol. The formation of this compound is very much favored by the presence of sodium hydroxide and by warming; it is prevented on the other hand by the presence of sodium tartrate. The analytical values of this compound correspond to 74.2% of bismuth and 2.7% of sodium values required by a compound $C_4H_2O_9Bi_3Na = 844$ of the following structure:



(Formula XI.)

We can only give hypothetical assumptions for the mechanism of this transformation as we have been unable so far to isolate intermediate products. By fractional precipitation with alcohol the bismuth content is gradually decreased and the last fraction contains practically pure sodium tartrate. The reaction might be explained as follows: It may be assumed that under the influence of the alkali on the bismuthyl bismutho tartrate (Formula V), the bismutho group containing the BiOH complex is transformed into a BiO complex while the hydrogen atom migrates to the oxygen atom of the hydroxyl group of the tartaric acid radicle (equation *d*):



(Formula X.)

This compound may be considered as a bismuthyl monobismutho sodium tartrate. The two BiO groups of this tartrate (Formula X) replace the hydrogen atoms of the free hydroxyl of the tartaric acid radicle in two other molecules, as indicated by the arrows, and in the presence of one molecule of sodium hydroxide, two molecules of bismuthyl dibismutho sodium tartrate and one molecule of sodium tartrate are formed (equation *e*):

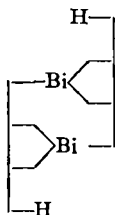
Formula number.	Preparation.	Per cent found.		Assigned structural formula.	Per cent required for assigned formula.		Name proposed.
		Bi.	Na.		Bi.	Na.	
IV.	Dissolved in conc. NaOH avoiding excess of water	54.9	6.1		55.3	6.0	Anhydride of dibismutho disodium ditartrate
V.	Hydrolyzed with water in the presence of 1 mol. NaOH	67.3	3.8		67.4	3.7	Bismuthyl bismutho sodium tartrate
VI.	Dried in the oven at 80°	68.5	3.8		68.5	3.8	Anhydride of dibismuthyl dibismutho disodium ditartrate
VII.	V. precipitated with NaCl	65.6	4.0 chlorine 5.5		65.4	3.6 chlorine 5.2	Bismuthyl chloro bismutho sodium tartrate
VIII.	V. decomposed with CO ₂	Not isolated					Bismuthyl bismutho tartaric acid
IX.	VIII. dried in the oven at 80°	72.1	...		72.0	...	Bismuthyl bismutho tartaric acid anhydride
X.	V. dissolved in the presence of alkali	Not isolated					Bismuthyl mono bismutho sodium tartrate
XI.	VI. dissolved in water in the presence of alkali	74.3	2.8		74.2	2.7	Bismuthyl dibismutho monosodium tartrate
XII.	X. decomposed with CO ₂	76.0	...		76.2	...	Bismuthyl dibismutho tartaric acid

SUMMARY.

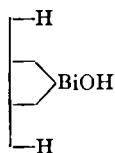
Table I shows the different compounds which we believe to be formed during the preparation of the bismuth tartrate with the Fabrègue method, with the preparation of the soluble bismuth sodium tartrate and a series of derivatives.

CONCLUSIONS.

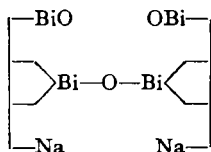
The preparation of the bismuth tartrate by the Fabrègue method passes through different compounds which were isolated and analysed. These are the aceto bismutho tartaric acid and the bibismutho tartaric acid anhydride



which might be considered as a bimolecular anhydride of bismutho tartaric acid, not isolated:

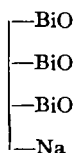


The preparation of the water soluble bismuth sodium tartrate passes also through different phases, the final product being an anhydride of dibismuthyl dibismutho disodium ditartrate of the composition $\text{C}_8\text{H}_4\text{O}_{15}\text{Bi}_2\text{Na}_2$; the structural formula



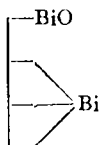
containing 68.5% of bismuth and 3.8% of sodium.

By dissolving the preparation in water in the presence of sodium hydroxide and reprecipitating with alcohol, a compound can be isolated which contains 74.3% of bismuth and 2.8% of sodium which corresponds to the formula $\text{C}_4\text{H}_2\text{O}_9\text{Bi}_3\text{Na}$ and which might be considered as bismuthyl dibismutho sodium tartrate.



Both preparations are decomposed by carbon dioxide with the formation of the free substituted tartaric acids. By drying in the oven at 80° , the dibis-

methyl dibismutho disodium ditartaric acid forms the corresponding anhydride, $C_4H_2O_7Bi_2$:



Both preparations, the bismuthyl bismutho sodium tartrate and the bismuthyl dibismutho sodium tartrate form precipitates with alkali salts; and by drying they tend to form condensation products with anhydride formation. In this respect the bismuthyl dibismutho sodium tartrate differs from the dibismuthyl monosodium citrate. We shall report on this difference of the chemical and physical properties of both compounds in another paper.

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NITROSYL CHLORIDE AND KETONES.

BY H. RHEINBOLDT AND O. SCHMITZ-DUMONT.

Under the above-mentioned title E. V. Lynn and Frank Andrew Lee¹ recently published a report, containing a detailed discussion of our investigation upon "Nitroschlorination" of methyl-ketones by nitrosyl chloride.² This review prompts the following comments:

By their experiments Lynn and Lee found no chlorisonitroso compounds but only isonitroso compounds. This led them to the conclusion—that the reaction without use of diluting agents would give another result, that it would come to a standstill at the first phase of the nitroso-chlorination.

We have already stated in our previously mentioned communication—that the reaction of liquid nitrosyl chloride on undiluted *acetone* also yielded chlorisonitroso-acetone. We are in a position to confirm this statement by a further experiment with *pinacolone*:

Six Gm. of pinacolone were added to 20 Gm. of liquid nitrosyl chloride, cooled to about $-10^{\circ}C$. At first no reaction was evident, but after removing the cooling mixture, a lively reaction took place, with evolution of nitric oxide and hydrochloric acid gas. After the evaporation of nitrosyl chloride, a yellow-colored oil remained, the temperature of which had risen on account of the heat of the reaction. On cooling, the product solidified completely and yielded, after washing with

¹ E. V. Lynn and F. A. Lee, *JOUR. A. PH. A.* (April 1927), p. 309.

² H. Rheinboldt and O. Schmitz-Dumont, *Ann.*, 444 (1925), 113.