

precipitated by Wagner's reagent,—for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up, multiplied by 0.3834, gives the amount of caffeine in that particular portion of the liquid.

ANN ARBOR, MICHIGAN.

ON THE FORMATION OF ANTIMONY CINNABAR.

BY J. H. LONG.

Received February 15, 1896.

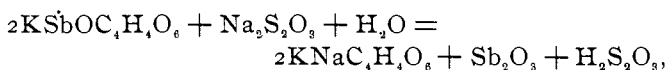
THE composition of the pigment known as antimony cinnabar has been stated by several different formulas, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula Sb_2S_2O . The formula, Sb_2S_3 , is found also in some of the older works, and Baubigny¹ has shown that this is undoubtedly the correct one. Experiments made by myself and described in this Journal, in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand, has a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given.²

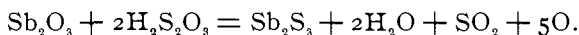
By analogy with other formulas established in the paper referred to I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation:

¹ *Compt. rend.*, October 22nd, 1894.

² *Loc. cit.*



the oxide and thiosulphate then acting on each other to form sulphide :



The oxygen and sulphur dioxide are not liberated as such but held as polythionates with the excess of thiosulphate used.

To throw further light on the reaction I have attempted the formation of the cinnabar by other methods. While the product is sulphide of antimony, it appears that it can be made with its characteristic color only by the decomposition of a thiosulphate. All attempts to obtain the true precipitate by action of hydrogen sulphide or alkali sulphides and sulphur dioxide on antimony solutions failed. The only body formed was the amorphous sulphide, often mixed with sulphur. On the other hand, by the action of a neutral or acid mixture of an antimony compound and a thiosulphate on each other, the cinnabar red product is the only one formed. If the mixture is made alkaline by the addition of a drop or two of ammonia water, no sulphide whatever precipitates. A small amount of hydrated oxide of antimony separates, but the decomposition of the thiosulphate is prevented. On the addition, now, of enough weak acid to neutralize the ammonia a yellow precipitate soon appears, but this speedily changes to deep bright red. The formation of the true cinnabar seems to begin by the appearance of a yellowish intermediate product, which is compatible with the above equations.

In this connection it is interesting to note the behavior of pure antimony trioxide with solutions of thiosulphate. The reaction of the latter with a soluble antimony compound is comparatively rapid, and experiments were made to show the action of the oxide under the same conditions. It was found that the latter, when added to a strong or weak neutral thiosulphate solution is unable to effect a decomposition, in the cold or by application of heat. When the mixture is boiled the oxide remains perfectly white. This is true even after heating in an autoclave under a pressure of eighteen atmospheres.

It was found, however, that with the addition of a little acid to the mixture of oxide and thiosulphate a reaction followed after a time, although it never became complete. In a series of experiments a constant weight, 0.576 gram, of the pure precipitated, washed, and dried oxide was taken and mixed with water and a constant weight of sodium thiosulphate in solution, in each case 0.992 gram of the salt. Definite volumes of half normal hydrochloric acid were then added and water enough to make the total volume fifty cc. in each case. The mixtures were made in small Erlenmeyer flasks, loosely stoppered, and were very frequently shaken. The amounts of hydrochloric taken are given in the table below. The reactions became apparent only after several minutes, and, after five hours, had advanced so far in the mixtures numbered one and two, that the products had become orange. The reactions in the other flasks were less marked, but later became strong. The mixtures were made on October 7th and were shaken many times daily through two months, in fact, as long as any change of color in them was noticed. On December third the amount of sulphide of antimony present was found by the method of Rivot, oxidation by chlorine after preliminary treatment with strong potassium hydroxide solution. The sulphur is found as sulphate and the amount of sulphide formed in each case is shown by the table.

No.	Amount of Sb_2O_3 .	$\text{Na}_2\text{S}_2\text{O}_3$.	$\frac{N}{2}\text{HCl}$.	H_2O .	BaSO_4 found.	Sb_2O_3 converted.
1	0.576 gram.	0.992 gram	2 cc.	48 cc.	0.155 gram.	0.064 gram.
2	0.576 "	0.992 "	4 "	46 "	0.293 "	0.121 "
3	0.576 "	0.992 "	8 "	42 "	0.384 "	0.158 "
4	0.576 "	0.992 "	12 "	38 "	0.427 "	0.176 "
5	0.576 "	0.992 "	16 "	34 "	0.454 "	0.187 "

In mixtures one and two no evolution of sulphur dioxide could be detected by the odor or by tests, but in the others it was apparent, weak in 3 and strong in 4 and 5. No free sulphur was precipitated in any case, or at any rate could not be found in the final product. Although but a small part of the oxide was actually converted the color of the products in mixtures 1 and 2, was a deep cinnabar, and perfectly characteristic. The amounts of sulphide formed or of oxide converted are not

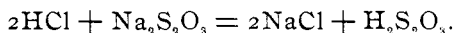
proportional to the volumes of acid used, and are much less than should be found on the assumption that the reaction begins by the production of antimony chloride from the oxide. If this were true, the sulphide formed by means of the soluble thiosulphate should increase with the acid taken. The reaction appears to take place between the oxide and thiosulphuric acid liberated by the hydrochloric acid, as was suggested by several experiments. In one case 0.500 gram of antimony oxide was treated with ten cc. of half normal hydrochloric acid and thirty cc. of water, as before, and allowed to stand twenty minutes, with frequent shaking. The mixture was then filtered and to the filtrate one gram of sodium thiosulphate in ten cc. of water was added. In a short time a precipitate of sulphur formed, perfectly light colored, showing the absence of even a trace of the antimony. The rapidity with which the thiosulphate was decomposed showed that the hydrochloric acid taken must be in the filtrate and not in the residue, as oxychloride for instance. Titration of the filtrate showed this in a similar case. In a second experiment the acid and thiosulphate, in amounts equal to those of the last experiment, were mixed, and after the lapse of one minute the now opalescent mixture was added to some antimony oxide. Although the reaction between the first substances had gone into its second stage, showing that the hydrochloric acid was now certainly in combination, a precipitation of antimony sulphide began almost immediately and in a short time the cinnabar color was distinct.

Thiosulphuric acid is usually spoken of as quite unstable, but Landolt has shown¹ that in dilute solutions it may exist many seconds, even minutes. The interval before precipitation is lengthened by dilution. If decomposition begins in presence of compounds of the heavy metals, a sulphide, sulphur dioxide, and polythionates may form. A large excess of thiosulphuric acid is necessary to complete the reaction in this manner, as suggested by the experiments of Vortmann.²

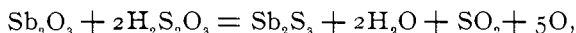
In experiment No. 1 of the table above the amount of hydrochloric acid taken is just one-eighth of that necessary to complete this reaction with the thiosulphate :

¹ *Ber. d. chem. Ges.*, 16, 2958.

² *Ber. d. chem. Ges.*, 22, 2307.



By full conversion enough acid would be liberated to complete the equation assumed at the beginning.



with the amounts of oxide and thiosulphate taken. It follows, therefore, that not over one-eighth of the antimony oxide taken should be found converted into sulphide, and the result of the experiment shows slightly less than this. According to this theory we should have 0.072 gram of oxide changed. The test shows 0.064 gram. In the second and following experiments the amount of oxide converted is relatively still less. The acid taken in the last experiment is sufficient to decompose all of the thiosulphate and thus permit the conversion of all of the oxide. But the result shows that slightly less than one-third the oxide has been changed. In the first experiment no escape of sulphur dioxide was noticed, while in the last it was quite marked and this fact has doubtless some connection with the low amount of sulphide formed. The reaction which takes place in a weak solution of thiosulphuric acid is evidently different from that in the strong solution, inasmuch as the greater portion of the sulphur seems to be given off as sulphide in the one case and as sulphur dioxide in the other.

In the somewhat similar reaction with arsenious oxide Vortmann¹ suggests this equation,



in which but one-sixth of the sulphur present is used to form sulphide. By increasing the amount of hydrochloric acid added to the thiosulphate the decomposition of the latter is hastened.

It is possible that after a time, with increased liberation of sulphur dioxide the formation of sulphide may be retarded, as was suggested by this experiment. I mixed half a gram of the antimony oxide with one gram of sodium thiosulphate in ten cc. of water, and added ten cc. of half-normal hydrochloric acid and thirty cc. of moderately strong solution of sulphur dioxide, free from air. By using water instead of the last solution, precipitation would appear in a few minutes, but in this case it was

¹ *Loc. cit.*

delayed several hours and then but a slight amount of yellowish product appeared. The thiosulphate is therefore protected from decomposition by the presence of the sulphur dioxide.

The cinnabar is easily formed from the oxychloride of antimony without addition of acid. Some recently precipitated and well washed oxychloride was mixed with water and thiosulphate solution of the strength used before. The characteristic color soon appeared and in a short time the whole product seemed to be cinnabar. The reaction is doubtless aided by the hydrochloric acid liberated by the decomposition of the oxychloride in presence of water. The acid in turn attacks the thiosulphate, and so the process becomes continuous and rapid. These reactions are all much hastened by application of heat and the quantitative relations are also altered, but at a temperature of 20° C. thiosulphuric acid seems to be the active precipitating agent in the cases investigated.

NORTHWESTERN UNIVERSITY,
CHICAGO.

PERHALIDES OF CAFFEINE.

BY M. GOMBERG.

Received February 25, 1896.

I. INTRODUCTION.

THE formation of periodides by organic bases has been known as far back as 1839.¹ Their methods of preparation, their composition and properties have been subjects of investigation at different periods since then. Jörgensen,² in 1870, made a complete review of the subject, and has contributed a long list of new periodides. In 1887, Gunther³ made a compilation of all the periodides known up to that time, and reported many new ones. More recently Prescott⁴ offered a classification of all known periodides of both organic and inorganic bases, presenting at the same time a history of the principal advances in the study of the subject.

A strict separation of the periodides as such into those of alkylamines and those of pyridine and of its derivatives, seems

¹ Bouchardat, 1838: *Compt. Rend.*, 9, 475.

² *J. prakt. Chem.* [2], 2, 347, 433, 1870.

³ *Ann. Chem.* (Liebig), 240, 66.

⁴ This Journal, 17, 775.