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REPORT
of
COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Lillian Marie Seyfried final oral examination for the degree of Master of Science..... We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

June 4 1917

A. H. Hunter
Chairman

F. H. MacDougall

F. B. Kingsbury

REPORT
of
Committee on Thesis

The undersigned, acting as a Committee of
the Graduate School, have read the accompanying
thesis submitted by Lillian Marie Seyfried
for the degree of Master of Science
They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of Master of Science.

J. A. Hunter
Chairman

F. H. MacDougal
F. B. Kingsbury

June 4 1917

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THE ACTION OF IODINE ON SODIUM TRICHLORPHENOLATE

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF MINNESOTA

by

LILLIAN M. SEYFRIED

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

June 1917

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THEORETICAL PART

During the study of the catalytic decompositions of the silver salts of the symmetrically trihalogenated phenols, it was shown that there resulted a white amorphous compound, the empirical formula of which corresponded to the formula of the original silver salt, less a molecule of silver halide. For instance, from the silver salt of tribromophenol¹, $C_6H_2Br_3OAg$, there resulted a compound $(C_6H_2Br_2O)_n$, and analogous compounds were obtained from the silver salt of trichlorophenol, which yielded $(C_6H_2Cl_2O)_n$, and from the silver salt of tribromoresorcinmonomethyl ether, which gave $(C_6H(OCH_3)Br_2O)_n$ ². It was shown that this reaction occurred by a splitting out of silver halide from the molecule, leaving an unsaturated residue of the general formula $C_6H_2X_2O$, which then polymerized to form the above compounds.

Further study of this reaction in this laboratory has shown that such unsaturated residues must be formed in the following reactions:

First, thermal decompositions of the silver salts of the above named phenols. In this, the silver salts were heated in benzene, splitting out silver halide and leaving the residues, which could be isolated from the benzene by precipitation with alcohol, and proved to be identical with those obtained by the catalytic decomposition.

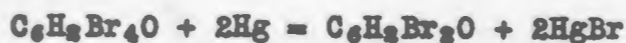
Second, the action of silver or mercury on tribromophenolbromide. This action was worked out by Mr. Woollett³, who found that bromine

¹Torrey and Hunter, Am. Soc. 33, 195 (1911)

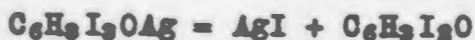
²W. H. Hunter and others, Am. Soc. 38, 1761 (1916)

³Unpublished work

was split out from the tribromphenolbromide when a solution in an indifferent solvent was shaken up with mercury or finely divided silver. It is interesting that the first recorded formation of the white amorphous compound, which we obtained from the tribromphenol, is the formation of a compound from tribromphenolbromide by the action of light to which Kastle¹ gave the erroneous formula $(C_6H_2Br_2O)_2$. Mr. Woollett was able to show that these compounds are both identical with the one obtained from tribromphenol silver salt. The action of the mercury may then be represented by the following equation:



Third, the action of iodine on the silver salt of triiodophenol². Mr. Woollett observed that when the silver salt was warmed with ethyl iodide, a reaction exactly like that shown by the tribromphenol silver salt occurred, yielding silver halide and an unsaturated residue which afterwards polymerised to the white amorphous oxide.



When the silver salt was treated with a very little iodine in water in the cold, a red amorphous substance was formed in place of the white oxide. This red substance was that first described by Lautemann³, and known as "Lautemann's Red." It has the identical composition of the white oxide. On the other hand, when the salt

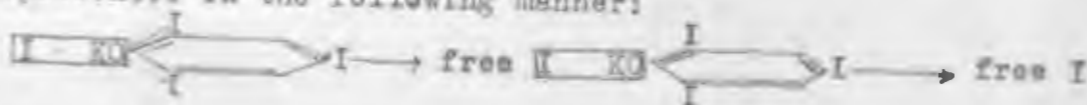
¹Am. Chem. J., 27, 34. 1902

²Am. Soc., 38, 2474 (1916)

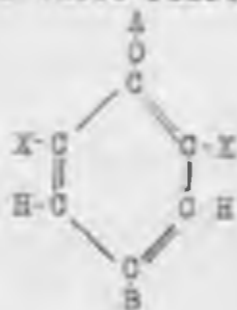
³Ann., 120, 309 (1861)

was treated with a very little iodine in benzene, the white amorphous oxide was again obtained.

This striking reaction led to the working out of the fourth method, the action of iodine on the potassium salt of triiodophenol in water solution, which led to the formation of "Lautemann's Red" only. A trace of iodine was sufficient to bring about this transformation, which proceeded very rapidly. It seems probable that the reaction takes place in the following manner: The iodine introduced splits out the potassium to form potassium iodide, whereupon, one iodine atom in the ring is set free in a nascent state, and in turn reacts with the potassium of another molecule. In that way a continuous splitting out of ring halogen is brought about and the potassium salt completely transformed to the unsaturated residue which polymerizes to form the amorphous product. The reaction may be represented in the following manner:

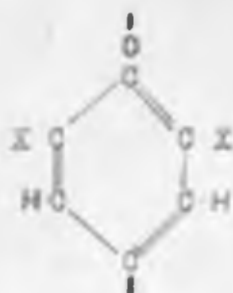


It will be seen then, that in all of these reactions, we start with a molecule of this general form



which loses the groups A and B, to form the unsaturated residue of

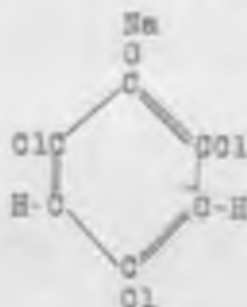
the type



This then polymerizes in every case to form amorphous compounds of high molecular weights.

One of the interesting questions suggested by this work arises from the action of iodine. This problem is, do the halogens, the iodine from the outside and the ring halogen, actually react in that way, could it be shown that the potassium and iodine split out together, which would then necessitate the ring halogen leaving the ring in the nascent state? Or does the potassium unite directly with the iodine in the ring under some catalytic influence of the "outside iodine?" The first of the two alternatives seem much the more likely, and the present research was undertaken with the idea of tracing the part taken by the ring and outside halogen.

In order to trace the halogens separately, the sodium salt of 2,4,6 trichlorophenol was selected for study.



The advantage of using this salt was in the fact that the ring halogen was different from that introduced. If the same halogen was

present in both cases, it would not be possible to follow separately the fate of both the "inside" and "outside" halogen.

It was decided to carry out the decompositions using two different concentrations of iodine, a $2/5$ gram atom equivalent and the gram atom equivalent, in order to show whether less than one atom equivalent could bring about the decomposition of a whole equivalent of sodium salt. The reaction was studied in three solvents; acetone, water and benzene.

Reaction in Acetone

When sodium trichlorophenolate was heated with a $1/10$ gram atom equivalent of iodine in acetone, only a small part (2%) of the sodium salt was transformed into the oxide. Heating under the same conditions and for approximately the same time with $1/5$ equivalent of iodine increased the salt transformation to 10.5%, while with $2/5$ equivalent, 66.0% of the sodium salt was converted to the amorphous oxide. Increasing the iodine concentration to a gram equivalent resulted in 71.6% of the salt transformed to the oxide. The oxides were all of the colorless type, and appeared identical with those prepared from analogous salts in the other ways. Analysis for chlorine showed entire agreement with the theoretical value for the oxide. When an attempt was made to trace the ring halogen and the iodine in this reaction, we discovered that our choice of solvent was an unhappy one. In the presence of halogen, acetone was far from being an indifferent solvent. Our attention was called to this by the very sharp odor of iodo-acetone given off from the reaction mixture. From this we concluded an attempt to

trace quantitatively the action of the two halogens would be unsuccessful. From qualitative experiments, however, we found the iodine present as free iodine, and combined with sodium as the iodide, in addition to that in the acetone derivatives. We were also able to show that the ring halogen, at least in part, existed as the chloride combined with sodium. The results of the acetone reaction were in accordance with our ideas, but for the reason mentioned, no further work was carried on ⁱⁿ this solvent.

Reactions in Water

The sodium salt when suspended in water with a 2/5 equivalent weight of iodine for 10 days, keeping the reaction flask in a dark place, yielded an amorphous substance slightly pink in color. Except for its color, the oxide was identical with that obtained in the acetone decomposition. The pink coloration here was extremely interesting, appearing to indicate the formation of the chlorine analogue of "Lautemann's Red", obtained when the potassium salt of triiodophenol was allowed to react with a trace of iodine in water. In the purification of the oxide by solution in chloroform and reprecipitation by alcohol, most of this color was removed, leaving the pure oxide a light tan color. At first it was thought the color might have been due to the adsorption of iodine on the colorless oxide, but no test for free iodine could be obtained from the alcohol used in reprecipitating the purified amorphous substance. Our conclusion here was that a small amount of the colored oxide, analogous to the Lautemann red, had temporarily formed in the crude oxide. The yield of the amorphous oxide was 63.4% of the original

sodium salt. When the same reaction was carried on using a gram equivalent of iodine the oxide formation increased to 79%, which showed that the 2/5 equivalent was sufficient to bring about a practically complete transformation of the sodium salt over to the oxide. A procedure of analysis was then worked out, and a complete examination was made on reaction mixture resulting when the salt was allowed to react with a 2/5 equivalent of iodine under the conditions observed in the preliminary experiments. The yield of oxide was 64.2% of the sodium salt taken, leaving 35.8% to be accounted for. "Unchanged salt" was determined by conversion into the phenol, and 13.4% was accounted for in this way. No other products could be demonstrated to check up the remaining 22.36%. However, it was found that our figures for "unchanged salt" were inaccurate, owing to the solubility of the phenol in water. This was determined, and was found to be more than sufficient to account for the missing 22.36%.

76.28% of the iodine added, that is of the 2/5 equivalent, was found as free iodine. The 22.72%, occurring in a non free state and apparently not used in the decomposition of the iodine salt, had no doubt been converted into hydriodic acid or even iodic. This conversion might easily have taken place in the presence of water and chlorine, especially when it was demonstrated that ionized chlorine appeared in the reaction.

We were able to demonstrate that the ring halogen behaved exactly in accordance with our ideas held of the reaction. For every molecule of the salt decomposed to form the oxide, one chlorine atom must have been set free, which then displaced the iodine attached to

the sodium to form sodium chloride. The ionized chlorine was determined as the silver salt. In this way the chlorine recovered was 62.9% of that available from the whole sample introduced. However, only 64.2 of the sodium salt was transformed into the amorphous oxide, and only this fraction could really provide the ionized chlorine. 97.8% of the actually available chlorine was therefore recovered. That is in agreement with the theory and shows that the view taken of the reaction is correct.

The formation of a quinone in this decomposition was held not improbable. We were not able to demonstrate the presence of any such compound at this time, although a study of that side of the reaction will be undertaken later. When the oxide from the water decomposition was washed with warm alcohol, the washings were pink in color. This deepened considerably on exposure to air, and the solution left on evaporation a slight amount of a purplish-red amorphous residue. This residue resembled the colored product obtained from a similar decomposition of the potassium salt of tri-bromophenolate, but was not nearly so intensely colored. It is our belief, at present, that this colored substance may be an alcohol-soluble amorphous product, a lower polymer of the unsaturated residue than the colorless variety.

The ease with which the analogous triiodo and tribromo salts decomposed as compared with the sluggish action of the trichlor salt was also observed. Previous work in this laboratory has shown that the transformation of the triiodophenolate over to the red oxide is almost instantaneous and that the tribrom salt undergoes practically complete decomposition, yielding a brownish-red oxide

after standing two to three hours, while our sodium salt showed apparently no change under such conditions. It was only after standing for a day that any formation of the oxide was apparent.

Reactions in Benzene

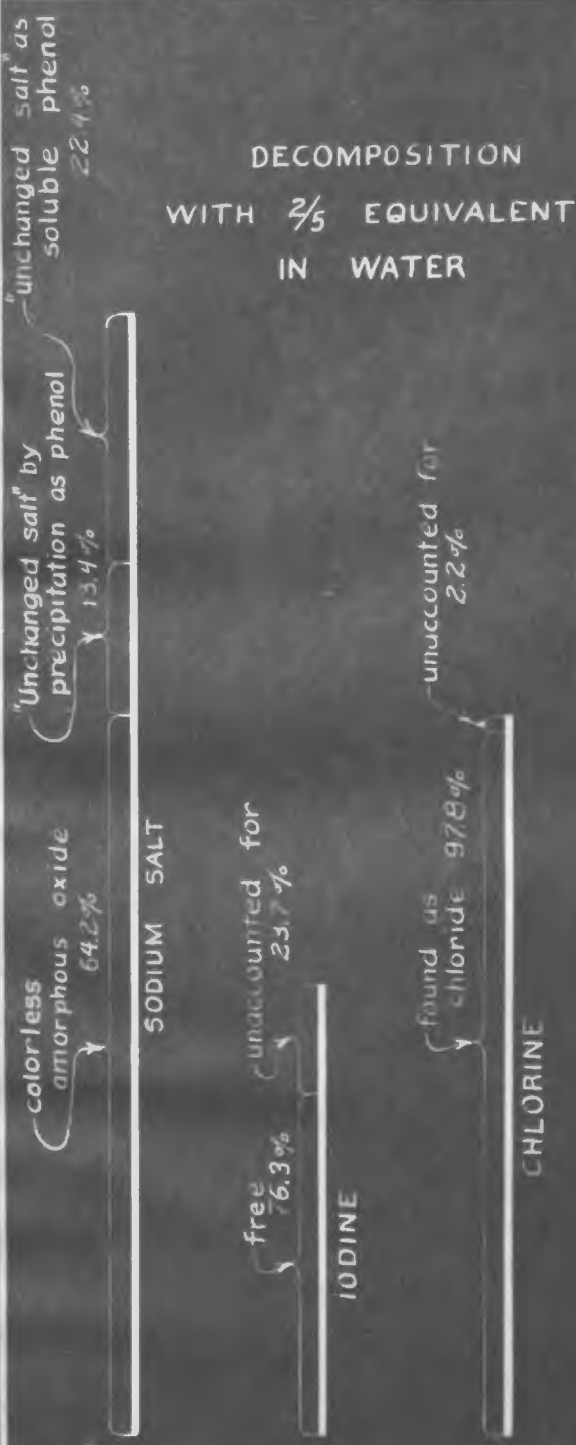
Preliminary experiments with the sodium salt in benzene showed that with the $2/5$ iodine equivalent just as complete a transformation of the sodium salt could be obtained as when using the full equivalent of iodine. A complete examination was then made on a reaction mixture resulting when the salt was heated with a $2/5$ equivalent of iodine. Analysis showed that 92.2% of the sodium salt went to form a colorless oxide, identical with that obtained in the previous decompositions. This when analyzed for halogen was found to contain nearly 1% more chlorine than that calculated. It is believed that this was due to some of the ionized chlorine substituting in the ring of part of the oxide molecules, in the presence of the iodine as carrier. Our belief for this was substantiated when an analysis for the ionized halogen was made. This, which represents the chlorine removed by the reaction, and which, according to our theory should appear in the nascent state at first, proved to be less in amount than expected. Only 85% of the available chlorine appeared in the reaction mixture as ionized chlorine. The only thing that could prevent this from appearing as ionized chlorine would be its disappearance by substitution. It will be remembered that in the water decomposition 97.8% of the chlorine appeared as ionized chlorine, and here the amorphous oxide had the calculated composition.

The iodine was traced to two positions 83.6% was found as free iodine, and 16.04% as sodium iodide. The presence of the iodide lends further proof to our theory. No doubt some of the iodine was still in the ionized form because the nascent chlorine was not available to replace it, as it had disappeared into the amorphous molecule as stated in the above section. That the iodine in this reaction has been fully traced is shown by the recovery of 99.64% of that introduced.

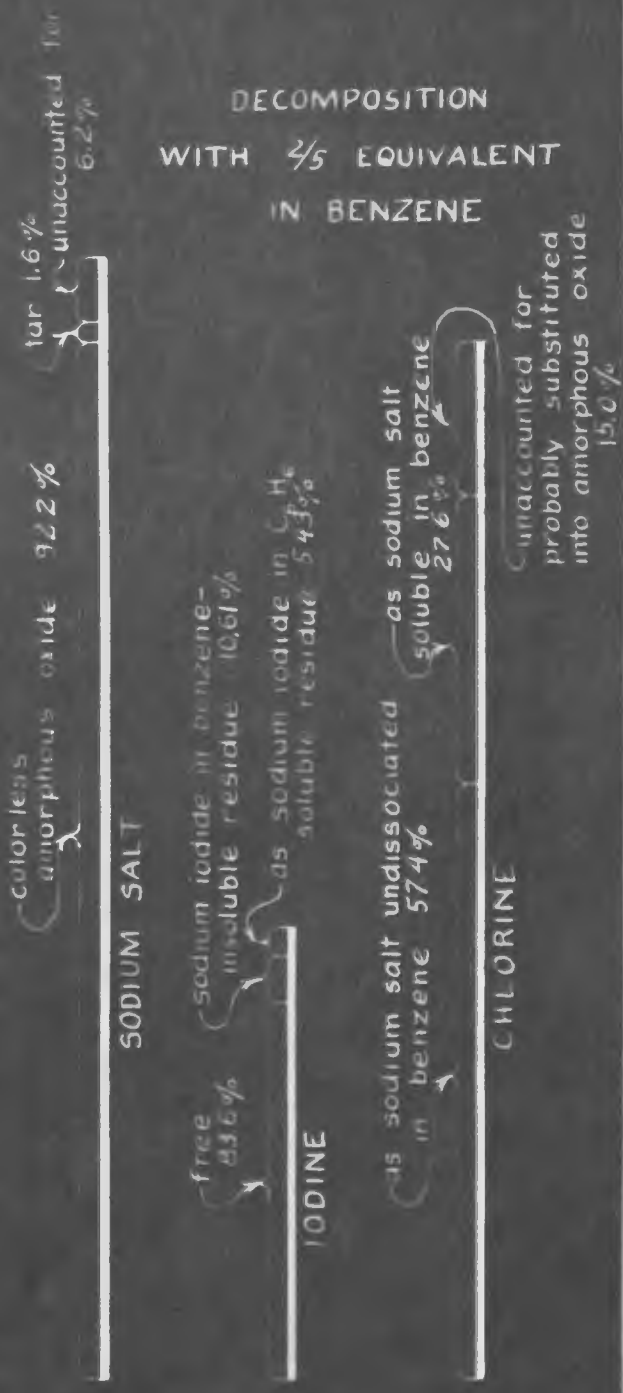
The brownish tar residue found when the alcohol used in the recovering the purified oxide was evaporated, although of no appreciable yield here, aroused considerable interest. It appeared to be identical with the tar residues formed in preliminary work when higher concentrations of iodine were used. With 1-1/2 gram equivalent or more, this tar residue was obtained in considerable amount. At that time, no particular stress was laid on the reaction, because it did not appear to have any relation with the formation of the amorphous oxide. Later, however, its appearance in the lower concentration of iodine decomposition warranted further study. It is our plan to attempt to isolate a sufficient amount of the tar for study. The occurrence of the tar with the amorphous oxide, differing only, so far as we know, by its solubility in alcohol, brings forth the suggestion that it may be another polymer of the unsaturated residue.

The results of analysis for the decompositions with a 2/5 gram equivalent of iodine in water and benzene is graphically shown by the following scales:

DECOMPOSITION
WITH $\frac{2}{5}$ EQUIVALENT
IN WATER



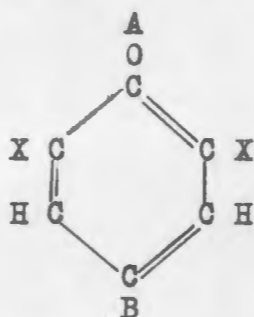
DECOMPOSITION
WITH $\frac{2}{5}$ EQUIVALENT
IN BENZENE



Summary

When sodium trichlorphenolate is allowed to react with less than a gram equivalent of iodine, in acetone, water, and in benzene, a practically complete transformation into the colorless amorphous oxide occurs.

The oxide has the formula $(C_6H_2Cl_2O)_n$, and is analogous to the amorphous substances formed from salts of the type



in other modes of decomposition.

The outside halogen acts indirectly as a catalyst, at the end of the reaction remaining practically unchanged, but forming an intermediate product with the sodium.

The ring halogen leaves the ring in the nascent state, replacing the iodine of the sodium iodide to form sodium chloride, and leaving the iodine free.

The velocity of the reaction with the trichlor salt is much less than that of the reactions with the analogous triiodo and tribrom salts, both of which proceed easily.

The reaction has been shown to take place in the following manner:

EXPERIMENTAL PART

Preparation of Sodium Trichlorphenolate

Pure trichlorphenol was dissolved in just enough alcohol to bring about solution, and to this was added a slight excess of the equivalent weight of sodium hydroxide which previously had been dissolved in a minimum quantity of water. After stirring well, the solution was evaporated on a water bath. A white residue of light, flaky crystals of the sodium trichlorphenolate remained. The crude salt was decidedly soapy to the touch, due to the presence of excess alkali. This salt was then dried in a oven for two hours at 120° , thus getting rid of any mechanically held water. It was then taken up with as small an amount of acetone as possible. At this point a slight precipitate of sodium carbonate and sodium hydroxide was filtered off and the acetone solution poured into fifteen volumes of toluene. At this point there was only a slight precipitation of the sodium salt, due to the fact that the salt was so very soluble in acetone. To bring about precipitation, the acetone had to be removed. Accordingly the solution was kept at a temperature ranging from 82° - 90° on the electric plate until the acetone had entirely boiled away, when the sodium salt readily precipitated from the hot toluene. The mixture was allowed to stand until cold to insure a complete separation of the phenolate. It was then transferred to a Huebner funnel, and the salt, after washing with benzene, was sucked dry. The yield, following this method of preparation, was about 75%.

An attempt to make the salt by adding to the trichlorphenol a

50% excess of sodium hydroxide solution was tried. This plan proved unsuccessful because it was extremely hard to recover an appreciable amount of the sodium phenolate on account of its great solubility in water, and in any liquid miscible with water.

A slight modification of the first method of preparation was finally used for making the salt. As in the first, the trichlorophenol dissolved in alcohol, was added to a water solution of an equivalent amount in slight excess of sodium hydroxide, and the mixture evaporated to dryness on a water bath. The residue of crude sodium salt was then heated in the oven at 150°C for three hours, and taken up with a minimum amount of water-free acetone. After filtering free from insoluble carbonate and excess alkali, the acetone solution was poured into fifteen volumes of toluene and the mixture boiled on the electric plate until the sodium salt precipitated. The mixture was allowed to cool to insure complete separation of the salt, and filtered on a Buechner. The salt was washed free from toluene with benzene and sucked dry. Following this method of preparation, a satisfactory yield of pure and practically anhydrous sodium salt was obtained.

Properties of Sodium Trichlorophenolate

The sodium salt crystallizes in white flakes. In contrast, the potassium salt of this phenol has a decided yellow color. The sodium salt is easily soluble in water, alcohol, ether, and acetone; but is practically insoluble in chloroform, toluene and benzene. The salt may exist in a hydrated form having one molecule of water of crystallization. This point was determined by heating to 150° a

weighed sample previously heated to 120°.

It is a remarkably stable salt, from all appearances remaining unchanged and displaying the same solubilities after heating to a temperature of 220°.

The Action of Iodine on Sodium Trichlorphenolate
in the Following Solvents:

Acetone, Water, and Benzene.

With Acetone as the Solvent.

The first work was done using a 1/10 gram atom equivalent of iodine. Two grams of the anhydrous sodium salt were dissolved with .115 grams of iodine in 20 c.c. of acetone. This was heated gently under a reflux condenser on a water bath at 45°-50° for about thirty minutes. To precipitate any amorphous compound found, 50 c.c. alcohol was added. A slight amount of colorless amorphous substance was thrown down, which represented but 2% of the original sodium salt. On examining the filtrate, it was found to contain mostly unchanged sodium trichlorphenolate, traces of sodium chloride and iodide. There was also a distinct odor of iodo-acetone to the filtrate. This compound might easily have been formed in the presence of free iodine and acetone. Although no determination of the amount of free iodine remaining in the solution was made, the acetone-alcohol filtrate was deeply colored with iodine. A second 2 gram sample of sodium salt was treated in a similar manner, only this time in place of using a 1/10 gram atom equivalent of iodine, a 1/5 gram atom equivalent was taken. The amount of amorphous substance similar to that previously obtained in this case increased the yield representing 20.7% of the original salt for the same time

of heating. After removing the amorphous substance, the acetone-alcohol filtrate was evaporated. The residue contained some sodium phenolate, free phenol, NaCl, a trace of NaI, and free iodine. On increasing the iodine concentration in a third sample to 2/5 gram atom equivalent, this time using 4 grams of sodium salt dissolved with .92 grams iodine in 75 c.c. acetone, and allowing the mixture to be warmed for three hours under a reflux condenser and to stand over night, the yield of amorphous product was greatly increased. On adding sufficient alcohol to completely precipitate the solid, filtering and weighing the dried sample, it was found to represent a 68.4% transformation of the trichlorosodiumphenolate. In the evaporated filtrate from the amorphous substance, small amounts of unchanged sodium salt, sodium chloride and free iodine were found. In all of these decompositions in acetone, no attempt was made to fully account for the halogens; for the present purpose it was considered sufficient to determine qualitatively the presence of chloride or iodide of sodium and free iodine. The chief purpose here was to show the amorphous substance as the main reaction product, and the effect of change in concentration of iodine. A final experiment with acetone as a solvent was made on a 2 gram sample of the salt, this time using one gram-atom equivalent, 1.16 grams of iodine in 50 c.c. acetone. The heating here was continued only 30 minutes, yet on isolating the amorphous substance, the highest yield yet obtained was found, 1.05 grams which represented a conversion of 71.6% of the original salt to the unsaturated residue. The above experiments showed that the completion of the decomposition of the sodium salt to form the amorphous oxide depended

upon two things, time and iodine concentration. The oxide obtained in acetone was analyzed for chlorine.

Substance .1577 : AgCl .2301

Calculated for $C_6H_2Cl_2O$: Cl, 44.07. Found 43.92.

Decompositions in Water Solution.

Action of 2/5 gram atom equivalent of iodine.

In a flask fitted with a glass stopper, was placed one gram of the sodium salt dissolved in about 50 c.c. water and .23 grams iodine previously dissolved in potassium iodide. This was allowed to stand in a dark place for one week. At this time a copious precipitate of a slightly colored substance had settled out. This was removed from the solution by filtration, washed free from iodine, and inorganic salts and dried. The dried substance, except for its slightly pink color appeared to be identical with the amorphous oxide obtained in the acetone decompositions, displaying the same solubilities. This pink coloration was extremely interesting, as it appeared to indicate the formation of the chlorine analogue of "Lautemann's Red"¹ which we hoped to obtain in the water decompositions, "Lautemann's Red" itself having been studied in this laboratory by Woollett², who made it by the decomposition of the silver salt of triiodophenol by iodine in water. However, this color was removed on dissolving the oxide in chloroform and reprecipitating by means of alcohol, leaving a perfectly colorless oxide, identical with that from the acetone.

¹Ann., 120, 309 (1861)

²J. Am. C. Soc., 38, 2475 (1916)

At first it was thought that the color might have been due to the adsorption of iodine on the colorless oxide, but no positive test for free iodine with starch paper (previously moistened with water) could be obtained from the alcohol used in reprecipitating the purified amorphous substance. Possibly, the color was due to a small amount of the red oxide of Lautemann temporarily formed in the crude oxide. The yield of amorphous substance was .23 grams, which represented 40.8% of the original sodium salt. The formation of a quinone in this decomposition was held not improbable. It was decided that if it were a reaction product, it would be found in the amorphous residue, being insoluble in water. The oxide was washed several times with warm alcohol. The washings were pink in color, a very delicate color at first, but on standing exposed to the air, this color deepened considerably, and after evaporating off the alcohol, a purplish-red residue remained. This residue resembled closely the oxide obtained in the action of iodine on the silver salt of triiodophenol. An attempt to isolate this colored residue will be made later for the purpose of comparison with "Lautemann's Red." At this time considerable interest was aroused by this fact that the amorphous substance from the 2,4,6-trichlorophenolate was practically free from the red oxide, while this red oxide was so easily obtained under the same iodine concentrations in cases where the sodium salts of the 2,4,6-triiodophenol and the 2,4,6-tribromophenol were used. In qualitative experiments it was found that no white amorphous oxide could be detected in the decomposition produced by the triiodophenol, while

with the 2.4.6 tribrom salt a slower decomposition occurred, yielding what was apparently a mixture of both forms of the oxide, the red and the white. The comparatively small yield of the amorphous oxide, representing but a 40.8% transformation of sodium salt, by a 2/3 equivalent of iodine in water left practically 50% of the salt unaccounted for. Either the sodium salt was present as such, unchanged in the filtrate, or other compounds, products of side reactions might have been formed.

Determination of "Unchanged Sodium Salt."

The 500 c.c. flask containing the filtrate from the initial crop of the amorphous oxide was allowed to remain in strong sunlight. Within an hour the mixture, previously clear, had been transformed into a decidedly turbid mixture, the turbidity caused thru the formation of additional oxide. This showed that much unchanged sodium salt still remained in the mixture; also the very interesting fact that sunlight aided the decomposition. To further demonstrate the presence of sodium salt, a 100 c.c. portion of the turbid filtrate was acidified with dilute acetic acid. A copious precipitate of the trichlorophenol settled out. This phenol carried down with it the additional precipitate of the amorphous oxide, formed during exposure to sunlight. The mixture of the two precipitates was transferred to a Gooch crucible, washed well with water, dried at 100°, and weighed. Later it was washed with alcohol until free from trichlorophenol, dried and weighed again, the difference representing the sodium salt as the phenol in 100 c.c., or 1/5 the sample.

Wt. of crucible oxide trichlorphenol	34.5800 gms.
Wt. of crucible oxide	34.5223 "
Wt. of trichlorphenol	----- .0577 "
Wt. of crucible oxide	34.5223 gms.
Wt. of crucible	34.4823 "
Wt. of oxide	----- .0390 "

.0577 gms. $\times 5 = .2885$, phenol in 500 c.c. 34.9% of the original sodium salt.

.0390 gms. $\times 5 = .195$ gms. oxide .23 gms. (wt. initial precipitate) = .43 gms. amorphous oxide or 63.4% of the sodium salt.

34.9% 63.4% = 98.3% of the salt accounted for.

Our attention was then turned to the fate of the halogens. According to the reaction for every molecule of sodium salt decomposed, one atom of chlorine should be set free, meaning that one-third of the chlorine content of any changed sodium salt must be accounted for. Obviously this chlorine would be tied to the sodium, and the iodine added should remain as free iodine except for any side reactions, such as formation of hydriodic acid. Even iodic acid might result in the presence of water and chlorine if the latter were free for any time. The solution from which the amorphous substance had been removed was made up to volume in a 500 c.c. flask, and 50 c.c. portions titrated with a standard solution of sodium thiosulphate. Eighty per cent of the iodine was shown to have remained free, leaving but 20% of the $2/5$ gram atom equivalent (8% of a gram atom equivalent to be accounted for). A qualitative test with $AgNO_3$ gave a slight precipitate of silver

iodide. Again, it is not improbable that some of the iodine might have been lost thru volatilization. Later in this paper will be found a complete quantitative analysis of a similar reaction mixture. The chlorine was also traced quantitatively in this later analysis. For this present work, a heavy precipitate on the addition of silver nitrate to a portion of the filtrate, with the confirming solubility test in ammonium hydroxide, was sufficient to show the presence of sodium chloride.

Summary of the Analysis

Reaction Mixture, filtered.

precipitate
amorphous oxide
weight .23 grams

.23 grams .195 g.
= .425 grams of
total oxide
63.4% sodium salt.

filtrate
iodine
sodium trichlorphenolate
sodium chloride
sodium iodide
made up to 500 c.c.

50 c.c. portions titrated for free iodine
Found for entire sample .179 grams
92% in terms of gram atom equivalent of
iodine in original sample

To 100 c.c. added dilute acetic acid
filter

precipitate
trichlorphenol
amorphous oxide
weight .0967 grams
wash with alcohol
Filter

Filtrate
sodium chloride
sodium iodide
Add AgNO₃,
Filtered

Residue
amorphous
oxide
weight .039
grams
.195 grams
for entire
500 c.c.

Filtrate
contained
trichlor-
phenol.
weight by
difference
= .0577
grams
.2885 grams
in the 500
c.c.
Represents
34.9%
sodium salt

Precipitate
silver chloride
silver iodide
Wash with 2%
ammonium
hydroxide

Residue
silver
iodide

Solution of
silver
chloride
acidified
with
nitric
precipi-
tate
silver
chloride

The Action of One Gram Equivalent of Iodine in Water.

One gram of the sodium salt was dissolved in about 50 c.c. water, to which had been previously added .63 gram iodine dissolved in potassium iodide. As before, the mixture was placed in a glass stoppered flask and allowed to stand in the dark for a week. An analysis, the procedure of which was similar to the one first completed, was undertaken. At this time a rather hurried analysis was made, as it was decided to run one more determination on a quantitative basis, using a larger sample. This first sample was examined simply for comparison with the sample run with a lower iodine concentration for oxide and iodine. With this sample, the reaction was practically identical with the former determination, the only difference being in the greater quantity of the amorphous residue formed, which, like the other, was colored in the crude form, but when purified by solution in chloroform and reprecipitation with alcohol remained as a colorless product. The results from this determination are given in the summary below.

Reaction mixture resulting after 1 gram sodium salt, dissolved in 50 c.c. H₂O was allowed to stand for 1 week in the dark with .63 grams iodine.

Filter

Precipitate = oxide
weight .52 grams
79% sodium salt

Filtrate made to 500 c.c.
contains iodine
sodium salt of trichlorphenol
sodium chloride
sodium iodide

Titration on 50 c.c. portions for free iodine resulted in accounting for .566 g. iodine or 89.8%

To 100 c.c. dilute acetic added very small precipitation of trichlorphenol. Weight neglected here.

Filter

Filtrate contains
sodium chloride
sodium iodide
Add AgNO₃, filter

Precipitate = AgCl
AgI
Wash with 2% NH₄OH

Residue =
AgI
no weight,
but positive
test

Filtrate = AgCl
Add HNO₃
precipitate =
AgCl
no weight taken
but substantial
precipitate
formed.

A third determination was made in this water-iodine decomposition, the purpose of which was to obtain a complete quantitative analysis of all the reaction products. This time, in place of using the solid sodium salt, 4.501 gram of the trichlorphenol, which was exactly equivalent to 5 grams of the anhydrous sodium salt, was added to 50 c.c. of .912 N/2 sodium hydroxide (this being the calculated amount necessary to react with 4.501 grams of the trichlorphenol). To this mixture was then added 2.7989 grams of iodine dissolved in a small quantity of potassium iodide. This solution, 380 c.c. in volume, stood in a dark place for 10 days. At the end of that time, a heavy precipitate of the oxide had settled out. This was filtered with suction, working quickly to prevent loss of iodine thru evaporation, and washed thoroughly with water, until the washings showed no iodine color. This amorphous product was a very light brownish pink, resembling the colored product obtained from a similar decomposition of the tribromophenolate, but not nearly so intensely colored. It was transferred to a watch glass and dried in the oven. It was observed that on raising the temperature to 140°, the oxide sintered. At this point heating was immediately discontinued, the oxide cooled in a desiccator and weighed. The color in the amorphous oxide had greatly decreased to light tan in the drying, showing that the former color was no doubt partially due to iodine adsorption. The weight of the amorphous product, 2.359 grams, corresponded to 3.213 grams sodium salt or 64.2% of the sample.

The filtrate from the amorphous substance, plus the washings

was collected in a liter flask and made up to volume. According to our idea of the reaction, this filtrate contained any unchanged sodium salt, the halogens, chlorine and iodine, present as such, or combined with sodium as the chloride or iodide. Several titrations for free iodine were made on 50 c.c. portions of the filtrate, and 76.28% of the original iodine accounted for as free, 23.72% remaining to be traced.

The unchanged sodium salt was then determined. To 250 c.c. of the filtrate dilute AgNO_3 was added until the solution was just slightly acid. This was done to convert the sodium salt in solution to the trichlorphenol. A flocculent precipitate of phenol indicating a fair amount of sodium salt trichlorphenol settled out. This was filtered on a Gooch crucible, washed carefully with distilled water, dried and weighed. The filtrate and the washings were saved, and an analysis for chloride made on it. From this weight, 1506 grams or .6024 gram in the entire sample, the equivalent sodium salt was calculated. The amount equivalent to the .6024 grams of phenol was .669 grams. This amount added to the amount equivalent to the amorphous product formed gave the weight of sodium salt accounted for as 3.882 grams, 77.64% of the original sample. The remaining 22.36% was yet to be traced. No other products of the sodium salt of any appreciable yield could be found and it was decided that one of the known products must have been made soluble in the water than anticipated. Either the amorphous oxide was somewhat soluble or the parts of the trichlorphenol representing the unconverted sodium salt might be in solution. On this

account it was decided to determine the solubility of the trichlorophenol. If this were appreciably soluble, the weight of trichlorophenol found would be too low, and the "unchanged sodium salt" calculated from this would be correspondingly low.

Solubility of Trichlorophenol

A mixture of distilled water and trichlorophenol was put in a flask and this stirred in a thermostat at 21.5° (room temperature) for two hours. After filtering, the filtration made in the thermostat bath, 50 c.c. portions were pipetted into beakers, and a 25 c.c. portion measured into a weighed glass evaporating dish. This latter portion was evaporated on a water bath to dryness, and the trichlorophenol remaining as the residue weighed. This was done because it served to determine in a way the volatility of the phenol. To each of the 50 c.c. portions of the water containing the dissolved phenol was added a small quantity of the dilute alkali (5 c.c. N/5 NaOH). After stirring with dilute acetic (about 1%) was added until the solutions were barely acid. Our idea here was to first convert the phenol to the sodium salt and to neutralize the excess alkali with the acetic acid. Silver nitrate was then added until there no longer was precipitated any of the yellow silver salt. On the first solubility determination the silver salts were allowed to stand over night at this point before transferring to Gooch crucibles. The next day it was noticed that the silver salts had changed from a yellow color to a blue-green, suggesting decomposition. They were transferred, however, to Gooch crucibles, dried in the oven at 120° and weighed. As expected, the

results did not check, so a second determination was run, this time transferring the silver salts within an hour after precipitation, to the crucibles, washing with alcohol, and drying at 80°. No decomposition of the silver salt appeared to occur under this treatment. The average weight of the silver salts from this determination was taken, and from that weight the equivalent amount of trichlorophenol calculated. From 25 c.c., silver salt to the amount of .04 gm. was obtained. The trichlorophenol equivalent to that weight was found to be .025 grams. That is, at the temperature of 21.5°, .025 parts of phenol was soluble in 25 parts of water.

It was also shown that when 25 c.c. of the same solution was evaporated to dryness on the water bath, a residue of trichlorophenol weighing only .002 grams remained. The difference, then, between .025 and .002 gave us some idea as to the volatility of the phenol.

To go back to the analysis proper, it was found that 22.36% of the original sodium salt was still unaccounted for. From the above determination it was found possible that 1.04 grams of trichlorophenol could have remained dissolved in the 1000 c.c. of water, and thus not be included in the determination of the unchanged sodium salt. 1.04 grams of phenol is equivalent to 1.18 grams sodium salt which would more than accounted for the 22.36% missing sodium salt amounting to 1.118 grams. Therefore, it appeared very reasonable to accept that explanation for the unaccounted for salt. It was of interest to note the close relationship between the percentages of unchanged sodium salt, 22.36% equivalent and the iodine existing in

a non free state, 23.72% equivalent. It was concluded here that all of the iodine not used in the decomposition of the sodium salt had been converted into the acid, hydriodic or iodic. This appeared all the more evident after the determination of the chlorine existing as sodium chloride was completed.

Determination of Ionized Chlorine

For the ionized chlorine determination, the filtrate and washings, remaining after the precipitation of trichlorophenol from the 250 c.c. taken for the "unchanged sodium salt" determination, was used. Though already slightly acid with HNO_3 , enough was added at the point to produce an acid solution. Silver nitrate was then added in excess, whereupon a heavy white precipitate settled out. This was transferred to a Gooch, washed free from acid and nitrate, dried and weighed. The weight of silver chloride, .4464 grams, represented .1104 grams ionized chlorine in the 250 c.c. sample, .4416 grams in the total sample. From the 5 grams original sodium trichlorophenol assuming one-third of the chlorine to be ionized, the weight of ionizable chlorine was calculated as .7978 grams. The chlorine recovered then, was 62.9% of that available from the whole sample introduced. However, the amorphous compound weighed corresponded only to 64.2% of the sample introduced, and only this fraction could really give ionized chlorine. Therefore, the recovery of actually available chlorine was 97.8%. This is a remarkable agreement with the theory and shows that the view taken of the reaction is correct. Each molecule of sodium trichlorophenolate which gives amorphous oxide, does actually give up an atom of chlorine

also.

Summary of the Analysis

Reaction mixture resulting when 4.501 grams trichlorphenol was added to .912 N/2 sodium hydroxide, amounts calculated to form 5 grams of the anhydrous sodium salt, and added to this mixture 2.799 grams iodine previously dissolved in potassium iodide, the whole made up to 380 c.c. and allowed to stand in the dark for 10 days, filtered

precipitate
amorphous oxide
weight, 2.3535
grams
64.2%
sodium salt

filtrate
iodine
sodium trichlorphenolate
sodium chloride
hydriodic and iodic acids
made up to 1000 c.c.

50 c.c. portions titrated for free iodine
weight of iodine for entire 1000 c.c. =
2.135 grams
76.28% amount used

250 c.c. filtrate acidified with dilute HNO₃
filtered

precipitate
trichlorphenolate
washed dried
and weighed
weight = .6024
.669 gram
sodium salt

13.4% of salt taken

filtrate
sodium chloride
add dilute HNO₃ and silver
nitrate. Filtered

Precipitate, silver chloride
weight .4464
.7979 grams ionizable
chlorine in entire sample.

97.8% available

Determination of Quinoid Group in Oxide Obtained
from a Water Decomposition.

A weighed sample was tested for quinoid oxygen by an alkaline solution of hydrazine after the manner of the quantitative determination worked out by Mr. Woollett (Doctor's thesis, unpublished). The principle of the method is the measurement of nitrogen evolved when the hydrazine is oxidized by quinoid oxygen. In the first of two determinations, a slight increase in volume was observed which was probably due to experimental error, as the second determination showed no effect.

Decomposition in Benzene Solution

Action of 2/5 gram atom equivalent of iodine on the
hydrated salt ($C_6H_2Cl_2ONa.H_2O$)

1.99 grams of sodium salt were added to 100 c.c. benzene containing .4621 grams iodine. This mixture was heated in an Erlenmeyer flask on a water bath attached to a reflux until the decomposition appeared complete, as the sodium salt of the phenol had become transformed into sodium chloride. When the mixture had cooled, the reflux was washed thru with small portions of benzene, and the contents of the flask filtered thru a Buchner funnel, using gentle suction. A slight residue remained, and this was washed free from iodine with benzene, and the washings added to the filtrate. This process was carried out as quickly as possible, so as to minimize the loss of iodine thru volatilization. This benzene solution was then transferred quantitatively to a 500 c.c. flask and made up to volume.

The residue was dried, taken up with water and the water solution made up to volume in a 250 c.c. flask. The residue was completely soluble in water, and contained as expected the inorganic sodium salts, along with any unchanged sodium trichlorophenolate. 100 c.c. of this solution was just acidified with dilute HNO_3 , with the result that almost no precipitation of trichlorophenol occurred. However, a slight amount settled out after the solution was allowed to stand two days. This was filtered on a Gooch, washed with a small amount of water, dried and weighed. Only .7 mgs. of the phenol was found for the entire 250 c.c. This small yield was of course due to the solubility of the phenol in water, as shown in the analysis of the water decomposition. The filtrate from the above was made distinctly acid with dilute HNO_3 , and AgNO_3 added. A silver precipitate, slightly yellowish in color, settled out, suggesting a mixture of chloride and iodide, but no determination of chlorine was made on this sample.

The 500 c.c. filtrate was investigated for the amorphous oxides, free iodine, and trichlorophenol.

Determination of Free Iodine.

50 c.c. portions of the filtrate were placed in an Erlenmeyer flask fitted with a ground stopper and titrated with sodium thio-sulphate. Here the iodine-benzene color was used as the indicator. The thio-sulphate was added in small portions, shaking the closed flask thoroughly after each addition. The average of two determinations of iodine from this gave .3876 grams, 83.9% of the weight of

iodine added (.4621 grams), leaving only 16.1% of the added iodine still unaccounted for.

Determination of Amorphous Oxide

200 c.c. of the filtrate was evaporated over a water bath, leaving a brown varnish-like residue, exactly like the residue obtained from evaporation of solutions of the polydibromophenylene oxide. This was taken up with chloroform, which on adding produced a red coloration unlike iodine color in chloroform. The color soon disappeared leaving the solution a light brown. The oxide was extracted from this with alcohol. It was colorless and appeared identical with that formed in the acetone and water decompositions. The amorphous oxide was filtered on a Buechner funnel, washed with alcohol and sucked dry. The alcoholic filtrate and washings were saved for the phenol determination. The oxide was then transferred to a weighed watch glass and heated at a temperature of 80° to constant weight. The amount of oxide, recovered from the 200 c.c. sample weighed .5336 grams. The oxide in the entire sample was then 1.3403 grams, representing a 91.5% transformation of the sodium salt.

The alcoholic filtrate and washings from the oxide determination were evaporated on a water bath. A slightly colored residue remained. This residue was extracted with water, and on the water soluble portion affirmative qualitative tests were obtained for chloride and iodide. The water insoluble portion appeared to consist mainly of trichlorphenol.

Summary of the Analysis

From 2/5 gram atom equivalent in benzene.

Benzene Solution, Filter

residue contains Na trichlorphenolate Na chloride Na iodide wash with benzene dry and take up with H ₂ O make up to 250 c.c.	Solution iodine amorphous oxide trichlorphenol 50 c.c. portions titrated for free iodine Found for entire sample .3876 gr. 83.9% iodine added		
To 100 c.c. added. HNO ₃ until slightly acid filter	200 c.c. evaporated to dryness. Taken up with chloroform and ex- tracted with alcohol. Filtered		
precipitate = trichlorphenol weight .00079 .0008 g. sodium trichlor- phenolate	filtrate Na chloride Na iodide add HNO ₃ and AgNO ₃ filter	filtrate, evaporated slight residue con- tained trichlor- phenol sodium chloride sodium iodide Extracted with water	Residue = amorphous oxide Found for entire sample 1.3403 grams to 91.5% sodium salt.
	precipitate = AgCl AgI weight = .1415 grams	Residue trichlor- phenol	Solution sodium chloride sodium iodide

Decomposition in Benzene using a Gram Atom
Equivalent of Iodine.

1.9941 grams of sodium salt were allowed to react with 1.1571 grams iodine under the conditions of the 2/5 gram atom decomposition, heating in 100 c.c. benzene until the action appeared complete. The same procedure of analysis was undertaken in this case, and practically the same results were attained, the only difference being in the relative weights of the recovered products. No determination was made for ionized chlorine or iodine.

The Analysis of Reaction Mixture from Equivalent

Amounts of Iodine

Benzene Solution, Filter

residue
sodium trichlorphenolate
sodium chloride
sodium iodide
washed with benzene, dry
and taken up with water.
Made up to volume in
250 c.c. flask

Solution
iodine
amorphous oxide
trichlorphenol

Titrated 50 c.c. portions for
free iodine
Found for entire sample
1.05 grams, 90.7% of the
amount of iodine added.

100 c.c. made slightly acid
with dilute HNO₃
Filter

200 c.c. evaporated to dryness.
Taken up with chloroform and
extracted with alcohol.
Filtered

precipitate
trichlorphenol
weight for
entire sample
= .115 g.
.013 grams so-
dium salt
.64%

filtrate con-
tains
sodium chloride
sodium iodide
Added HNO₃ and
AgNO₃
Filtered

precipitate
silver chloride
silver iodide
no weights
taken

precipitate
amorphous
oxide
weight for
entire
sample
1.2975 gram
83.4% of
sodium salt
taken.

Filtrate
evaporated
found
sodium chloride
sodium iodide
trichlorphenol

A third determination in benzene was made, this time using a larger sample of sodium salt with a $2/5$ gram atom equivalent of iodine. This was for the purpose of obtaining a complete analysis of all the products. The solution of 3.3365 grams of the salt with .8682 grams of iodine in 150 c.c. benzene was made in a flask ground to fit the reflux. In this way the use of a connecting cork was done away with, in that way preventing any loss of halogen incurring thru adsorption on the connecting cork. To detect, and measure if necessary, loss of iodine and chlorine by volatilization a U-tube containing glass beads moistened with silver nitrate solution, was attached to the reflux. In this way, any escaping halogen would be taken up by the nitrate and converted to the corresponding silver salt. The flask was heated at 85° for three hours when the U-tube was removed as no change in the silver nitrate was apparent. The heating was then continued until the sodium salt no longer appeared as a residue. An analysis of the reaction mixture was made following the general procedure used in the analysis of the other decompositions made in benzene. The reaction mixture was filtered on a Buchner funnel using gentle suction, and the residue washed with benzene until free from iodine. The filtrate and washings were transferred quantitatively to a 500 c.c. flask and made up to volume.

Analysis of Residue

The above residue was sucked dry and taken up with water. This water solution was made slightly acid with nitric acid to precipitate any "unchanged sodium salt" as trichlorophenol. No precipitate was obtained here, but an absence of phenol at this point did

not indicate a complete transformation of the sodium salt, because the solubility of the phenol in water, as already determined, would prevent the detection of even appreciable quantities of sodium salt, a saturated solution containing the equivalent of .03 parts sodium salt to 25 parts water. The solution was then made distinctly acid with dilute nitric acid and silver nitrate added in excess. A voluminous precipitate consisting of silver chloride and silver iodide settled out. The silver salts were transferred to a Gooch crucible and washed free from silver nitrate and acid. Two o/o ammonium hydroxide was run through the Gooch until all of the silver chloride had been dissolved out, leaving the silver iodide as a residue. The weight of silver iodide obtained was .1708 grams. The iodine equivalent to this was .0921 grams which represented 10.61 o/o of the amount of iodine added recovered as iodide. The silver chloride was recovered from the ammonia solution by acidifying with nitric acid. The mixture was allowed to stand several hours before filtering in order that a complete and coagulated precipitate of silver chloride be obtained. The silver salt was then filtered on a Gooch and after washing and drying, was weighed. The weight of the chloride was 1.1026 grams, the chlorine content of which was calculated to be .2728 grams. This was 57.18 o/o of available ionisable chlorine, .5435 grams.

An analysis of the benzene soluble products was then undertaken.

Determination of Free Iodine

The same method of titration was used here as in the other titrations made in a benzene solution.

Three portions of the benzene filtrate made to 500 c.c., referred to in the above section, were titrated with sodium thiosulphate for iodine, and the average of the ratios taken.

	Benzene filtrate	Thiosulphate	Ratio
Titration 1	49.23 c.c.	5.89	8.358
Titration 2	45.68	5.53	8.262
Titration 3	41.44	5.02	8.254

Average ratio 8.291

1 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ = .01203 grams iodine.

The iodine determined for the total filtrate was .7260 grams.

This was 83.6 o/o of the sample added, .8682 grams.

Determination of Amorphous Oxide

250 c.c. of the benzene filtrate was evaporated to dryness on a water bath. A brown varnish-like residue identical in appearance with those obtained in the previous benzene decompositions remained. This was taken up with chloroform and as before, a deep red coloration was observed which gradually disappeared leaving a light brown solution. The oxide was extracted by the addition of alcohol in great excess, and transferred to a Gooch, washed with alcohol and sucked dry. The alcoholic filtrate and washings were heated on the electric plate to drive off any remaining chloroform which would tend to hold oxide in solution. This was found to be the case because after gentle heating for one-half hour a second slight precipitation of oxide was observed. This was added to the first and the whole again washed thoroughly with alcohol and dried, first by suction and later, after removing the oxide to a weighed watch

glass, by heating at 80° in the oven. The weight of the oxide was 1.1334 grams for 250 c.c., or 2.2668 grams for the whole sample. This was equivalent to 3.088 grams of sodium salt and represented a 92.2 o/o recovery of the sample taken.

An analysis of the oxide for halogen after the method of Carius was made.

Substance	.1654; AgCl,	.3007
Calculated for	(C ₆ H ₂ Cl ₂ O) _n	44.07
Found		44.97

Analysis of Alcohol Filtrate

The filtrate and washings from the oxide determination were evaporated to dryness on a water bath. A slight residue, brownish in color, remained and appeared to consist mainly of inorganic salts and a brown tar. In preliminary experiments in the early part of this work, a brown tar similar to this was easily obtained in appreciable amounts when iodine in greater quantities than a gram atom equivalent was used. This tar product will be studied later. The residue was extracted several times with water and to the water soluble portion was added nitric acid and silver nitrate. A fairly heavy white precipitate of silver salt was thrown down, a mixture of chloride and iodide. This was allowed to completely separate out, and after several hours was transferred to a Gooch. By washing with 2 o/o ammonium hydroxide until the washings showed an absence of silver chloride when acidifying with nitric acid, and reprecipitating with nitric acid, it was possible to separate the chloride from the iodide. The weight of silver iodide was .0436 grams, or

.0872 grams for the entire sample. The weight of iodine corresponding to this was .0471 grams. That is, 5.43 o/o of the iodine added was recovered as iodide from the benzene filtrate. The silver chloride found was .3007 grams, the chlorine content of which was .0744 grams. The percent of chlorine recovered from the benzene as chloride was 27.6 o/o of that available as ionized chlorine. It was not expected to find this inorganic salt present in benzene solution. Either sodium chloride and iodide were soluble in benzene to that extent or a small amount of water was present. Our conclusion here was that if water was present, it was there thru the sodium salt as great care had been taken to have the apparatus thoroughly dry for this work. A determination for water was made on the sodium salt by heating a weighed sample for two hours at 150°. The salt was found to contain a very small amount of water, 77 centigrams of the salt containing 2 milligrams of water. From the 3.3365 grams of salt introduced 9 milligrams of water would be freed. In view of the great solubility of the sodium chloride and iodide in water, this amount was judged sufficient solvent.

Summary of Analysis

Reaction mixture resulting when sodium salt was heated with 2/5 gram atom equivalent of iodine in benzene. Filtered.

Residue
sodium trichlorphenolate
sodium chloride
sodium iodide
Taken up with water acidified
with nitric acid
No precipitation of phenol

Filtrate
amorphous oxide
iodine
alcohol residue
made up to 500 c.c.

Slight amount of nitric acid
added
Silver nitrate in excess added
Filtered

Portions titrated for free iodine.
Found for sample .7260 grams.
83.6 o/o iodine added.

250 c.c. evaporated.
Residue chiefly amorphous oxide. Taken
up with chloroform and extracted with
alcohol. Filtered.

precipitate
silver chloride
silver iodide
washed with 2 o/o
ammonium hydroxide

Filtrate
thrown
away

Precipitate
oxide
found for
sample
2.2668
grams
3.088
grams
sodium
salt
92.2 o/o
of that
added

Filtrate evaporated
brown residue
taken up with water

residue
silver iodide
weight .17089
.0921 g.
iodine
10.61 o/o
iodine added

Solution
silver
chloride
acidified
with
dilute
nitric
acid
filtered

Residue
brown
tar
weight
.0398
.0542
sodium
salt(?)
1.6

Solution acidified
with nitric.
Silver nitrate
added. Filtered

precipitate
silver chloride
silver iodide
washed with 2 o/o
ammonium hydroxide

precipitate
silver
chloride
weight
1.10269
.2728 grams
chlorine
57.18 o/o of
chlorine
available in
sample

residue
silver
iodide
washed
and
dried
weight
for
sample
0.0872
grams
.0471
grams
iodine
5.45
o/o of
iodine
added

Solution
silver
chloride
Acidified
with nitric
acid.
Filtered.

precipitate
silver
chloride
weight for
sample .3007
.0744
chlorine or
.1487 for
total sample
27.6 o/o of
possible
ionized

chlorine

Methods for Determining Free Iodine in Benzene Solution

When the first benzene decomposition mixture was analysed for free iodine, the method of titrating the solution directly with standard thiosulphate was used. The titration was done in an ordinary beaker, stirring the two nonmiscible liquids together with a glass rod. The amounts of iodine calculated were so low, only 50 o/o of what was expected, and it was evident another method would be needed. Titrating directly a benzene solution of iodine with sodium thiosulphate appeared to be impossible.

Determination of Partition Coefficient of Iodine Between Benzene and Potassium Iodide

As a second method of determining free iodine in benzene, the use of the partition coefficient of iodine between benzene and potassium iodide was considered. Our idea was to determine this partition for a range of iodine concentrations, the minimum and maximum of which were to correspond with the concentrations used in the benzene decompositions. Having determined the partition coefficient, we would then shake together equal volumes of the unknown iodine solution and potassium iodide of the same strength used in the partition determinations, for a definite length of time. After the two liquids had separated, the potassium iodide solution was then to be poured away from benzene and titrated with thiosulphate for iodine. Having the partition value, it would be a simple matter to calculate the free iodine in the benzene solution. For the partition determinations, the following samples of iodine were used:

1. .3832 grams
2. .4309 grams
3. .4589 grams
4. .4621 grams
5. .5138 grams

These were all dissolved individually in benzene and made up to 100 c.c.; 50 c.c. portions were then shaken with the small amount of approximately N/10 potassium iodide in tightly stoppered separatory funnels for the same periods of time. This was done at room temperature. After the two liquids had separated into two well defined layers, the potassium iodide was poured away, transferred to a burette and titrated with thiosulphate for iodine, using starch solution as an indicator. The amount of iodine remaining in the benzene was found by the difference between the iodine dissolved and iodine determined in the potassium iodide solution. The ratio between these two values was taken as the partition coefficient.

The following values were obtained:

Sample 1. Weight of iodine .3832 grams.

	KI ₃	Na ₂ S ₂ O ₃ (factor 1 c.c. = .01212 I)
Titration 1	25.26 c.c.	5.37
Titration 2	23.32 c.c.	4.97

Partition from 1 = 2.049, from 2 = 2.068

Average 2.06

Sample 2. Weight of iodine .4309 grams.

Partition from first titration 2.207

Partition from second titration 2.202

KI ₃	Na ₂ S ₂ O ₃
26.44	6.47

added in small quantities, and the flask vigorously shaken after each addition. The amount of iodine determined checked with the amount used in making up the sample. A solution was then made containing a known amount of iodine to which was added some of the amorphous oxide; the point here was to ascertain whether or not the presence of the oxide would interfere with the titration. The average of several titrations was taken and the iodine calculated agreed with that used.

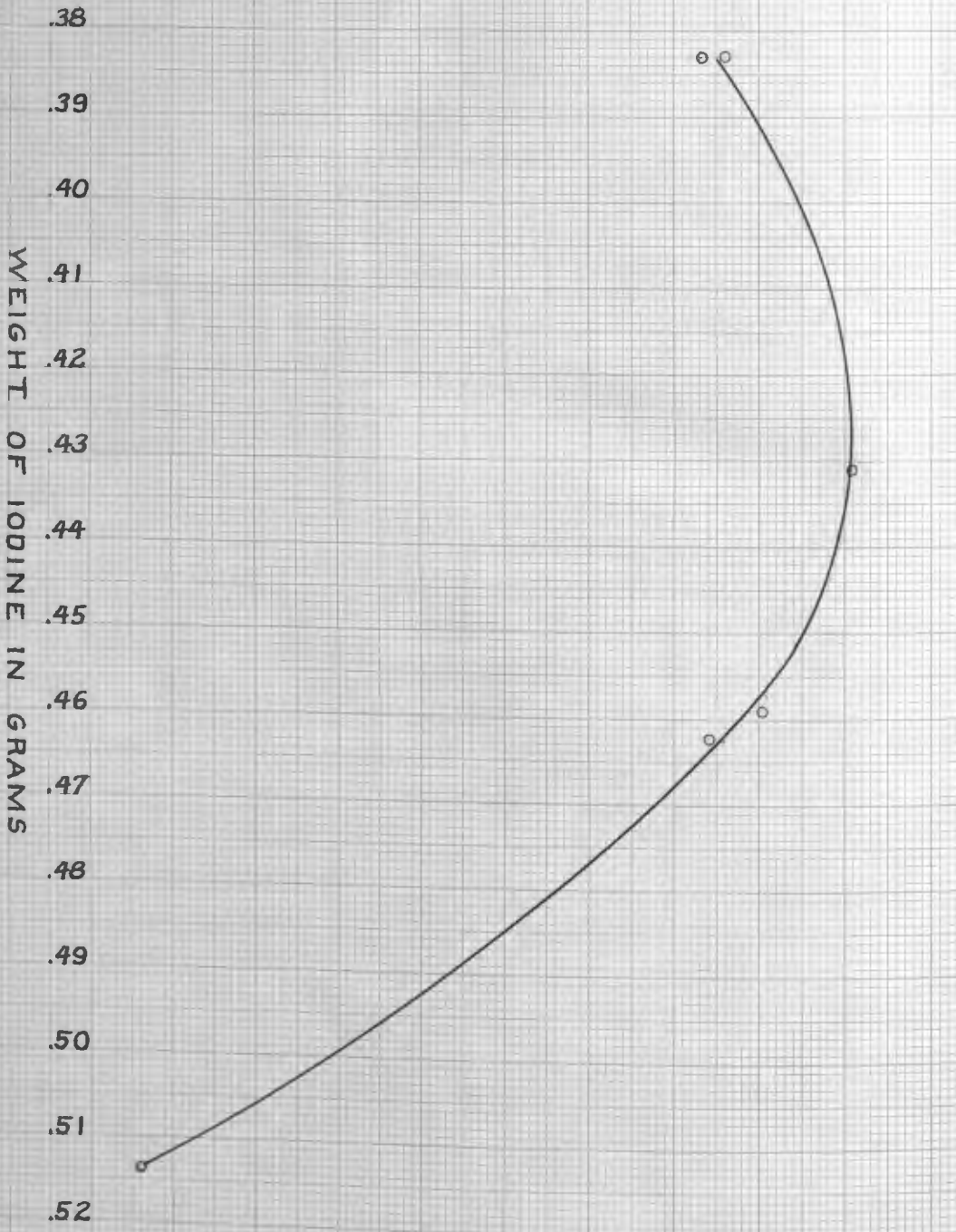
Iodine taken .5301, iodine found .5332.

PARTITION COEFFICIENT

2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30

.38
.39
.40
.41
.42
.43
.44
.45
.46
.47
.48
.49
.50
.51
.52

WEIGHT OF IODINE IN GRAMS



Sample 3. Weight of iodine .4589 grams.

	KI ₃	Na ₂ S ₂ O ₃
1	25.33	6.43
2	24.16	6.20
3	9.96	2.58

Coefficient 1 2.035
2 2.103
3 2.167
Average 2.101

Sample 4. Weight of iodine .4621 grams.

	KI ₃	Na ₂ S ₂ O ₃
1	18.93	4.83
2	18.45	4.77

Average
18.69 4.8

Coefficient = 2.04

Sample 5. Weight of iodine .5138

	KI ₃	Na ₂ S ₂ O ₃ c.c.
1	24.25 c.c.	7.78
2	26.13 c.c.	6.76

Average
25.19 7.02

Coefficient = 1.360

It was decided to work out a method of direct titration. A known amount of iodine was dissolved in benzene and an aliquot part titrated with the thiosulphate. The titration was carried out in an Erlenmeyer fitted with a ground stopper. The thiosulphate was