THESIS

The Determination of Silver in Organic Compounds.
The Silver Salts of Pentabromophenol.

by

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PART I

THE DETERMINATION OF SILVER IN ORGANIC COMPOUNDS.

Introduction

During the last few years some work has been done both in this country and in Germany on the silver salts of halogen substituted phenols, thus giving rise to some exceedingly interesting results. As most of the work done concerned the lower halogen substituted compounds, it was thought that an investigation of the silver salts of the higher halogenated phenols might prove valuable.

As this investigation would necessitate a large number of analyses, a more satisfactory method for the determination of silver in such compounds has been studied.

Review of Methods

There have been a large number of methods described in the literature for the estimation of silver in organic compounds, but in every case they are lacking in one or more of the qualities which determine their value, namely, speed, accuracy, and applicability.

The universal method which is described in all of the text books covering the subject is that of Carius.[1] This method involves heating the silver compound with fuming nitric acid in a long, heavy, sealed glass tube, by means of a specially constructed furnace, at

[1] Ber., 3, 697 (1870)

about 200°C for several hours. This treatment decomposes the organic part of the compound, thus freeing the silver, which in turn is dissolved by the acid. The contents of the tube are then carefully rinsed out into a beaker, the excess of acid neutralized with pure sodium carbonate and the silver precipitated and weighed as halide.

This method, although it is so universally used, has serious defects. The greatest objection to it is its extreme tediousness, (as is revealed in the foregoing description.) Moreover the tubes often explode with great violence, thus making the method a dangerous one.

Aside from determining silver in explosive substances like silver oxalate, silver acetylide, silver picrate, etc., and also in cases of a number of compounds which are not completely decomposed by the treatment within the tube, the Carius method has wide applicability. It is also capable of yielding very exact results if extreme care is exercised in the manipulation.

There are many other methods which depend upon decomposition of the silver salts, using either oxidizing or reducing agents to accomplish it.

The method of Dupont and Freundler,[1] which like the Carius method employs acid for the decomposition, deserves mention. This method consists in heating the silver salt in an open vessel with aqua regia, whereby the silver is converted into silver chloride and determined as such. If bromine is present in the compound, they find that the presence of a small amount of a bromide, which generates hydrobromic acid, greatly assists in the decomposition.

[1] Manuel Operatoire de Chemie Organique, P. 80 (1898) - Rindl and Simonis.

Dupont's and Freundler's method has found little favor with chemists; this probably being due to its inapplicability. Datta and Fernandes[1] have shown that aqua regia is a very strong chlorinizing agent and produces chlorination in cases of a very large variety of compounds. It is true also that aqua regia does not effect decomposition in cases of some compounds which are not halogenated by it.

The only method of any significance which does not depend upon the decomposition of the compound is that of Vanino[2]. This method is based upon the reducing action of formaldehyde in strong alkaline solution. The silver is reduced to the metal and weighed as such. Due to the fact that only soluble silver salts could be analyzed by this method, it is therefore of little value.

The Cyanide-Sulfide Method.

The method of determining silver in organic compounds worked out in this laboratory by the author is based upon the separation of the silver from a cyanide solution of the silver compound by its precipitation as a sulfide and its estimation as such.

Cyanides such as sodium and potassium cyanides have a decided action on silver salts in general; even upon those which have only a very slight solubility such as the halides, thiocyanate, oxalate, cyanide, etc., forming the quite stable argenti cyanide ion according to the following typical reaction in which A represents the organic part of the silver salt molecule

$$A\ Ag + 2\ NaCN = Na\ Ag(CN)_2 + A\ Na$$

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[1] J. Am. Chem. Soc., 38, 1809-13.
[2] Ber., 31, 1763.

It is seen from the above equation that in every case, when this reaction takes place, the sodium or potassium salt of the compound is formed according as sodium or potassium cyanide is employed. In practically every case either the sodium or potassium salt or both are very soluble, giving at the completion of the reaction a solution of the alkali salt and the argenticyanide.

It might be thought that the determination of silver in the argenticyanide solution would offer considerable difficulties. If only a slight excess of the cyanide solution were used and some substance added which would combine with the silver given by the dissociation of the complex cyanide ion to form an insoluble compound yielding a still lower concentration of silver ion than is present from the argenticyanide, the complex would be destroyed with the formation of cyanide ion. As silver sulfide is the most insoluble of all the silver salts, a sulfide would therefore be the best suited for this purpose. The reaction is as follows:-

$$NaAg(CN)_2 + Na_2S = Ag_2S + 4NaCN$$

The free cyanide generated in the above reaction would dissolve an appreciable amount of the silver sulfide if no precautions were taken to prevent it. If, however, an excess of the sulfide solution is added the concentration of the silver ion coming from the silver sulfide would be so greatly depressed due to the common ion effect that this difficulty would be overcome.

In some cases the alkali salt formed in the first reaction might be hydrolized to an insoluble precipitate of the acidic compound, but if a small amount of an alkali is added, this action will be prevented. Only in the cases of very insoluble weakly acidic compounds would this difficulty be expected.

The Cyanide-Sulfide method is carried out as follows:-

About 0.3000 gm. of the sample is weighed out into a 400 ccm. beaker; two or three drops in excess over the theoretical of a 0.25 Nor. solution of sodium cyanide are added. The solution is then warmed to assist the solvent action of the cyanide. After the silver salt is dissolved the solution is diluted to 300 ccm. with distilled water. If a precipitate should appear at this point in the operations due to hydrolysis of the alkali salt, a few drops of a dilute alkali solution are added to dissolve it. About 25 ccm. of a 0.25 normal sodium sulfide solution in excess over the theoretical amount required for complete precipitation of the silver present, are added slowly with stirring. The solution is then heated and stirred until the silver sulfide precipitate has coagulated nicely. The silver sulfide is then filtered from the hot solution into a previously weighed Gooch crucible, washed completely free from soluble sulfide with distilled water, and finally washed, first with a little alcohol and then ether. The Gooch crucible is then transferred to an oven, dried one-half hour at 100°-110°C, cooled and weighed. It is then dried during 15 min. periods until the weight remains constant. More than two weighings are seldom necessary. The percentage of silver is calculated from the weight of the sample and the silver sulfide by the following formula.

$$\log_{10}\%Ag = 1.93982 + \log_{10}(\text{wt. of } Ag_2S) - \log_{10}(\text{wt. of sample}).$$

In comparison with the other methods of determining silver in organic compounds, the Cyanide-Sulfide method is an exceptionally speedy one; the entire determination from the time the weighing of the samples is started until the Gooch crucibles are placed in the oven seldom takes more than one hour and a half. Working with silver salts which are very soluble in the cyanide solution the author has made the determination within an hour's time.

It might be expected that silver sulfide would oxidize when heated in air at 110°. When washed with alcohol and ether, however, constant weight is maintained by the sulfide during several hours of heating.

The cyanide sulfide method is very easy of manipulation, greatly excelling the Carius method in this respect. Its accuracy leaves little to be desired. Working with a 0.3 gm. sample, 0.1 mg. of silver sulfide is equivalent to 0.03% of silver. If practical, larger samples can be used thus reducing the error coming from errors in weighing.

Another decided advantage of the author's method over those which depend upon decomposition of the compound lies in the fact that by the cyanide-sulfide treatment the compound, from which the silver salt is derived, is not destroyed but can easily be recovered by merely acidifying the filtrate from the silver sulfide. If the compound is an insoluble solid, it can then be separated by filtration. If it is soluble or a liquid, some means of extraction with solvents may be employed. The product recovered in the case of the insoluble pentabromophenol showed after only one crystallization a high degree of purity. When much time has been spent preparing a compound to be investigated in respect to its silver salts, this refinement of the method can well be appreciated.

There remains one more factor in the method to consider: that is its applicability. It is essentially on this factor that its success will depend.

There are a great variety of organic silver salts derived from acidic organic compounds. Wherever a hydrogen atom of sufficient acidity exists in an organic compound, there is a possibility of salt formation. The largest group of such compounds is, of course, the carboxylic acids. Sulphonic acids, acid amids, imids and phenols are other examples of groups of organic compounds from which silver salts are derived. The fact that a large percentage of these silver salts are difficultly soluble crystalline or amorphous bodies is what makes them such a very important class of compounds, for they can easily be investigated in the laboratory.

Silver salts have been, from the very beginning of organic chemistry, of great assistance in determining the basicity and molecular weight of organic compounds.

Coming back now to the application of the Cyanide-Sulfide method to the analysis of such a large variety of silver salts, there are apparently only two possible limiting factors. In the first place some silver salts may exist which are not soluble in the cyanide solution. This could only be expected in cases where the silver ion concentration from the salt when covered with cyanide is so low that the silver cyanide complex cannot form. A case of this kind was discovered with the silver salt of diazoaminobenzene which dissolved only slightly in the cyanide solution. As there are but a comparitively small number of such compounds, the applicability of the method is not seriously affected.

Another possible difficulty might arise in the case of silver salts, in which very easily reducible nitro groups are present in the molecule, thus making it possible for the dilute sulfide solution to reduce the nitro body to a difficultly soluble substance which might not form a sodium salt on account of its basic character, but would precipitate out and contaminate the silver sulfide. Due to the very slight reducing action of such a very dilute alkaline solution of the sulfide which is present and the probability that an insufficient number of amino groups would be formed to render the compound too basic for the formation of the sodium salt, little difficulty could be expected from this source.

The Cyanide-Sulfide Method

Experimental

The method was first tried out by analyzing some rather impure but homogeneous silver pentabromophenolate with the following results:

% Ag	Sample I	15.48
% Ag	Sample II	15.47

The fact that such good checks were obtained gave much encouragement so samples of pure silver salts were prepared and analyzed.

Analysis of Silver Oxalate

The theoretical amount of a dilute solution of C. P. silver nitrate was added slowly to a dilute solution of C. P. oxalic acid which was kept shaken. The white amorphous precipitate of silver oxalate was filtered and thoroughly washed with distilled water upon a Büchner funnel. The product was sucked as dry as possible upon the filter, separated carefully from the filter paper and allowed to dry for a day on a watch glass which was set in the desk and protected from dust. It was then powdered and dried over phosphorus pentoxide in vacuo for several days. As silver oxalate is easily decomposed in contact with sunlight, considerable care was exercised to avoid this difficulty. The product was very slightly darkened which was no doubt due to reduction.

Analysis

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_2O_4Ag_2$
No. I	0.2832	0.2311	71.04	71.03
No. II	0.3893	0.3178	71.09	71.03
No. III	0.2523	0.2065	71.12	71.03

The slight reduction of the silver oxalate may have caused the results to run high.

Analysis of Silver Benzoate

The silver benzoate was prepared by dissolving a few grams of benzoic acid, containing 0.1 - 0.2% of combined chlorine in a large volume of hot distilled water. The hot acid solution was then carefully neutralized with a dilute sodium hydroxide solution containing a small amount of halogen. A few drops of a very dilute solution of silver nitrate was added and the solution filtered free of the silver halide. A slight excess over the theoretical of a very dilute solution of C.P. silver nitrate was then added slowly with constant shaking. The large flocculent precipitate of silver benzoate which separated was dissolved in the solution by boiling and adding the necessary amount of distilled water. After the silver benzoate had dissolved, the solution was filtered. Upon cooling, the fine needles like cyrstals of silver benzoate which separated were recrystallized twice from boiling water, the final crystallization yielding a slightly darkened product. This was first dried in air and then over phosphorus pentoxide in vacuo. The product like silver oxalate had to be protected from the light.

Analysis

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_7H_5O_2Ag$
I	0.3187	0.1728	47.18	47.12
II	0.3263	0.1762	(47.01)*	47.12
III	0.4475	0.2429	47.23	47.12

*During the analysis of sample II a few specks of silver sulfide were lost.

The fact that the results show a high percentage of silver is probably due to the slight reduction of the silver benzoate.

Analysis of Silver Cinnamate

Pure recrystallized cinnamic acid m.p. 132.5 was carefully neutralized with dilute sodium hydroxide solution which contained a small amount of halide. This neutral solution was freed from soluble halide by adding a few drops of silver nitrate and filtering. From this point the operations were the same as in the preparation of silver oxalate.

The product was a snow white amorphous body.

Analysis

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_9H_7O_2Ag$.
I	0.2866	0.1390	42.22	42.32
II	0.2722	0.1321	42.25	42.32
III	0.2734	0.1327	42.26	42.32

Analysis of Silver Anisate

Pure anisic acid m.p. 185°C was employed in the preparation of the silver salt. The operations were the same as those employed in the preparation of silver benzoate. The product after five crystallizations still exhibited a slight pink color.

Analysis

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_8H_7O_3Ag$.
I	0.2438	0.1164	41.57	41.66
II	0.2400	0.1147	41.61	41.66
III	0.2314	0.1107	41.65	41.66

Analysis of the Pink Amorphous Silver Salt of Pentabromophenol[1]

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for C_6Br_5OAg.
I	0.3043	0.0627	17.94	18.11
II	0.3475	0.0716	17.94	18.11
III	0.4734	0.0975	17.93	18.11

Analysis of the White Amorphous Silver Salt of Pentabromophenol[2]

Preparation I

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for C_6Br_5OAg.
I	0.3918	0.0807	17.93	18.11
II	0.4131	0.0851	17.93	18.11
III	0.4701	0.0965	17.88	18.11

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[1] Thesis Part II, p 22

[2] Thesis Part II, p 23

Preparation II

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc.
I	0.2544	0.0523	17.91	18.11
II	0.2118	0.0439	18.06	18.11

Analysis of the Lemon Yellow Silver Ammonia Salt of Pentabromophenol.[1]

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_6Br_5OAg(NH_3)_2$
I	0.2907	0.0570	17.07	17.10
II	0.2715	0.0532	17.06	17.10
III	0.2470	0.0487	17.17	17.10

Analysis of the Pink Silver Salt of Pentabromophenol.[2]

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag Calc. for C_6Br_5OAg.
I	0.3457	0.0781	18.10	18.11
II	0.4492	0.0935	18.12[2]	18.11
III	0.2806	0.0584	18.12	18.11

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[1] Thesis, Part II, P. 27

[2] Thesis, Part II, P. 23

PART II

The Silver Salts of Pentabromophenol.

Introduction

In 1910 Torrey and Hunter[1], working in the Harvard laboratory, discovered upon allowing the red silver salt of 2-4-6 tribromophenol to stand over night on a filter paper that it had turned white. Upon analysis of the white product results were obtained indicating that it was isomeric with the red form. This change they thought might have been brought about by the action of the ammonia present in the laboratory. They then proceeded to prepare the red and white in a pure condition for analysis.

The red silver salt was prepared by precipitating it with silver nitrate from a solution of its sodium salt. The white salt was found to be best prepared by precipitating it with silver nitrate from a solution of its sodium salt to which ahd been added a few drops of ammonia, thus making use of the fact that ammonia affects the transformation from the pink to the white form. The analysis of the two salts so prepared proved their identical composition.

Two different forms of the same silver salts were discovered by the above investigators in the cases of 3-4-6 tribromoguaiacol and 2-4-6 tribromoresorcinol monomethyl ether, but only the white salts in each case could be obtained for analysis as the red forms changed too rapidly into the white. No other cases in which two forms of the same silver salt existed were discovered.

Torrey and Hunter attempted to discover a difference in the chemical behavior of the two forms of silver tribromophenolate but

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[1] J. Amer. Chem. Soc., 33,194-205.

failed to find any.

Hanzsch[1] working in the same field confirmed Torrey's and Hunter's results and added another case of the kind. He also investigated a number of the silver salts of halogenated phenols and prepared the following table which gives the color and forms of the silver salts which he prepared:

Silver Salts of:

Chlorophenols	Bromophenols	Iodophenols
o-m-p chlorophenol colorless	p bromophenol colorless	p iodophenol colorless
2-4 dichlorophenol colorless	2-6 dibromophenol colorless	2-6 diiodophenol colorless
2-6 dichlorocresol yellow	2-6 dibromo-p-cresol yellow colorless	2-6 diiodo-p-cresol colorless
tetrachlorophenol yellow	2-4-6 tribromophenol brick red colorless	**2-4-6 triiodophenol colorless
penta chlorophenol yellow	tetrabromophenol colorless	
	*pentabromophenol colorless	

** A yellow silver salt of 2-4-6 triiodophenol has been prepared by Woollett.[2]
*The author has prepared a pink silver salt of pentabromophenol.

Hanzsch made a number of generalizations which in view of the observations of later investigators are open to serious criticism.

Taking account of the fact that two cases have already been found which do not correspond with the table of Hanzsch, a systematic investigation of the silver salts of halogenated phenols should throw more light upon the existence of other isomeric forms. There is no

[1] Ber. 40, ~~4332~~ 4875 (1907)
[2] J. Amer. Chem. Soc. 38, 2474.

reason to suppose that the silver salt of tetrabromophenol, for instance, does not exist in isomeric forms as it differs from the silver salts of the tri- and pentabromophenols by one bromine atom.

Discussion of Results.

Two silver salts of pentabromophenol were described in the literature at the time this research was taken up. Bodroux[1] obtained a rose colored amorphous precipitate upon adding silver nitrate to a solution of the potassium salt. Hanzsch[2] obtained a reddish amorphous precipitate in the same manner as Bodroux but mentioned that the color was probably due to the impurity of his pentabromophenol, which after repeated crystallization retained a reddish color. Hanzsch also described a colorless amorphous form of silver pentabromophenolate which he obtained by precipitation with alcoholic silver nitrate from a solution of the ammonium salt in alcohol. Hanzsch himself pointed out that alcohol affects the transformation of the colored into the colorless form in the case of other isomeric silver salts but he evidently failed to realize the possibility of such an action in the case of the silver pentabromophenolate, which he describes as existing only in the colorless form.

Although two differently colored silver salts of pentabromophenol have been prepared, no one has shown them to be isomeric.

Previous to the authors investigation the silver salts of 2-4-6 tribromophenol described by Torrey and Hunter[3] and the silver

[1] Compt. rend., 126, 1282-1285 (1898).
[2] ~~Loc. cit.~~ Ber., 40, 4882,
[3] Loc. cit.

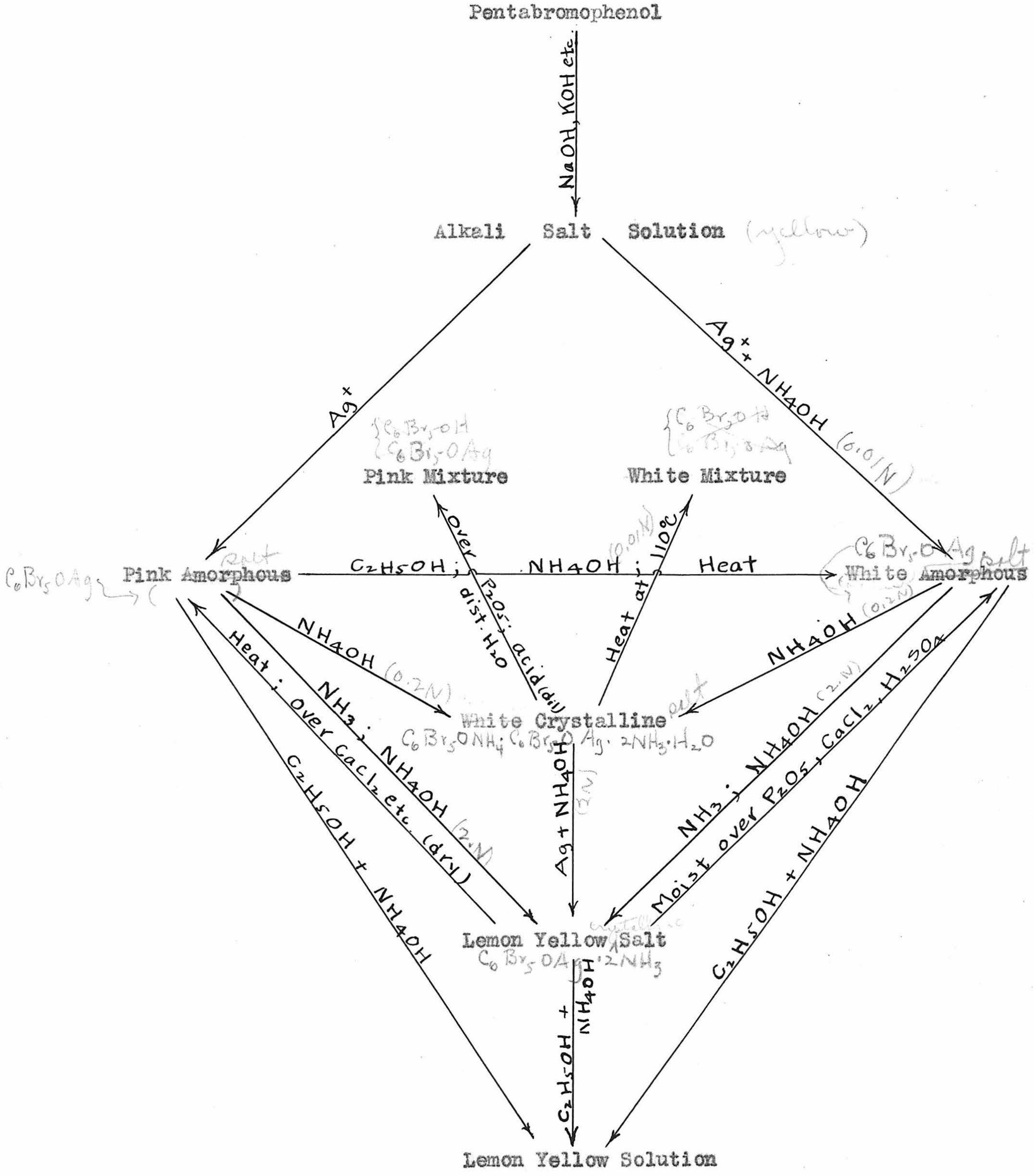
salts of 2-6 dibromo-p-cresol described by Hanzsch are the only cases of the kind mentioned in the literature where the salts have been shown to be isomeric by analysis.

A study of the conditions under which the colored and colorless forms of silver pentabromophenolate are formed has shown that the pink amorphous form, obtained by adding silver nitrate to an aqueous solution of an alkali phenolate, is readily transformed into the white amorphous salt in the presence of ammonia or alcohol and upon standing in a damp condition. The analysis of both salts has shown them to be isomeric.

As Hanzsch has stated that the color in the reddish silver salt of pentabromophenol may be due to an impurity and since the appearance of a paper by Furcht and Lieben[1], who describe a white and yellow levulinate of silver but ascribe the color in the yellow salt to an impurity, it is worth while to state the reasons for believing that the color in the case of the colored silver salt of pentabromophenol is not due to impurities. In the first place the pentabromophenol used in the preparation of the colored salt was of exceptional purity and perfectly colorless. Some of the colored and colorless amorphous silver salts were converted into pentabromophenol and from these products the colored salt was obtained just as in the case of the freshly prepared phenol. The analysis of colorless and pink salts agree with the theoretical percentages. Moreover the transformation of the pink into the colorless form takes place without the appearance of any colored by-products.

[1] Bull. Soc. Chem. (4) 5, 1069, (1909)

CHART


Pentabromophenol
NaOH, KOH etc.
Alkali Salt Solution (yellow)
Ag+
Ag+ + NH4OH (0.01N)
{C6Br5-OH
{C6Br5-OAg
Pink Mixture
{C6Br5OH
{C6Br5OAg
White Mixture
C6Br5OAg → (
Pink Amorphous
salt
C2H5OH ; NH4OH ; Heat
(0.01N)
C6Br5-OAg
White Amorphous
salt
(0.2N)
Over P2O5 ; acid (dil)
dist. H2O
Heat at 110°C
NH4OH (0.2N)
NH4OH
White Crystalline
salt
C6Br5ONH4 ; C6Br5OAg · 2NH3 · H2O
Heat ; over CaCl2 etc. (dry)
NH3 ; NH4OH (2N)
Ag + NH4OH
(2N)
NH3 ; NH4OH (2N)
Moist over P2O5, CaCl2, H2SO4
C2H5OH + NH4OH
C2H5OH + NH4OH
Lemon Yellow Salt
crystalline
C6Br5OAg · 2NH3
C2H5OH + NH4OH
Lemon Yellow Solution

The author has also prepared two crystalline silver salts of pentabromophenol which contain ammonia of addition. These two salts consist of a colorless and a lemon yellow crystalline form. They are best prepared by adding silver nitrate to an ammoniacal solution of an alkali salt of pentabromophenol; the precipitation of the different forms depend upon the concentration of the ammonia present.

The analysis of the lemon yellow salt has shown it to be an ammonia addition product with the molecular formula $C_6Br_5OAg.2NH_3$. Analysis shows the white crystalline salt as possessing the following formula: $C_6Br_5ONH_4$, $C6Br_5OAg.2NH_3.H_2O$.

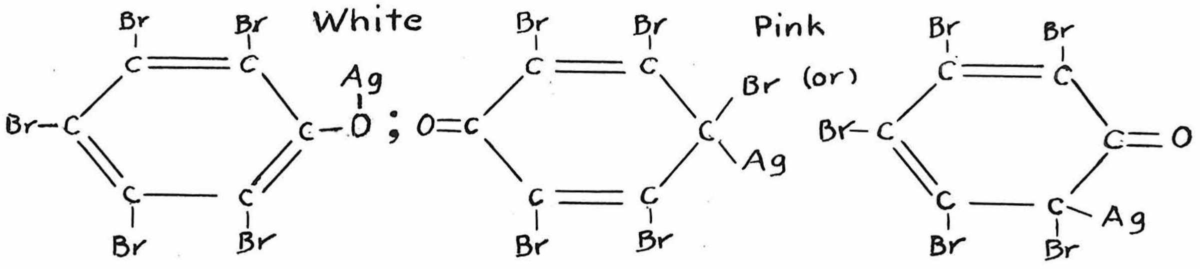
Two semi-crystalline products have been prepared from the above mentioned white crystalline salt. One of these products is white and is obtained by heating the dry white crystalline salt. The other product is pink and is obtained by drying the moist white crystalline salt over phosphorus pentoxide. These products may be definite compounds but every indication points to the conclusion that they are mixtures.

The accompanying chart shows in a concise way the numerous changes that the silver salts of pentabromophenol undergo. The details of these changes are discussed more fully in the experimental part.

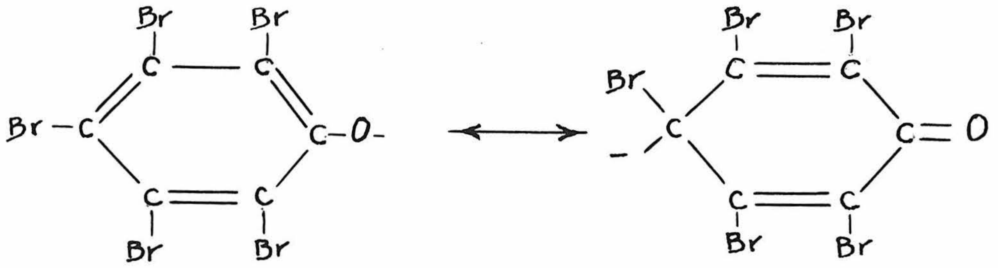
The investigation of the amorphous silver salts of pentabromophenol has thus far indicated no difference in their chemical behavior. These salts therefore are apparently analogous to the silver salts of tribromophenol described by Torrey and Hunter.

That the color in the case of the pink amorphous form of silver pentabromophenolate cannot be due to an impurity has already been shown. The only way to account for colored and colorless forms of the same silver salt seems therefore to consider them as differing in structure.

To consider the salts as exhibiting a quinoid-benzenoid isomerism is the most logical hypothesis to assume as it best accounts for the chemical and physical properties of the isomers. According to this hypothesis the salts would have the following formulas:



Solutions of the sodium, potassium and ammonium salts prepared by dissolving the purest pentabromophenol in the bases of these metals exhibit a decided yellow color. This color is undoubtly due to the presence of quinoid salts. There is probably a tantomeric equilibrium between the quinoid and benzenoid forms of the anion as follows:



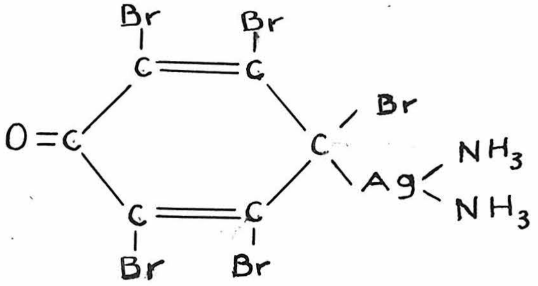
Upon addition of silver nitrate to the solutions of the alkali salts a mixture of the isomers is probably precipitated. Direct evidence to this effect is shown by the fact that the solid yellow silver ammonia salt when treated acetic acid changes to a much redder product than is obtained by direct precipitation.

In ascribing a structural formula to the lemon yellow silver ammonia salt the remarkable thing to consider is its color. Hanzsch[1] observed that the isomeric silver salts of tribromophenol absorb ammonia to form the same colorless ammonia addition product. Recently Bruni and Levi[2] have prepared a large number of ammonia addition products of the silver salts of organic acids. These are all described as colorless products.

The absorbtion of ammonia by the isomeric silver salts of pentabromophenol gives the same lemon yellow salt. The absorbtion of ammonia by the white amorphous salt is, however, very much slower than in the case of the pink form indicating that there must first be a rearrangement to the quinoid structure before the ammonia can add on readily.

It seems rather remarkable that the isomeric silver salts of pentabromophenol should give a lemon yellow ammonia addition product while the closely allied isomeric tribromo- derivatives give a colorless ammonia salt.

If considered as exhibiting a para quinoid structure, the lemon yellow silver ammonia salt would have the following formula:



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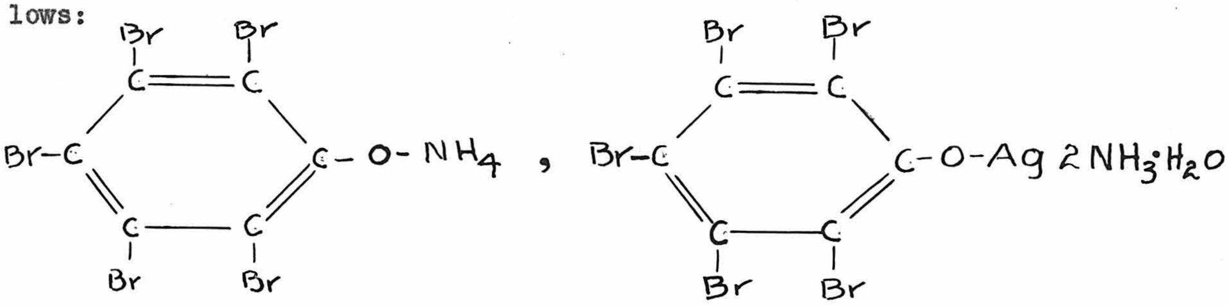
[1] Loc. cit.
[2] Gazz. Chem. ital 46, II 17-42, 235-46 (1916)

The lemon yellow color of the above salt and also the yellow color exhibited by solutions of the alkali salts may be cited as evidence supporting the para quinoid arrangement.

The analysis and properties of the white crystalline double silver-ammonium salt indicate that its structural formula is as follows:



The avove formulas are only proposed tentatively. Further investigations must be carried out before the question of structure of these salts can be satisfactorily settled.

From an investigation of other metallic salts of pentabromophenol it appears that isomerism is not limited to the silver salts. The salts of mercurous mercury and cadmium show strong evidence of existing in isomeric forms.

Summary.

Part I

1. A review of the methods used for the estimation of silver in organic compounds.
2. A new method for determining silver in organic silver salts based upon the precipitation of the silver as silver sulfide from cyanide solution of the salt and its estimation as such.

Part II

1. A short review of the previous work done on the silver salts of

halogenated phenols.

2. The preparation and properties of two isomeric and two ammonia addition silver salts of pentabromophenol.

3. A discussion of the possible structural formulae of silver salts of pentabromophenol.

4. Other metallic salts of pentabromophenol.

PART II

Experimental Part.

Preparation of Pentabromophenol.

The pentabromophenol was prepared according to the method of Bodroux[1] which consisted in treating phenol with bromine in the presence of anhydrous aluminum bromide. The product after bromination was treated with cold 95% ethyl alcohol to extract the aluminum bromide and the lower halogenated products. The residue which was mainly pentabromophenol was dissolved in boiling 95% ethyl alcohol, the solution boiled for about one half an hour with refined bone charcoal, filtered and allowed to cool, whereby, the pentabromophenol crystallized out in long needles. This final process of boiling with charcoal and crystallizing was repeated several times, yielding a perfectly snow-white product. One more crystallization of the snow-white product from pure 95% alcohol was found to be suffieient to give a preparation having a constant melting point. Separate batches gave (corrected) melting points as follows: 229°; 229.5°; 229.3; 229.4; 230; 229.5; 229°; 230°.

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[1] Compt. rend, 126, 1282-85 (1898).

Previous investigators[1] give 225° as the melting points of their preparations of pentabromophenol.

In taking the melting points the author used two high quality thermometers. One was nitrogen filled; range 20° to 400°C. The other was an Anchütz normal nitrogen filled; range 200° to 250°. Both thermometers were calibrated at 218.1°C with naphthalene vapor.

Preparation of the Pink Amorphous Silver Salt of Pentabromophenol.

As the sodium salt of pentabromophenol is the most soluble of the alkali salts, the silver salts were prepared from a solution of it made by dissolving the phenol in an equivalent quantity of normal sodium hydroxide which was practically free from chlorides. The solution thus prepared was yellow and alkaline to phenolphthalein.

The pink amorphous silver salt was prepared by adding a slight excess of 0.05 normal silver nitrate to a 0.01 normal solution of the sodium salt with frequent shaking. The precipitate after the addition of the silver nitrate was brown due to the presence of a considerable amount of silver oxide. To dissolve out the silver oxide and give a pure product 0.01 normal acetic acid was added carefully until the liquid showed a slight acid reaction with litmus. The precipitate which at this point appeared pink, was shaken up vigorously to coagulate it and filtered upon a Büchner funnel. After filtration the solid was separated carefully from the filter paper, shaken up with about 500 ccm. of distilled water and refiltered. After washing a few times on the filter, the precipitate was sucked as dry as possible, transferred

[1] Korner, annalen 137, 210
Bodroux, Compt. rend., 126, 1282-85 (1898)
Auwers, Ber 32, 3596.

carefully to a watch glass and allowed to dry in a clean desk for a day. It was then pulverized, spread out thin on a watch glass and dried over phosphorus pentoxide for several days in vacuo. The product was analyzed for silver by the cyanide-sulfide method.

Sample	Wt. of Sample	Wt. of Ag_2S.	Pink % Ag. Deter.	% Ag. Calc. for C_6Br_5OAg. from
I	0.3043	0.0627	17.94	18.11
II	0.3475	0.0716	17.94	18.11
III	0.4734	0.0975	17.93	18.11

Some of the pink salt was prepared by heating the lemon yellow ammonia addition product for several hours at 120°.

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter,	% Ag. Calc. for C_6Br_5 OAg. from
I	0.3457	0.0781	18.10	18.11
II	0.4492	0.0935	18.12	18.11
III	0.2806	0.0584	18.12	18.11

A comparison of the above analyses shows that the pink salt prepared by the latter method yields the purer product.

Preparation of the White Amorphous Silver Salt of Pentabromophenol.

This salt was prepared by adding a slight excess of 0.05 normal silver nitrate to a 0.01 normal solution of the sodium salt of pentabromophenol. In this case, however, the latter solution contained ammonium hydroxide of 0.01 normal which affected the transformation of the pink form into the white and at the same time prevented the formation of silver oxide. The product after washing and drying as in the case of the pink amorphous salt was very light creamy color. Two separate batches gave the following analyses for silver:

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. ~~for~~ from C_6Br_5OH.
I	0.3918	0.0807	17.93	18.11
II	0.4131	0.0851	17.93	18.11
III	0.4701	0.0965	17.88	18.11
IV	0.2544	0.0523	17.91	18.11
V	0.2118	0.0439	18.06	18.11

Samples I, II, and III, preparation I
Samples IV, and V, preparation II

Both the pink and white amorphous salts are difficultly soluble in water, alcohol, ether, ligroin, benzene, carbon tetrachloride, bromobenzene, etc. They both dissolve in alcohol to which has been added a little ammonium hydroxide, yielding a deep lemon yellow solution. Both salts seem to react identically with ethyl iodide and in the sunlight this action is analogous to the catalytic decomposition observed by Torrey and Hunter[1] in the case of silver tribromophenolate and later studied in detail by other investigators[2]. The color changes in the case of the silver pentabromophenolate were, however, different from those observed by Torrey and Hunter. When covered with ethyl iodide the silver pentabromophenolate first became green, then black and finally yellow; at no time was a color observed in the liquid. The products from this reaction have not been studied.

Preparation of the White Crystalline Silver-Ammonium Salt of Pentabromophenol.

Instead of making the solution of the sodium salt 0.01 normal in respect to ammonium hydroxide as in the preparation of the white amorphous salt, a much larger concentration up to 0.1 or 0.2 normal is used, a beautifully irridescent white crystalline precipitate separates. Under

[1] Loc cit.

[2] Hunter, Olson and Daniels, J. Am. Chem. Soc., 38, 1761-71; Woollett, J. Amer. Chem. Soc., 38, 2474.

the microscope the crystals appear as very thin plates which revolve rapidly upon their axes as they migrate through the solution. The crystals were filtered upon a Büchner funnel and washed with 0.2 normal ammonium hydroxide. That this salt in a moist condition is only stable in the presence of a certain vapor pressure of ammonia is shown from the fact that when washed with distilled water or dilute acids and when dried over phosphorus pentoxide in vacuo it turns pink. An analysis of the pink product in the latter case has shown that it contained no nitrogen. The aqueous tension may also influence the stability of the salt. One batch was dried in a des~~si~~iccator over sodium hydroxide and another in a dessicator over a mixture of anhydrous ~~acid~~ and hydrated sodium sulfate. In both cases a little ammonia was introduced in the dessicator. The dried products from both dessicators retained their color and crystalline structure and were apparently stable upon exposure to air. The analyses of the white crystalline salt for silver from the two des~~si~~iccators are:

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. ~~for~~ from $C_{12}H_{12}O_3N_3Br_{10}Ag$
I	0.5913	0.0637	9.38	9.35
II	0.5760	0.0621	9.39	9.35
III	0.7476	0.0796	9.27	9.35
IV	0.3474	0.0374	9.37	9.35
V	0.3203	0.0342	9.30	9.35

I, II, and III were dried over sodium sulfate
IV and V were dried over sodium hydroxide.

Two nitrogen and two bromine determinations were made on the white crystalline salt dried over sodium hydroxide.

Determination of Nitrogen by the Method of Kjedahl.

Sample	Wt. of Sample	ccm. of HCl (0.4942N) used	% N_2 Deter.	% N_2 Calc. for $C_{12}H_{12}O_3N_3Br_{10}Ag$.
I	1.065	5.32	3.46	3.64
II	1.319	6.90	3.62	3.64

These results indicate three atoms of nitrogen to one of silver.

Some of the white crystalline salt dried over sodium hydroxide was heated in the oven for several hours at 120° until it lost to constant weight with the following results:

Wt. of sample 0.6825 gm; loss in weight 0.0430 g. % loss 6.30; % loss calculated for loss of three molecules of ammonia and one of water from $C_{12}H_{12}O_3N_3Br_{10}Ag$ = 5.98%

Analysis of the White Crystalline for Bromine by the Method of Carius.[1]

Sample	Wt. of Sample	Wt. of Ag_2S	% Br. Deter.	% Br Calc ~~for~~ from $C_{12}H_{12}O_3N_3Br_{10}Ag$.
I	0.1720	0.1834	68.76	69.31
II	0.1970	0.2100	68.74	69.31

These results show ten atoms of bromine to one of silver.

Some of the pink product obtained by drying the white crystalline over phosphorus pentoxide was analyzed for silver.

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag Deter.	% Ag. Calc ~~for~~ from $C_{12}HO_2Br_{10}$ Ag.
I	0.3515	0.0401	9.93	9.95
II	0.2938	0.0335	9.93	9.95

These results indicate that three molecules of ammonia and one of water were lost from $C_{12}H_{12}O_3N_3Br_{10}Ag$.

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[1] The silver bromide taken from the tube which was mixed with broken glass was analyzed for silver by the cyanide-sulfide method.

When boiled with alcohol the white crystalline salt is broken up yielding a residue of the white amorphous silver salt and a filtrate containing pentabromophenol in solution; approximately equal quantities of the phenol and silver salt are obtained. The same action takes place when the white crystalline salt is warmed with dilute sodium hydroxide whereby the filtrate in this case is a solution of the sodium salt.

The ammonium salt prepared from the pure phenol exhibits a slight pink color. When heated in the oven at 110° it loses its ammonia and gives a snow-white residue of the pure phenol.

From the above data it appears that the white crystalline silver salt of pentabromophenol is a double salt with the formula $C_6Br_5ONH_4, C_6Br_5OAg\cdot 2NH_3\cdot H_2O$ and that upon loss of water and ammonia it breaks up according to the following reaction yielding either the white or the pink amorphous silver salt depending upon conditions:

$$C_6Br_5ONH_4, C_6Br_5OAg\cdot 2NH_3\cdot H_2O = C_6Br_5OH + C_6Br_5OAg + 3\ NH_3 + H_2O.$$

The loss of ammonia from the ammonium radical in the double salt when dried over phosphorus pentoxide may be due to a greater instability than is shown by the ammonium salt of pentabromophenol, itself which does not lose ammonia under these conditions.

Preparation of the Lemon Yellow Silver Ammonia Salt of Pentabromophenol.

A solution of the sodium salt was made about 2 normal in respect to ammonium hydroxide, an excess of silver nitrate over the amount necessary to precipitate the amorphous salts was added and the white crystalline salt which separated was dissolved by warming the solution. Upon cooling and standing several hours long, lemon yellow needle like crystals separated. The crystals were filtered upon a Büchner funnel, washed with 2 normal ammonium hydroxide and dried in a dessicator containing sodium hydroxide and an ammonium salt which generated ammonia. The crystals upon drying retained their color and crystalline structure. The dry salt loses its ammonia very slowly at ordinary temperatures but when heated in the oven at 100°-110° the ammonia is liberated rapidly and the pink salt is formed as was previously indicated. Like the other silver salts it dissolves in a mixture of ethyl alcohol and ammonia to give the characteristic lemon yellow solution. (See chart).

The lemon yellow salt was analyzed for silver by the cyanide sulfide method with the following results.

Sample	Wt. of Sample	Wt. of Ag_2S	% Ag. Deter.	% Ag. Calc. for $C_6Br_5OAg.2NH_3$
I	0.2907	0.0570	17.07	17.10
II	0.2715	0.0532	17.06	17.10
III	0.2470	0.0487	17.17	17.10

A sample of the lemon yellow salt was heated in the oven at 110° until it had lost ammonia to constant weight.

Wt. of sample 1.249 gm; wt lost 0.0684 gm.; % loss 5.46; % NH_3 Calc. in $C_6Br_5OAg.2NH_3$ 5.40.

Absorbtion of Ammonia by the Amorphous Silver Salts of Pentabromophenol.

As can be seen from the foregoing chart, both the pink and white amorphous silver salts of pentabromophenol absorb ammonia and form the same lemon yellow ammonia addition product.

Samples of the dry white and pink amorphous salts were weighed out upon watch glasses and placed in the same dessicator containing ammonia generated as previously described. The salts were taken out at intervals and weighed.

	% NH_3 in the pink salt	% NH_3 in the white salt
After 3 hrs.	4.96%	0.70
After 6-1/2 hrs.	4.96%	0.88
After 22 hrs.	4.96%	1.29
After 27-1/2 hrs.	4.96%	1.29

After the salts would no longer absorb ammonia at room temperature, the dessicator was placed in an ice chest beside the ice. After remaining for three hours the salts were again weighed but no change was found. The salts were then transferred to a dessicator containing a much higher partial pressure of ammonia and allowed to stand 36 hours at room temperature with the result that the percentage of ammonia in the pink salt increased from 4.96 to the theoretical percentage (5.40%) while that in the white increased from 1.29% to 5.01%. After standing four days in the same dessicator, the % of ammonia in the white increased to 5.09%.

The above data show that the absorbtion of ammonia by the white salt is very much slower than in the case of the pink. This could not be due to a difference in the physical state as the white salt was light and fluffy while the pink was very compact. The total absorbtion of ammonia by both salts seems to depend upon the partial pressure of the ammonia in the dessicator.

Other Salts of Pentabromophenol

Various salts were prepared by adding neutral solutions of metallic salts to a dilute solution of the sodium salt of pentabromophenol. The following is a list of the metallic ions which form difficultly soluble salts with pentabromophenol.

Colored Amorphous Salts		White Amorphous Salts	White Crystalline Salts
Ions	Color	Ions	Ions
Cu^{+}	light brown	Ba^{++}	K^{+}
[1]Cu^{++}	red	[3]Cd^{++}	NH_4^{+}
Co^{++}	light pink	Ca^{++}	Li^{+}
Fe^{+++}	brown	[4]Ni^{++}	Mg^{++}
Fe^{++}	yellow	Mn^{++}	
Pb^{++}	light yellow	Zn^{++}	
[2]Hg^{+}	orange	Th^{+}	
Hg^{++}	yellow		

[1] Dissolves in warm 6N ammonium hydroxide which upon cooling deposits dark brown needles.

[2] Changes to a perfectly colorless salt upon standing exposed to sunlight.

[3] Changes to a deep violet salt upon standing exposed to sunlight. The violet precipitate dissolves in warm 6N. ammonium hydroxide from which lemon yellow needles separate upon cooling.

[4] Dissolves in warm 6N ammonium hydroxide from which light green needles deposit upon cooling.

Either "Baker's Analyzed", or a high grade of Kalbaum's Chemicals was used throughout this investigation in preparing salts for analysis.