

the disodium salt separating in the cold. Recrystallized from 50% alcohol it forms almost black aggregates of microscopic hairs with a greenish reflex and dissolving in water with a deep red color.

Analyses. Calc. for $C_{13}H_{14}O_6N_3AsNa_2 \cdot 8.5H_2O$: H_2O , 23.84. Found: 23.64.

Calc. for $C_{13}H_{14}O_6N_3AsNa_2$: N, 8.59; As, 15.33. Found: N, 8.56; As, 15.81.

The free acid, when liberated in much 50% alcohol slowly separates as red-brown microcrystalline aggregates which do not melt below 285°.

Analyses. Calc. for $C_{13}H_{16}O_6N_3As \cdot H_2O$: H_2O , 3.89. Found: 3.96.

Calc. for $C_{13}H_{16}O_6N_3As$: N, 9.44. Found: 9.49.

2 - Hydroxy - 5 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid.—Neutral A \rightarrow alkaline *o*-hydroxy-phenoxyacetic acid solution. The neutralized solution was concentrated to small bulk *in vacuo*, and the dye precipitated by adding strong sodium hydroxide solution. Dissolved in hot 50% alcohol and treated with an excess of acetic acid, the monosodium salt separated as yellow, indefinitely crystalline, microscopic globules.

Analyses. Calc. for $C_{14}H_{12}O_7N_2AsNa$: N, 6.70; As, 17.93. Found: N, 6.42; As, 18.33.

The free arsonic acid separated from a solution in dil. sodium hydroxide as an emulsion which soon crystallized. Dissolved in boiling 85% alcohol, and the filtrate diluted with water, the acid separated as brown, microscopic platelets which do not melt below 280°. It dissolves in boiling alcohol, and gives a bright orange solution in dil. sodium hydroxide. The color in conc. sulfuric acid is a deep red-orange.

Analyses. Calc. for $C_{14}H_{13}O_7N_2As \cdot 0.5H_2O$: H_2O , 2.2. Found: 2.4.

Calc. for $C_{14}H_{13}O_7N_2As$: N, 7.07; As, 18.92. Found: N, 6.99; As, 18.61.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY. No. 7.]

CHROMO-ISOMERIC SILVER SALTS OF PENTABROMOPHENOL AND A THEORY OF CHROMO-ISOMERISM OF SOLID COMPOUNDS.

BY HOWARD J. LUCAS AND ARCHIE R. KEMP.

Received March 4, 1921.

1. Previous Investigations.

Two silver salts of pentabromophenol have been described. Bodroux¹ obtained a rose-colored amorphous precipitate upon adding silver nitrate to a solution of the potassium salt. Hantzsch and Scholtze² also obtained a reddish amorphous precipitate in the same manner, ascribing the color to an impurity present in the pentabromophenol; but they also described a colorless, amorphous form, which precipitates when alcoholic silver nitrate is added to an alcoholic solution of the ammonium salt, and they apparently regard it as a purer lot of the same salt, which they describe as colorless, and existing in only one form. Isomeric silver salts of other

¹ Bodroux, *Compt. rend.*, **126**, 1282-85 (1898).

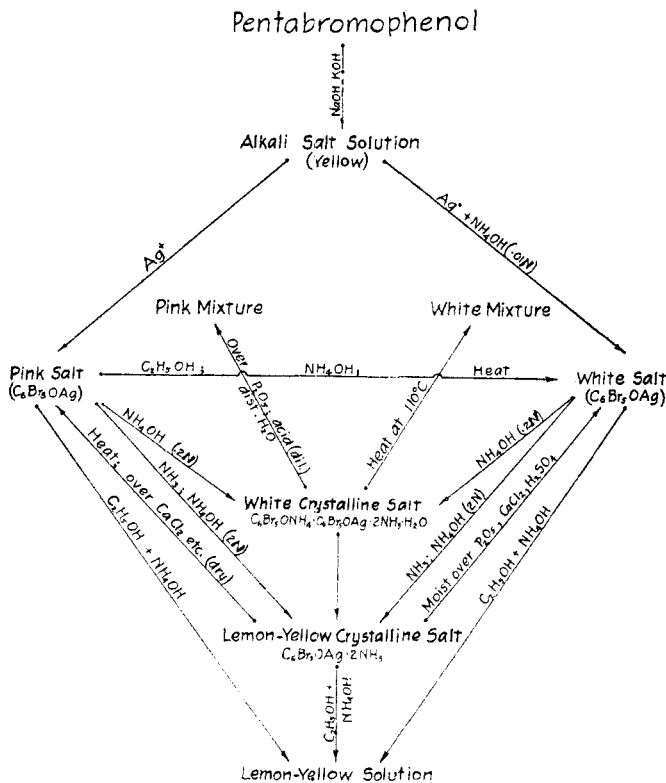
² Hantzsch and Scholtze, *Ber.*, **40**, 4882 (1907).

phenols are described by Hantzsch and Scholtze,² by Torrey and Hunter,³ and by Hunter and Joyce.⁴

2. Outline of This Investigation.

In the work described in this article, in order to eliminate the possibility of the color being due to impurities, the pentabromophenol was carefully purified by repeated crystallizations from alcohol and by boiling with animal charcoal until a colorless product was obtained and the melting point of successive crops did not change.

The determination of silver in the various salts was carried out by the cyanide-sulfide method as described by Lucas and Kemp.⁵ The accuracy of this method was demonstrated in the case of the salt of the formula C_6Br_5OAg , which is stable and can be obtained in a high degree of purity. This salt was prepared by heating the yellow crystalline ammoniate of the formula $C_6Br_5OAg \cdot 2NH_3$. The formula C_6Br_5OAg requires 18.11% of silver. Three analyses gave 18.10%, 18.12%, and 18.12%—results which show that the method is highly accurate.



³ Torrey and Hunter, THIS JOURNAL, 33, 194-205 (1911); Ber., 40, 4332 (1907).

⁴ Hunter and Joyce, THIS JOURNAL, 39, 2640 (1917).

⁵ Lucas and Kemp, *ibid.*, 39, 2074 (1917).

When pentabromophenol is treated with a solution of sodium hydroxide it dissolves, and the solution has a yellow color. The color is intensified on heating, but fades again on cooling. Diluting the solution causes a gradual fading out of the color. The sodium salt of pentabromophenol crystallizes from this yellow aqueous solution in colorless featherlike needles. The color of the solution is not due to impurities; for it persists after repeated crystallizations of the white pentabromophenol.

The pink silver salt separates when silver nitrate solution is added to the sodium pentabromophenolate solution; but, if the silver nitrate is 0.01 *N* in ammonium hydroxide, the colorless form precipitates. The concentration of ammonia must not be much greater, because at about 0.2 *N* another salt, consisting of an ammoniate, separates—a colorless shimmering crystalline compound, which has a satiny appearance as it moves through the liquid. If the concentration of ammonia is still greater, another ammoniate which can be obtained in well-defined yellow needles, separates after standing.

The accompanying chart shows the relationships between the phenol, the colored and colorless silver salts, and the two ammoniates.

3. Discussion of the Color Relations and a New Theory of Chromoisomerism.

It seems unreasonable to ascribe the color of the solution of the sodium salt to tautomerism of the benzoid-quinoid type, because it must then be assumed that sodium is linked to carbon. Compounds in which sodium is known to be joined to carbon are decomposed by water with formation of sodium hydroxide. Thus the carbides of sodium and potassium⁶ react vigorously with water, and so does sodium phenyl,⁷ forming sodium hydroxide and benzene. The fact that the colorless salt gives rise to a colored solution must therefore be ascribed either to some other structural change or electronic condition. Now, since in solution the sodium salt is largely ionized, it is clear that the difference in color must be due to some difference in the powers of absorbing light possessed by the ion and by the un-ionized molecule. According to present views, however, the absorption of light is caused by the vibration of electrons, and this must increase with the looseness with which the electrons are bound and with the corresponding tendency of the compound to undergo structural changes or shifting of the valence bonds. Now the production of the anion is accompanied by the formation of a powerful negative electrostatic field, which decreases the effective attraction of the carbon atoms for the electrons; and the latter, being under less restraint, vibrate in

⁶ Matignon, *Compt. rend.*, **125**, 1033-5 (1897).

⁷ Acree, *Am. Chem. J.*, **29**, 590 (1903).

longer periods. The ion absorbs in the visible violet, and the solution is yellow. This greater vibration may well correspond to an oscillation of the double and single valences between the carbon atoms of the benzene ring. It is known in general that the introduction of halogen into the benzene nucleus causes a shifting of the absorption bands towards the red,⁸ and that the addition of a strong base to solutions of phenols also causes a shifting of the absorption bands towards the red.⁹

When an ionized substance passes from solution into the solid state, either of two conditions may result, according to the theory of chromo-isomerism here presented.

(1) As has been shown by the recent X-ray work on the structure of crystals, the atoms or atom-groups that form the ions in solution, such as the sodium and chlorine atoms in sodium chloride, maintain in most crystalline substances their separate identities and probably still carry the same charges that they do in aqueous solution. It is evident, however, that the powerful electrostatic fields which accompany the atoms in the ionized condition will be weaker in the crystalline state; for, instead of existing in the solution more or less independently of other ions, each atom is now surrounded by atoms carrying charges of opposite sign. The intensity of vibration of the electrons will therefore be less and the frequency of vibration shorter, so that the absorption will be displaced toward the violet end of the spectrum, and the crystalline substance may become of a paler red or yellow color than that of its ions in solution, or it may even become colorless.

(2) The compound which first crystallizes from solution may be an unstable form, changing to a more stable form under favorable conditions. Whenever such a transition takes place energy is lost from the system. This means that the rearrangement is due to the tendency of the atoms and atom-groups to assume the position in which the electrostatic fields about them are most completely neutralized. Either the ions may still retain their identities in the more stable packing, or they may become chemically united, in other words as intimately associated as the atoms within the atom-group that constituted the ion in solution. Whatever the actual condition, the weakening of the electrostatic fields strengthens the attraction between atoms and electrons, and the latter now vibrate in still shorter periods, so that absorption of light is displaced farther towards the violet. A solid substance which was still colored in the unstable form, will become less highly colored or even colorless in the stable form; in other words, a change in the electrostatic environment of the absorbing atoms or atom groups brings about

⁸ Baly, *J. Chem. Soc.*, **99**, 856 (1911); Purvis, *ibid.*, **99**, 825 (1911); **107**, 966 (1915).

⁹ Ewbank, *ibid.*, **87**, 1347 (1905); Baly, Tuck and Marsden, *ibid.*, **97**, 582 (1910); Wright, *ibid.*, **100**, 676 (1900).

a corresponding change in the wave length of the light absorbed, and the wave length is longest when the electrostatic fields are the strongest.

The fact that the solid sodium salt of pentabromophenol is colorless while its anion is yellow may be attributed to either of these conditions. But the existence of two solid silver salts, one of which is pink and the other white, requires for its explanation both assumptions. The facts in regard to these silver salts and their bearing upon this explanation may therefore be more fully considered. They may be briefly summarized as follows.

The analyses of the salts show that they have the same percentage composition. The pink salt is the more reactive. Thus, when the freshly precipitated moist salts are covered with about 20 cc. of alcohol-free ether and 5 cc. of ethyl iodide is added, both give the same product, pentabromophenyl ethyl ether, but the reaction takes place more rapidly with the pink salt. Its color fades slowly, and it is largely changed to silver iodide within one-half hour; whereas the white salt under the same conditions is not completely converted during a much longer time. When put in an atmosphere containing ammonia both salts finally give the same ammonia addition product, but the rate of ammonia absorption by the pink form is more rapid.

All these facts are simply accounted for by the hypothesis that the pink salt is the unstable, more reactive form, and that the white salt is the stable, less reactive form.

That the pink salt is unstable is shown by the ease with which transformation to the colorless form takes place. When the pink form is brought into solution, even to a very slight extent, as may be done by heating it in contact with water or by the addition of a small amount of alcohol or ammonia, the white form results. Thus the color of the pink salt may be ascribed to the same factor as that which gives the color to the solution of the sodium salt, namely, to a strong electrostatic field about the pentabromophenolate ion; while in the white salt the ions have taken up the positions in which their electrostatic fields are most completely neutralized. Thus also the pink salt results when precipitation takes place so rapidly that there is not time for the ions to arrange themselves in the final, more intimate, association characteristic of the more stable white salt.

The color of the yellow ammoniate of silver pentabromophenolate can be readily accounted for on the basis of this theory, since the electrostatic environment is modified by the association of two molecules of the polar compound ammonia with each silver atom, an increase in the strength of the electrostatic fields resulting.

The production of color in the cases mentioned above, *viz.*, the aqueous

solution of the sodium salt, the pink silver salt, and the yellow silver ammoniate, is ascribed to the vibration of the electrons between the carbon atoms of the benzene ring. If such is actually the case, then we should expect visible light to be absorbed by the same mechanism in the case of complex benzene derivatives, particularly when they are in strong electrostatic fields.

The theory that chromo-isomerism in solid salts may arise not only from a difference in molecular structure, but from a difference in crystal structure, when this produces a variation in the strength of the electrostatic field which is associated with the atoms or atom groups of the compound, is applicable to inorganic compounds. For example, the cubic modification of mercuric sulfide is black, the trigonal is red; the cubic modification of thallos iodide is deep red, the rhombic is yellowish-green; the tetragonal modification of mercuric iodide is red, the rhombic is yellow; the trigonal modification of antimony tri-iodide is red, the rhombic is yellowish-green, and the monoclinic is greenish-yellow. It will be noted that the more symmetrical crystal form has the darker color. This seems to justify the conclusion that whenever a compound exists in two or more colored forms, the crystal structure of the darker colored one possesses the greater symmetry. Moreover, the study of crystal structure by means of X-rays indicates that compounds in which the union is entirely polar have the most symmetrical structure and that the presence of more or less firmly bound groups of atoms, *i. e.*, radicals, usually leads to a less symmetrical crystal structure. For example, rock salt crystallizes in the cubic system and calcite in the trigonal. It is probable that greater symmetry goes with a more polar condition, and therefore with greater freedom of vibration owing to the presence of more free charges. It is not surprising, then to find that the deeper colored form of a compound possesses the greater symmetry.

That a difference in crystal structure may account for the different colors of the so-called chromo-isomeric salts of organic acids is shown in the case of thallos picrate. Red thallos picrate is monoclinic, and yellow thallos picrate is triclinic. On the basis of the theory presented, the picrate ion is absorbing light of longer wave length in the former case, because the electrostatic field surrounding it is stronger than in the yellow modification.

When dealing with solutions of colored compounds, it is observed that here also the wave length of the light absorbed varies with the electrostatic environment, in general being greatest in the polar, and least in the non-polar solvents. Thus the head of the absorption band of 4-nitro-*o*-xylene lies closer to the red in alcoholic than in petroleum ether solution, and in the case of nitroquinol dimethyl ether the absorption band progressively shifts to the red in the following solvents in the order

named: light petroleum ether, benzene, alcohol, chloroform, pyridine, water, aniline and conc. sulfuric acid.¹⁰

Finally, on the basis of this theory, it is not necessary to assume a different structural formula for each differently colored modification of a compound. The whole field of the relationship between color and constitution could be much clarified by applying the principles discussed above.

4. The Experimental Work.

The pentabromophenol used in this work was prepared by the method of Bodroux,¹¹ which consists in treating phenol with bromine in the presence of anhydrous aluminum bromide. The crude product was treated with cold 95% alcohol to extract the aluminum bromide and lower halogenated products. It was dissolved in hot alcohol, boiled with refined bone charcoal, and allowed to cool slowly, when it crystallized in long needles. This operation was repeated several times, yielding a snow-white product, melting at 229.5° (corr).

The pink silver pentabromophenolate.—A solution of the sodium salt was made by dissolving the phenol in an equivalent quantity of sodium hydroxide in solution which was practically free from chlorides. The solution thus prepared was yellow, and alkaline to litmus. It was diluted until about 0.01 *N*; then a slight excess of 0.05 *N* silver nitrate was added slowly with stirring. The precipitate was brown, due to the presence of silver oxide, but changed to pink on the addition of 0.01 *N* acetic acid until the liquid showed a slight acid reaction with litmus. The precipitate was filtered, the solid removed from the filter and shaken up with much water, filtered again, and after washing thoroughly to remove impurities, sucked as dry as possible. It was placed on a watch glass, allowed to dry for one day in a clean cupboard, 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.⁵

ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag ₂ S. G.	Ag. found. %.	Ag. calc. from C ₆ Br ₅ OAg. %.
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

The pink salt was also prepared by heating the yellow ammoniate for several hours at 120°.

ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag ₂ S. G.	Ag. found. %.	Ag. calc. from C ₆ Br ₅ OAg. %.
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

When prepared by the latter method it is much purer than by precipitation, because the yellow ammoniate can be obtained very pure.

The pink salt is insoluble in water, alcohol, ether, ligroin, benzene, carbon tetrachloride, bromobenzene, etc. It dissolves in alcohol to which a little ammonium hydroxide has been added, yielding a deep lemon-yellow solution. With ethyl iodide the dry salt

¹⁰ Baly, Tuck and Marsden, *loc. cit.*; Baly and Rice, *J. Chem. Soc.*, **101**, 1478 (1912).

¹¹ Bodroux, *Compt. rend.*, **126**, 1282-5 (1898).

seems to decompose in a manner analogous to the catalytic decomposition first observed by Torrey and Hunter³ in the case of silver tribromophenolate, and later studied by other investigators.¹² The insoluble pink silver pentabromophenolate first becomes green, then black, and finally yellow; the liquid is not colored during the course of the reaction. No effort was made to study this reaction further. When the moist freshly precipitated salt is covered with about 20 cc. of ether and 4 to 5 cc. of ethyl iodide, the pink color slowly fades until after about one-half hour the solid appears to be entirely silver iodide. If the ether layer is filtered, the solid thoroughly extracted with ether and the solvent allowed to evaporate, pentabromophenyl ethyl ether separates in long slender needles, melting¹³ at 131° to 134° (corr.), and after one crystallization from alcohol at 134° to 135° (cor.). From 1.3 g. of the phenol there was obtained 1.1 g. of the ether, a yield of 80%.

The moist pink silver salt is converted into the more stable colorless form on heating, also in the presence of a small amount of alcohol or ammonia. If treated with stronger aqueous ammonia the white ammoniate forms, which goes over into the yellow ammoniate when warmed with strong ammonia solutions. These transformations can be carried out either in the presence or absence of excess silver ion.

The White Silver Pentabromophenolate.—This may be prepared from the pink salt, as described above, or directly by the addition of 0.05 *N* silver nitrate solution to the 0.01 *N* solution of the sodium salt made 0.01 *N* with respect to ammonia. The product after washing and drying is a very light cream color.

Sample.	ANALYSES.			
	Wt. of sample. G.	Wt. of Ag:S. G.	Ag. found. %.	Ag. calc. from C ₆ Br ₅ OH. %.
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

The white salt closely resembles the pink in being insoluble in the solvents named above, and dissolving in alcohol containing ammonium hydroxide to form a lemon-yellow solution. It also decomposes with dry ethyl iodide. The moist salt reacts slowly with a solution of ethyl iodide in ether to form the pentabromophenyl ethyl ether. The freshly precipitated white silver salt from 1.8 g. of pentabromophenol was covered with a solution of ethyl iodide in ether, but the rate of reaction was so slow that there was no noticeable change in the color of the solid during an hour, in marked contrast to the more rapid reaction of the pink salt. After standing for 12 hours, there was obtained 1.4 g. of white solid melting at 132-4° (corr.), which was recrystallized from alcohol in the form of long, slender needles that melted at 134-5° (corr.). The yield of pentabromophenyl ethyl ether was about 70%.

In contact with ammonium hydroxide of about 0.2 *N* the silver salt goes over into the white crystalline ammoniate, which dissolves in more concentrated ammonia on heating. From this solution the yellow ammoniate crystallizes if the dilution is not too great.

The White Crystalline Ammoniate.—This is formed from either the pink or white salt, as described above, or directly from silver nitrate and the sodium salt, if the concentration of ammonia in the solution is 0.2 *N* or greater. It has a beautiful satiny appearance, reflecting light much as does precipitated mercurous chloride. Under the

¹² Hunter, Olson and Daniels, *THIS JOURNAL*, 38, 1761-71 (1916); Woollett, *ibid.*, 38, 2474-8 (1916).

¹³ Bonneau, *Bull. soc. chim.*, 7, 776-81 (1910), gives 136° for the melting point.

microscope the small particles appear as very thin plates, which revolve rapidly as they migrate through the solution.

The salt was filtered and washed with dil. ammonium hydroxide and dried in desiccators containing a small amount of ammonia, one desiccator having sodium hydroxide, and another a mixture of hydrated and anhydrous sodium sulfate as drying agents. That the moist solid has an appreciable vapor pressure of ammonia is shown by the fact that when washed with water or dil. acids, or when dried over phosphorus pentoxide *in vacuo* it turns pink. The dried products from both desiccators retained their crystalline appearance, and were apparently stable upon exposure to air. Analysis for silver and for bromine (by Carius' method) gave the following results, which show the presence of 10 atoms of bromine to one of silver.

Instead of determining the silver bromide, which was mixed with broken glass, the silver contained in it was determined by the cyanide-sulfide method, and the percentage of bromine calculated from the weight of silver sulfide.

ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag ₂ S. G.	Ag. found. %.	Ag. calc. from C ₁₂ H ₁₂ O ₃ N ₃ Br ₁₀ Ag. %.
I.....	0.5913	0.0637	9.38	9.35
II.....	0.5760	0.0621	9.39	9.35
III.....	0.7473	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.

ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag ₂ S. G.	Br. found. %.	Br calc. from C ₁₂ H ₁₂ O ₃ N ₃ Br ₁₀ Ag. %.
I.....	0.1720	0.1834	68.76	69.31
II.....	0.1970	0.2100	68.74	69.31

Nitrogen was determined by the method of Kjeldahl, with the following results, which indicate 3 atoms of nitrogen to 1 of silver.

ANALYSES.

Sample.	Wt. of sample. G.	HCl (0.4942N) used. Cc.	N found. %.	N calc. from C ₁₂ H ₁₂ O ₃ N ₃ Br ₁₀ Ag. %.
I.....	1.065	5.32	3.46	3.64
II.....	1.319	6.90	3.62	3.64

Loss on heating was determined by heating 0.6825 g. of the salt dried over sodium hydroxide at 120° to constant weight of 0.6395 g. The loss was 0.0430 g., or 6.30%. Calculated as 3 molecules of ammonia and 1 molecule of water from C₁₂H₁₂O₃N₃Br₁₀Ag, the calculated loss is 5.98.

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

ANALYSES.

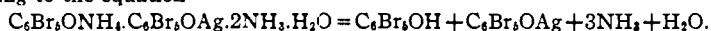
Sample.	Wt. of sample. G.	Wt. of Ag ₂ S. G.	Ag. found. %.	Ag. calc. from C ₁₂ H ₁₂ O ₃ Br ₁₀ Ag. %.
I.....	0.3515	0.0401	9.93	9.95
II.....	0.2938	0.0335	9.93	9.95

These results indicate that 3 molecules of ammonia and 1 of water were lost from C₁₂H₁₂O₃N₃Br₁₀Ag.

Ammonium pentabromophenolate is stable over phosphorus pentoxide and when heated to 110° loses ammonia to give a snow-white residue of the pure phenol.

When boiled with alcohol the white crystalline salt leaves a residue of white silver pentabromophenolate and a filtrate containing pentabromophenol in solution, the two approximately equal in amount. If dilute sodium hydroxide is used the same decomposition is observed, except that the phenol is now dissolved as the sodium salt.

From the above data it appears that the white crystalline ammoniate is a double salt of the formula $C_6Br_5ONH_4 \cdot C_6Br_5OAg \cdot 2NH_3 \cdot H_2O$, and that it is easily decomposed according to the equation



The silver salt resulting from this decomposition is pink or white, depending upon the conditions.

The Lemon-yellow Ammoniate of Silver Pentabromophenolate.—This may be obtained from the salts already described, but is best prepared directly from the solution of the sodium salt by first making it 2 *N* in ammonia and then adding an excess of silver nitrate. The white crystalline salt which first separates is dissolved by warming the solution, which is filtered and the filtrate allowed to stand several hours, when long lemon-yellow needles crystallize. They are filtered with suction, washed in strong ammonia solution, and dried over sodium hydroxide in a desiccator containing a little ammonium chloride. The crystals upon drying retain their color and crystalline structure. The dry salt loses ammonia very slowly at ordinary temperatures, but when heated at 100° to 110° the decomposition is rapid and the pink form of the silver salt remains. This is a deeper red than when formed by precipitation. The yellow salt dissolves in alcohol containing ammonia to give the characteristic lemon-yellow solution (see Fig. 1).

Sample.	ANALYSES.			
	Wt. of sample. G.	Wt. of Ag ₂ S. G.	2Ag. found. %.	Ag. calc. from C ₆ Br ₅ OAg · 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

When 1.249 g. was heated at 110° to constant weight it lost 0.0684 g., corresponding to 5.46%; the percentage of ammonia calculated from $C_6Br_5OAg \cdot 2NH_3$ is 5.40.

Absorption of Ammonia by Silver Pentabromophenolate.—Under the proper conditions the two forms of this salt absorb ammonia to form the yellow ammoniate. But when the vapor pressure of ammonia above the salts is low, only partial absorption takes place, and at different rates for the two salts. Samples of the two salts were weighed out on watch glasses and placed in the same desiccator containing sodium hydroxide and a small amount of ammonium chloride. The salts were taken out at intervals and weighed.

Time elapsed. hours.	Percentage of NH ₃ .	
	Pink salt. %.	White salt. %.
3	4.96	0.70
6.5	4.96	0.88
22	4.96	1.29
27.5	4.96	1.29

After the salts would no longer absorb ammonia at room temperature, the desiccator was placed in an ice-chest beside the ice. After remaining for 3 hours the salts were again weighed but no change was found. The salts were then transferred to a desiccator containing a much higher partial pressure of ammonia and allowed to stand for 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 for 4 days in the same desiccator, the percentage of ammonia in the white increased to 5.00%.

The above data show that the absorption of ammonia by the white salt is very much slower than by the pink form. This cannot 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 absorption of ammonia by both salts seems to depend upon the partial pressure of the ammonia in the desiccator.

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 positive ions which form difficultly soluble salts with pentabromophenol.

Salts. Colored, not distinctly crystalline.			Salts, White, not distinctly crystalline.		White crystalline salts.	
Ions.	Color.		Ions.		Ions.	
Cu ⁺	light brown		Ba ⁺⁺		K ⁺	
Cu ⁺⁺⁺	red		Cd ⁺⁺		NH ₄ ⁺	
Co ⁺⁺	light pink		Ca ⁺⁺		Li ⁺	
Fe ⁺⁺⁺	brown		Ni ⁺⁺⁺		Mg ⁺⁺	
Fe ⁺⁺	yellow		Mn ⁺⁺		
Pb ⁺⁺	light yellow		Zn ⁺⁺		
Hg ^{+b}	orange		Tl ⁺		
Hg ⁺⁺	yellow		

^a Dissolves in warm 6 *N* ammonium hydroxide which, upon cooling, deposits dark brown needles.

^b Changes to a perfectly colorless salt upon standing exposed to sunlight.

^c Changes to a deep violet salt upon standing exposed to sunlight. The violet precipitate dissolves in warm 6 *N* ammonium hydroxide from which lemon-yellow needles separate upon cooling.

^d Dissolves in warm 6 *N* ammonium hydroxide from which light green needles deposit upon cooling.

5. Summary.

1. The silver salt of pentabromophenol exists in two forms, one pink, the other colorless; and in both forms silver is joined to oxygen.

2. Two ammoniates of silver pentabromophenolate are described, one a yellow salt, C₆Br₅OAg.2NH₃, and the other a double salt of the formula C₆Br₅ONH₄.C₆Br₅OAg.2NH₃.H₂O.

3. A new theory of chromo-isomerism is proposed, on the basis of which the wave length of the light absorbed by a substance will change as the electrostatic environment of the absorbing atoms or atom-groups changes, and will be longest when the electrostatic fields are the strongest.

4. The theory satisfactorily accounts for the yellow color of aqueous solutions of the colorless sodium pentabromophenolate, for the color of the two forms of the silver salt, and for the yellow color of the ammonia addition compound of the latter.

5. Absorption of light in these cases is ascribed to the isorropesis of the benzene ring. It is undoubtedly a factor in color production in the case of other benzene derivatives.

6. The theory satisfactorily accounts for the different colors of polymorphic forms of inorganic compounds, such as mercuric iodide, thallos iodide, etc. The more symmetrical form is the darker colored, because the electrostatic fields about the atoms are stronger in the more symmetrical forms.

7. According to the theory presented, it is not necessary to assign a different formula to each colored modification of a compound. The entire field of color and constitution should be re-examined on the basis of this theory.

In conclusion, the assistance and valuable criticism of Dr. Arthur A. Noyes and Dr. Roscoe G. Dickinson in connection with the development of the theory are gratefully acknowledged.

PASADENA, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

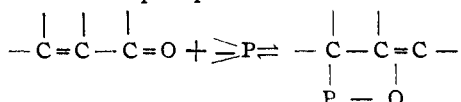
ADDITION REACTIONS OF PHOSPHORUS HALIDES. II. THE 1,4-ADDITION OF PHOSPHENYL CHLORIDE.

BY JAMES B. CONANT AND S. M. POLLACK.

Received March 17, 1921.

I. Introduction.

Phosphorus trichloride readily combines with the carbonyl group of aldehydes¹ and with the conjugated system of α,β unsaturated ketones.² This combination involves the formation of a ring containing as one of its members a pentavalent phosphorus atom.



The reaction is reversible and the product cannot be isolated, but may be transformed by suitable reagents into a stable phosphonic acid or its derivative.

These addition reactions are analogous to the formation of the pentahalides by the addition of chlorine or bromine to phosphorus trichloride. The trivalent phosphorus atom is unsaturated, as shown by its combination with the halogens, the carbonyl group or the ends of a conjugated system in unsaturated ketones. The organic derivatives of phosphorus trichloride (the chloro-phosphines) are also unsaturated since they readily unite with two atoms of chlorine. It is, therefore, to be expected that they will combine with certain unsaturated organic substances in a manner completely parallel to phosphorus trichloride itself. Michaelis, in fact, in his exhaustive study of these compounds showed³ that benzaldehyde combined

¹ THIS JOURNAL, 42, 2337 (1920).

² *Ibid.*, 39, 2679 (1917); 42, 830 (1920).

³ Michaelis, *Ann.*, 293, 193 (1896).