

THESIS.

The Silver Salts of Tetrabromphenol.

by

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Introduction.

Before 1910 only one silver salt of 2-4-6 tribromphenol had been prepared. This salt was prepared by Purgotti¹ in 1886. In 1910, Torrey and Hunter³ of Harvard University, succeeded in preparing two forms of the silver salt of tribromphenol, a pink and a white variety, which they proved by analysis to be isomers. The form of the silver salt prepared by Purgotti was described by him as an orange yellow precipitate. The salt prepared by Torrey and Hunter was a white amorphous salt. These men prepared the white salt from a slightly ammoniacal solution of the sodium salt. They failed to find any difference in the behavior of the two salts.

Two other cases in which two isomeric forms of the silver salts of the halogenated phenols occur have been named by Torrey and Hunter: namely, silver salts of tribromresorcinol monomethyl ether and of 3-4-6 tribromguaiacol. However, the red forms in both cases were very unstable and no analyses could be made of them.

Hantzsch² working along these lines, confirms the observations of Torrey and Hunter and also added some other results. The sum of these results gives as a total five halogenated phenols which were known to have existed in two isomeric forms of the silver salt, altho, as has been stated, it was not possible to prove this in every

case because of the unstability of the pink form. Three of these have already been mentioned but will be given again for simplicity.

1. 2-4-6 tribromphenol.
2. 2-4-6 tribromresorcinol monomethyl ether
3. 3-4-6 tribromguaiacol.
4. tetrabromguaiacol
5. dibromoparacresol.

Hantzsch also investigated many other halogenated silver salts and has prepared the following table, which has since been modified by later investigators.

Silver Salts of:

<u>Chlorphenols.</u>	<u>Bromphenols.</u>	<u>Iodophenols.</u>
o-m-p chlorophenol colorless	p bromphenol colorless	p iodophenols 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
tetrachlorphenol yellow	2-4-6 tribromphenol colorless pink	2-4-6 triiodo-phenol colorless (yellow) ^c
pentachlorphenol yellow	tetrabromphenol colorless (pink) ^a pentabromphenol colorless (pink) ^b	

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^a This salt has been prepared by the author.

^b This salt has been prepared by Kemp. Thesis, T.C.T. 1917

^c This salt has been prepared by Woollett. J.A.C.S. 38,2474

It has been shown by later investigators that this table is by no means complete. Kemp and Woollett have both added to it, and the author has prepared another salt of tetrabromphenol as indicated. In view of these facts, a systematic investigation of the silver salts of the halogenated phenols would be of value in determining the existence of other isomeric forms.

The silver salts of tetrabromphenol have been investigated by the author and the results are tabulated in the following pages.

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Discussion of Results.

Only one silver salt of tetrabromphenol was described in the literature at the time this research was taken up. Two forms of both tribromphenol³ and pentabromphenol² had been prepared. Torrey and Hunter showed these two forms in the case of tribromphenol to be isomers. Hantzsch describes two forms of the silver salt of 2-6 dibromo-p-cresol which were proven to be isomers. Hantzsch also describes two forms of the silver salt of pentabromphenol but one of these he thinks is the other form containing impurities. (pink) There was no apparent reason for believing so, however, since the pink salt retained its color after repeated recrystallization. It has since been shown by Kemp⁵ in his work upon pentabromphenol that the pink salt was an isomer of the white salt. Hantzsch himself pointed out that in the case of some of the other forms

of the isomeric silver salts that the transformation of one form into the other was accelerated by the presence of alcohol. He apparently failed to realize this possibility in the case of the higher phenols.

The author has prepared two forms of the silver salt of tetrabromphenol and an ammonia addition product in which there are two molecules of ammonia for every atom of silver present. One of these silver salts is colorless. The other comes down as an orange yellow precipitate but turns pink on drying. These two forms have been shown to be isomers by analysis. The results of these analyses are given in the following pages.

By means of a few simple experiments and a study of the conditions under which the colored and the colorless forms of the silver tetrabromphenolates are formed has shown that the pink form is the unstable form and the white the stable form. The pink salt, was prepared from a neutral solution of the alkali salt by the addition of silver nitrate, is readily transformed into the white form by the addition of a few drops of dilute ammonia to the freshly prepared wet salt. The analysis of the two forms thus prepared has shown them to be isomers, just as in the case where the white salt was prepared by the direct addition of the nitrate to the slightly ammon-

iacal solution of the alkali salt of tetrabromphenol.

In as much as some authors ⁶ have stated that the colored forms of some of these silver salts were probably due to impurities, it is worth while to state some reasons for believing that this is not true in the case of the silver tetrabromphenolates. In the first place, since two isomeric forms of the silver salt have been prepared in the cases of tribromphenol and pentabromphenol, it follows from a consideration of the corresponding properties of the phenols that there would be two forms of this kind in the case of tetrabromphenol silver salts. The tetrabromphenol used in this work was of a very high grade of purity (99.98%-99.80% pure), as shown by analysis. It crystallized from alcohol in long silky white needles, absolutely free from color of any kind. The analyses of both the colored and the colorless forms agree with the theoretical percentages. Moreover, the transformation of the colored form into the colorless form takes place without the liberation of any colored by-products.

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Experimental.

Preparation of Tetrabromphenol.

The method of preparation of this acid from tribromphenol and bromine, by heating at 170° - 180° for several hours in a combustion furnace, as outlined by Korner⁷, is not at all satisfactory since it requires a great deal of careful attention, very pure products to start with, etc., and also the possible nuisance of the combustion tube breaking and discharging its contents.

Werner⁸ prepared tetrabromphenol by first making the body tetrabromcyclohexadienone by the addition of the necessary amount of bromine in a saturated aqueous solution to a solution of phenol in water. The resulting yellow body is carefully dried and heated for some time with concentrated sulphuric acid at the melting point of the body, 118° C. The product is poured into water and the tetrabromphenol separated and purified. The author failed to obtain any satisfactory results with this method.

Orton and Coates⁹ prepared tetrabromphenol in one of their experiments by decomposing tetrabromodiazobenzene and obtained a tetrabromphenol which melted at 115° C. This method is a 'round-a-bout' method of obtaining the tetrabromphenol since it requires the preparation of the diazo body to start with, and would probably never be

used where it is desired to prepare tetrabromphenol in a large quantity as it was in this research.

The author prepared tetrabromphenol by the direct bromination of tribromphenol in the presence of anhydrous aluminum bromide, by a method similar to that of Bodroux¹⁰ for the preparation of pentabromphenol. The tribromphenol was carefully dried and fused in a side-necked flask over a water bath. Bromine (liquid) containing 2% of Al in the form of anhydrous aluminum bromide, was run into the fused mass, over a period of 8 hours, in order to insure complete bromination. When the theoretical amount of bromine had been added and just before the product in the flask solidified 25% excess bromine was run in at once and the mixture shaken and cooled. The reaction between the bromine and the tribromphenol continues after the product has cooled just as well as in the fused material, but it is necessary to fuse the tribromphenol in the beginning in order to have thorough mixing of the phenol and the Bromine. The product in the flask, which consisted mainly of tetrabromphenol with small amounts of tri- and penta-bromphenols and bromine and aluminum bromide, was separated from the flask by cracking the flask away from it, after the product had been allowed to cool and stand for several hours. Results of one bromination are as follows:

Tribromphenol taken.....	108 gms.
Bromine used.....	66 "
Aluminum used.....	1.5 "
Theoretical Yield.....	134 "
(crude incl. Al)	
Actual Yield.....	136 "
Yield pure product (m.p. 114°).....	56.5 "

The HBr given off was absorbed in water and titrated with NaOH to determine the completeness of the bromination. From the results of the titration the bromination was shown to be 95% complete.

1/5 of sample titrated.

NaOH used.....	62.0 c.c.
Sample contains-HBr.....	25.1 gms.
Theoretical.....	26.4 "
Bromination.....	95%

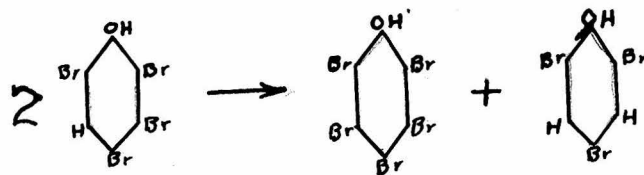
The additional weight of the crude tetrabromphenol was bromine held in suspension in the solid material.

The product from the flask was leached with cold alcohol (95%) and later heated until all soluble matter was in solution. The solution was then boiled with charcoal (animal) refined, until on filtering, the resulting solution was colorless. The alcohol was then diluted to 80% and the pentabromphenol allowed to crystallize out. This was a very small amount. The solution was then diluted to 66% and the tetrabromphenol allowed to crystall-

ize out. This carried a small amount of tribromphenol with it as an impurity. Several recrystallizations resulted in the production of long silky white needles of tetrabromphenol which were later analyzed to determine their purity. The tetrabromphenol thus separated was found to be 99.98%-99.80% pure. m.p. 114° C. Yield 56.5 gms.

On another batch of the crude tetrabromphenol thus prepared, a series of experiments were made in an attempt to purify the crude product in a much simpler manner, since the purification by fractional recrystallization from alcohol is very difficult. It was thought that this might be possible by dissolving the product in sodium hydroxide, filtering off any impurities in the form of insoluble matter and precipitating again by the addition of an acid. By virtue of the differences in solubilities of the three bromphenols a separation was expected. It was found however, that no separation was effected, and a product was obtained which invariably melted at 78° - 85° , far below the melting points of the three bromphenols, 93° , 120° , 229.5° resp. Very little work was done upon the product thus obtained other than an attempt to separate it by means of fractional crystallization from alcohol. The product once obtained however, would not separate appreciably from alcohol in this manner, but gave the same product after repeated recrystallization. It was thought that the NaOH

might be acting as a catalyset in the presence of small amounts of tri- and penta- bromphenols causing the reaction



to take place. There was very little to confirm this theory however since pure tetrabromphenol was separated from a solution of the sodium salt which had stood for some time, and which was prepared by dissolving the free acid in NaOH, by the addition of dilute HAc. Apparently no reaction of the type just mentioned had taken place.

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Preparation and Analysis of the Two Silver Tetrabromphenolates.

Preparation of The Anhydrous Pink Salt.

As the sodium salt of the acid tetrabromphenol is the most soluble of the alkali salts, the silver salt was prepared from a solution of this salt.

3 gms. of pure, dry tetrabromphenol (m.p. 114°C.) was treated with enough 1 N. NaOH to dissolve and the solution diluted to 150 c.c. Dilute (.05 N) HAc was then added until the solution was neutral. This condition was noticeable by a slight cloudiness of the solution due to the separation of the free acid caused by the addition of a slight excess of HAc. The solution was diluted to 300 c.c.

and one or two drops of silver nitrate added to free the solution of any chlorides or bromides which might be present. The solution was then filtered thru a very high grade of filter paper until the resulting solution was clear. This solution was diluted to four times its original volume and enough .05 N. silver nitrate added to completely precipitate the tetrabromphenol present as the silver salt. This precipitate was orange yellow. Dilute HAc was then added until the solution was slightly acid. This was to prevent the separation of any silver oxide in the precipitate. The yellow precipitate was very gelatinous. It was filtered on a Buchner funnel and removed to a 500 c.c. flask, HAc added and shaken to free from any silver oxide which might have been formed in the filtration. It was filtered again and removed to the flask. This time it was agitated with pure water and filtered. The precipitate was sucked as dry as possible on the funnel, removed to a clean porous plate and placed in a clean desk to dry. It was removed some time later, having turned pink in the process of drying, and thoroughly pulverized and given a final drying over phosphorous pentoxide, for several days. Analyses were made on it for silver, by the method of Kemp and Lucas¹¹. Results of these analyses are given as follows:

No.	Wt. Sample.	Wt. Ag ₂ S.	%Ag deter.	%Ag calc from C ₆ HBr ₄ OAg
I.	0.2991 gm.	0.0720 g.	20.90	20.89
II.	0.4060 "	0.0976 "	20.94	20.89
III.	0.3141 "	0.0756 "	20.96	20.89
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Preparation of the White Amorphous Salt.

As in the preparation of the pink salt, this salt was prepared from a solution of the sodium salt.

3 gms. of the pure, dry salt (m.p. 114°) was dissolved in the requisite amount of 1 N. NaOH and the solution diluted to 150 c.c. Dilute HAc was then added until the solution was neutral. One or two drops of silver nitrate were then added to free the solution from any chlorides or bromides which might be present and the solution diluted to 300 c.c. and filtered thru a high grade of filter paper until the solution coming thru was absolutely clear. This solution was made slightly ammoniacal with dilute ammonium hydroxide and diluted to four times its original volume. Enough .05 N. silver nitrate was then added to completely precipitate the tetrabromphenol present as the silver salt. This salt came down snow white. (It might be slightly brown due to the separation of a small amount of silver oxide. If this should happen, HAc should be added until the color is destroyed). HAc was added anyhow as a preventative toward any separation of the kind indicated, until the solution

was faintly acid. The white amorphous silver salt prepared in this manner was filtered on a Buchner funnel and transferred to a 500 c.c. flask. The salt was thoroughly agitated with dilute HAc and refiltered. It was again removed to the flask and shaken up with water. Finally the precipitate was sucked as dry as possible on the funnel and transferred to a clean porous plate in a clean desk to dry. Later the salt was removed, thoroughly pulverized and given a final drying over phosphorous pentoxide for several days. Analyses were made upon it for silver as before. The results of these analyses are as follows:

No.	Wt. Sample.	Wt. Ag ₂ S.	%Ag.Deter.	%Ag. Calc from C ₆ HBr ₄ OK ₄
I.	0.3147 gm.	0.0758 gm	20.97	20.89
II.	0.4998 "	0.1205 "	20.99	20.89
III.	0.3593 "	0.0858 "	20.80	20.89

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Preparation and Analysis of the Yellow Ammonia Addition Product.

The ammonia addition salt was prepared by treating the still moist silver salt (either color) with ^{just} enough conc. ammonium hydroxide to dissolve it. An excess prevents the precipitation of the ammonia salt. Very soon after the solution of the silver salt, the ammonia addition salt precipitates from the solution as a cream yellow amorphous salt.

About 5 gms. of the freshly prepared pink silver salt were treated in the manner outlined above. The ammonia addition product which separated was filtered on a Buchner funnel and placed in a dessicator in an atmosphere of ammonia over solid sodium hydroxide to dry. After several days the salt was removed and analyzed for ammonia by the Kjeldahl method. The results of this set of analyses is given as follows:

No.	Wt. Sample.	c.c. HCl used 0.0252 N.	%NH ₃ deter.	% calc from C ₆ HBr ₄ OAg(NH ₃) ₂
I.	0.8610	60.21	6.21	6.1719
II.	0.8015	56.10	6.23	6.1719

Previous to the analyses a portion of ammonia salt was weighed out onto a watch glass and dried in an electric oven for 1 hr. The salt lost weight corresponding to 2(NH₃)

Wt. Salt taken.....	0.8473 gms.
Wt. After Heating.....	0.7947 "
Loss Ammonia.....	0.0526 "
% Ammonia Lost.....	6.21%

Samples of the dried white and pink silver salts were placed in an atmosphere of strong ammonia for several hrs. to see if they would absorb ammonia. They would not absorb ammonia as was noted by weighing them occasionally. The salts were dampened and the process repeated with the same results. Concentrated ammonium hydroxide failed to have any effect on the dry salts. Before drying the salts

they are very readily acted upon, but after drying the converse is true. The ammonia salt on being heated gives rise to the white silver salt.

	Wt.
Sample Taken.....	0.3578 gms.
After 1 hr.....	0.3581 "
After 4 hrs.....	0.3585 "
After 12 ".....	0.3584 "
After 24 ".....	0.3585 "

This is data from the pink salt which should be the most active since it is the unstable form. The small addition to the weight is due to entrained ammonia in the salt.

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Other Salts of Tetrabromphenol.

Other metallic salts were prepared from neutral solutions of the sodium salt with the following results. Some of these salts so prepared act as tho there are isomeric forms of other metallic^{salts} than silver.

	<u>Colored Amorphous Salts.</u>	<u>White Amorphous Salts</u>	<u>White Crystalline Salts.</u>
a	Co ⁺⁺ light pink	Pb ⁺⁺	K ⁺
b	Cu ⁺⁺ chocolate brown	d Cd ⁺⁺	NH ₄ ⁺
	Hg ⁺⁺ light yellow	Zn ⁺⁺	Mg ⁺⁺
	Ni ⁺⁺ light green	Sb ⁺⁺	Sr ⁺⁺
	Fe ⁺⁺⁺ cream yellow	Sn ⁺⁺	Ca ⁺⁺
	Fe ⁺⁺ dark yellow	As ⁺⁺⁺	Ba ⁺⁺
	Hg ⁺ light yellow	Bi ⁺⁺⁺	Li ⁺⁺
	Mn ⁺⁺ light pink	Sn ⁺⁺⁺⁺	
c	Cu ⁺ light brown		

With ammonium hydroxide some of these salts undergo changes as follows:

Cu^{++} - Precipitate turns very light blue and finally with more NH_4OH dissolves giving complex copper-ammonium^a salt solution.

Hg^+ - Completely dissolves and slightly decomposes giving a small amount of metallic mercury.

Fe^{++} - Precipitate turns red, (Prob. due to some $\text{Fe}(\text{OH})_3$)

Fe^{+++} - Turns dark green and then upon standing turns dark brown.

Hg^{++} - Turns creamy white.

Bi^{+++} - Changes to amorphous orange yellow salt.

Mn^{++} - Changes to creamy brown precipitate.

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^a Light pink crystals.

^b Turns blue on standing.

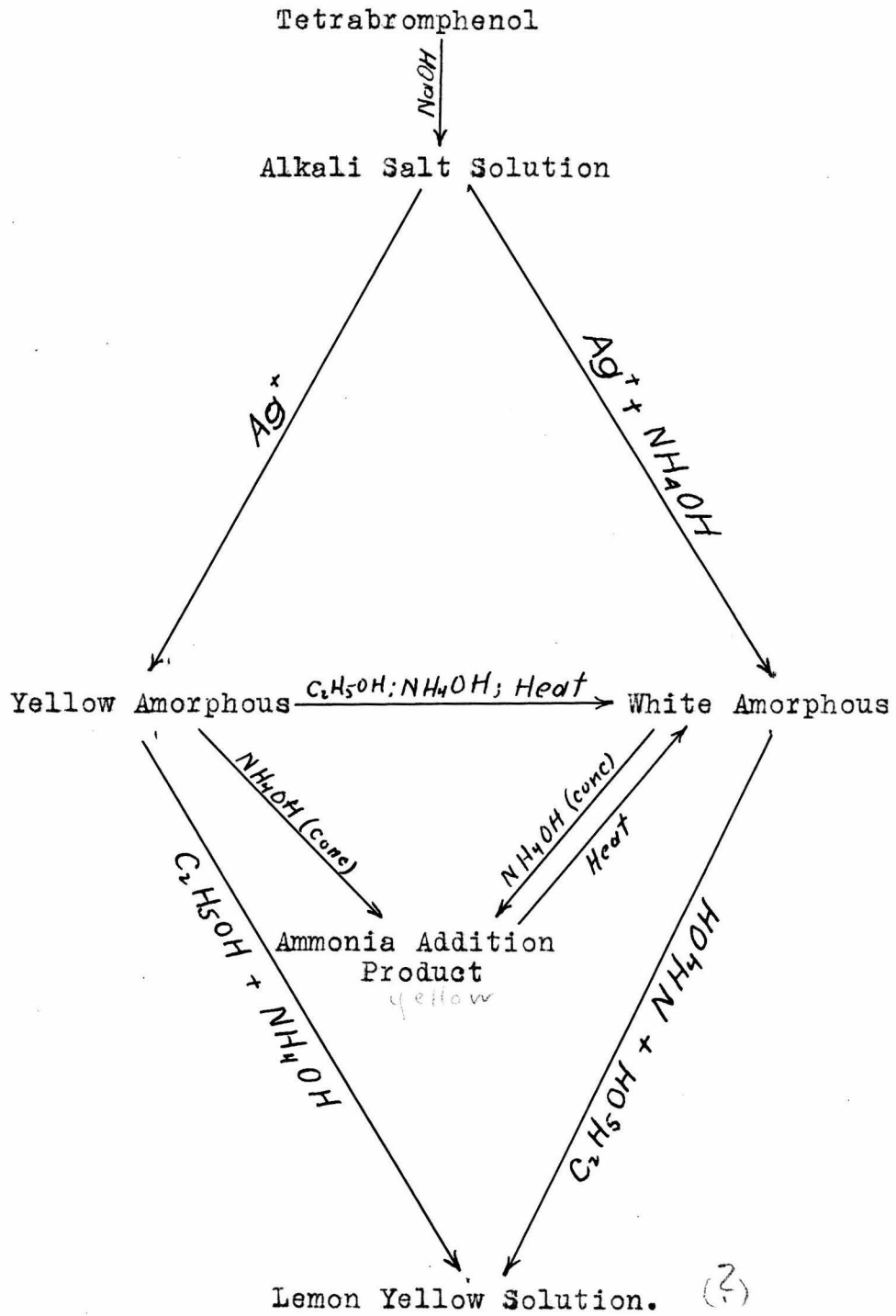
^c Turns orange on standing.

^d Precipitates light blue crystals on being exposed to sunlight for a long time.

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Either Baker's "Analyzed" or a high grade of Kahlbaums chemicals were used throughout this thesis.

CHART



Reference Sheet.

1. Gazz. Chim. Ital. 16, 527 (1886)
2. Ber. 40, 4332 (1907)
3. Torrey and Hunter, Jour, Am. Chem. Soc. 33,194-205.
4. Hantzsch, Same as 2.
5. Kemp, Thesis, Throop College of Technology. 1917.
6. Hantzsch, No. 2. Also Furcht and Lieben, Bull.Soc. Chem.
(4) 5,1069, (1909)
7. Körner, Annalen, 137,209.
8. Jour. der russ. Chem. Gesell. 18, 105.
9. Jour. ^{Chem.} Lond. Soc. 91,51.
10. Comp. Rend. 126, 1282-85(1898)
11. Jour. Am. Chem. Soc. 39-9-2074.