## Summary.

The amorphous oxides resulting from the catalytic decomposition of symmetrically trihalogenated phenol salts, occur in 2 isomeric forms when derived from tribromophenol and from tri-iodophenol. Of these, one is colorless, the other colored.

Several lines of evidence lead to the view that the colorless ones are mixtures, all made of varying numbers of residues of the 2 formulas
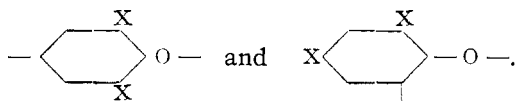


The colored ones contain, in addition, residues of the formula



No definite structure can be assigned to any of the polymerized compounds, which must be considered simply as "piles" of residues.

The point of most importance for the present research is the existence of quinoid residues of the composition $(= C_6H_2X_2 = 0)$.

MINNEAPOLIS, MINN.

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# A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. V. THE ACTION OF IODINE ON THE SODIUM SALT OF TRICHLOROPHENOL.

BY W. H. HUNTER AND LILLIAN M. SEYFRIED.

In the preceding paper it has been shown that very small amounts of iodine bring about the transformation of the potassium salt of tri-iodophenol into chromo-poly-di-iodophenylene oxide. In the first paper of this series[1] it was shown that traces of iodine were sufficient to change the silver salts studied into the colorless polyphenylene oxides.

The product of the reaction is in every case a substance of very high molecular weight, differing in composition from the phenol salt only by a single molecule of metal halide. For instance, omitting the iodine added, the equation for the transformation of the potassium salt of tri-iodophenol may be written

$$nC_6H_2I_3OK = nKI + (C_6H_2I_2O)_n.$$

[1] THIS JOURNAL, **38**, 1761 (1916).

This equation is identical in form with the one which expresses the thermal decomposition of silver salts of symmetrically trihalogenated phenols,[1] but it takes no account of the iodine with which the potassium salt reacts. Yet it appears impossible to accept any view of the action of the iodine, which does not consider it as abstracting the metal from the phenol salt in the first stage of the action. This first stage would be represented most simply by the equation

$$2C_6H_2I_3OK + I_2 = 2KI + 2C_6H_2I_3O—$$
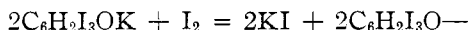
This explanation brings to light a new problem, that of the way in which the residue $C_6H_2I_3O$—loses an atom of iodine, to become the molecule $(C_6H_2I_2O)_n$, and it was for the purpose of gaining evidence on the nature of this action that the work described in this paper was undertaken.

It was decided that a simple method of attack would be to work out quantitatively the reaction between iodine and a salt such as sodium trichlorophenolate, with the object of demonstrating the fate of the iodine added, of the benzene ring, and of the sodium.

Our first experiments were designed to show the effect of using various amounts of iodine. Three solutions of sodium trichlorophenolate, in acetone, were heated for equal times with 0.1, 0.2, and one gram-atom equivalents of iodine, the other conditions being kept the same, except that more acetone was necessary in the third experiment. Yields of 2, 21 and 71% showed that the action increased with increasing amounts of iodine, as would be expected. A sample of the resulting amorphous substance was analyzed and found to be the expected poly-dichloro-phenylene oxide, first obtained by the thermal decomposition of silver trichlorophenolate.[1] This showed that the action of the iodine was entirely analogous to that on the potassium salt of tri-iodophenol, and as far as the ring was concerned, was represented by the statement

$$C_6H_2Cl_3ONa + I_2 \longrightarrow —C_6H_2Cl_2O—.$$
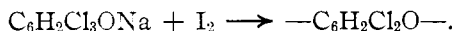
By longer action of $^2/_5$ of a gram-atom equivalent of iodine, over 65% of the salt was transformed into oxide, showing that the final yield which may be obtained is not limited by the amount of iodine added. Further, free iodine was still present when the action was stopped, so that the limit of action presumably had not been reached.

Two things are demonstrated by these experiments. First, the final yield of oxide which may be obtained, is not determined by the amount of iodine added, but by the time of contact. Second, the presence of free iodine at the end of the time allowed for the reaction, shows either that the iodine acts by its presence only, or that it is regenerated as fast as it is converted into sodium iodide. The latter hypothesis is much to be pre-

[1] THIS JOURNAL, 38, 1767 (1916).

ferred, and leads to the explanation of the fate of the chlorine atom which leaves the ring, although it does not give any explanation of the way in which it leaves the ring.

Quantitative determinations of all the reaction products were next undertaken. For this purpose the reaction was carried out in 2 ways. In one case, aqueous solutions of the sodium salt and of iodine in potassium iodide were allowed to react. In the other case, the dry salt was suspended in benzene and treated with free iodine. The results were alike in both cases, and are summarized below. Two-fifths of a gram atom of iodine was used in all experiments.[1]

Fate of Iodine.

| | Found free at end. % | NaI. %. | Unaccounted for. %. |
|---|---|---|---|
| Water solution | 76.3 | .. | 23.7 |
| Benzene solution | 63.6 | 10.6 | 5.8 |

There can be no doubt that most of the "iodine unaccounted for" in the water reaction was present as iodide, but determination of this was prevented by the use of potassium iodide as vehicle for the iodine. Possibly there was some loss by volatilization, in each case, though glass stoppers were used.

Fate of Sodium Trichlorophenolate.

| | Found as amorphous $(C_6H_2Cl_2O)_n$. %. | As trichlorophenol. %. | Tar. %. | Not found. %. |
|---|---|---|---|---|
| Water solution | 64.2 | 13.4 | ... | 22.4[a] |
| Benzene solution | 92.2 | .. | 1.6 | 6.2[b] |

[a] Remaining dissolved (by diff.).
[b] Presumably did not react.

Fate of Chlorine Removed from Ring.

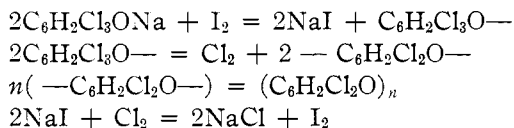| | Found as ionized chlorine. %. | As NaCl precipitate. %. | Unaccounted for. % of calc. yield. |
|---|---|---|---|
| Water solution | 97.8 | .. | 2.2 |
| Benzene solution | .. | 85.0 | 15.0 |

The fate of the various factors is thus made clear. The sodium salt which is not converted into oxide remains unchanged. The iodine added appears at the end in the free state, because the chlorine combines with the sodium. The chlorine which leaves the ring is finally converted into chloride, completely in the water solution, not completely in benzene.

The last statement is important. In the benzene, 15% of the lost chlorine does not appear as chloride. In this case, it was suspected that some of it might have substituted in the oxide, and on analysis this was found to contain 44.97% chlorine, as against 44.07% calculated. Also, 11% of the added iodine appeared as sodium iodide. This obviously

[1] Experiments were carried out in benzene using the hydrated salt, with closely agreeing results. They are not included in the table, as the analysis was not complete.

means that the chlorine did not split out as sodium chloride in the first instance, and makes it more certain that the iodine did actually attack the metal atom, only to be expelled by the chlorine.

It seems certain that every point in the action of the iodine has been cleared up, except the means by which the chlorine atom leaves the ring. This problem has been thrown into sharper relief by the work here described, and is being attacked further in this laboratory. Meantime, the action of the iodine may be expressed most simply by the following equations.

$$2C_6H_2Cl_3ONa + I_2 = 2NaI + C_6H_2Cl_3O—$$
$$2C_6H_2Cl_3O— = Cl_2 + 2 — C_6H_2Cl_2O—$$
$$n( —C_6H_2Cl_2O—) = (C_6H_2Cl_2O)_n$$
$$2NaI + Cl_2 = 2NaCl + I_2$$

## Experimental Part.

**Sodium Trichlorophenolate.**—Pure trichlorophenol was dissolved in the least possible quantity of hot alcohol, a slight excess of sodium hydroxide dissolved in a small amount of water was added and the mixture was evaporated to dryness on the water-bath. The residue was then heated at 150° in an air-bath for 3 hours, and allowed to cool. It was taken up in a minimum amount of dry acetone, in which it is very soluble, and the filtered solution of the sodium salt was poured into 15 volumes of toluene. This mixture was boiled until the salt started to precipitate, showing that most of the acetone had disappeared. On cooling, a heavy precipitate appeared, which was filtered, washed with benzene, and dried. A very satisfactory yield of practically pure and anhydrous salt resulted.

*Properties.*—The dry salt gives white, flaky crystals, easily soluble in water, alcohol, ether and acetone. A monohydrate can be obtained, which is stable in the air. The water content was determined by heating an air-dried sample to 100°.

> Subs., 0.995; loss, 0.078
> Calc. for $C_6H_2Cl_3ONa.H_2O$: $H_2O$, 7.60.    Found: 7.84.

The anhydrous salt is apparently unchanged by heating for a time at 220°.

**Action of Iodine in Acetone.**—Two g. of the anhydrous salt was dissolved with 0.12 g. of iodine ($^1/_{10}$ atom equivalent) in 20 cc. of acetone, and heated carefully at 45 to 50° for $^1/_2$ hour. Fifty cc. of alcohol was then added. A slight amount of amorphous oxide resulted, equivalent to a 2% yield. A distinct odor of halogen-substituted acetone was also observed.

A second 2-g. sample was treated in the same manner, with double the amount of iodine ($^1/_5$ gram-atom). The yield was increased to 20.7% of amorphous oxide.

Next a 4-g. sample was treated with 0.92 g. of iodine ($^2/_5$ gram-atom equivalent) in 75 cc. of acetone, heated 3 hours, and allowed to stand overnight.   Here a 65.4% yield was obtained, although free iodine was still present in the acetone.   The filtrate contained unchanged phenol salt and much sodium chloride.

Finally, a 2-g. sample was heated for 30 minutes with one gram-atom equivalent of iodine (1.26 g.) in 50 cc. of acetone.   This resulted in a 71.6% yield of amorphous compound.

A sample of this oxide was analyzed for chlorine.

Calc. for ($C_6H_2Cl_2O$): Cl, 44.07.   Found: 43.92.

**The Action of Iodine in Water.**—One g. of the salt was dissolved in water in a glass-stoppered flask, 0.23 g. of iodine ($^2/_5$-atom equivalent) in potassium iodide solution was added, and the whole made up to 500 cc. This mixture was allowed to stand in a dark place for one week.   A copious precipitate settled out, which was dried.   It was very slightly pink, but on dissolving in chloroform and precipitating with alcohol in the usual manner, it became white.   It amounted to 41% of the calculated yield.

*Effect of Light.*—The original filtrate from the water solution, containing unchanged salt and free iodine, was placed in sunlight.   The reaction was greatly hastened by this, as shown by the fact that within an hour a relatively large amount of precipitate appeared, which weighed about 0.2 g., or almost as much as had been obtained in the dark in a week.

*Presence of Ionized Chlorine and Unchanged Salt.*—The final filtrate from the action of light contained unchanged sodium salt, as a portion was acidified with dilute acetic acid, giving a heavy precipitate of trichlorophenol, readily soluble in alcohol.

Silver nitrate gave a voluminous precipitate, a large part of which was shown to be chloride by solution in dilute ammonia and subsequent precipitation with nitric acid.

For the purpose of a complete analysis of the reaction mixture, 4.501 g. of trichlorophenol was placed in a glass-stoppered Erlenmeyer flask and treated with the calculated amount of alkali necessary to make 5.00 g. of anhydrous salt.   To the mixture was added 2.799 g. of iodine ($^2/_5$ atom equivalent) dissolved in potassium iodide.   The final volume was 380 cc.

The mixture was allowed to stand in the dark for 10 days, with occasional shaking.   At the end of that time, a heavy precipitate was visible. This was filtered off with suction, as rapidly as possible, to avoid loss of iodine, and washed well, till the washings showed no iodine color.   The precipitate, which was a very light brownish-pink, was heated in the oven

to 140°, when it sintered somewhat, but gave no evidence of decomposition. It weighed 2.359 g., corresponding to 3.213 g. of sodium salt, or 64.2% of the original sample.

*Free Iodine.*—The filtrate and washings were collected in a liter flask and made up to volume. Three hundred and fifty cc. portions were taken out and titrated for free iodine, with the result that 76.3% of the original iodine was found to be free in the solution. The checks were very satisfactory.

*Unchanged Salt.*—Two hundred and fifty cc. of the solution were made slightly acid with nitric acid. A flocculent precipitate of trichlorophenol settled out, which was filtered on a Gooch crucible, washed, and weighed. The filtrate and washings were saved. The weight of trichlorophenol obtained was 0.1506 g., or 0.6024 g. for the whole reaction mixture. The equivalent amount of sodium salt is 0.669 g., or 13.4% of the original amount, making 77.6% accounted for. Since no other product than the amorphous oxide could be demonstrated in parts of the reaction mixture examined, it seemed that the rest of the sodium salt, 22.4%, was to be accounted for by assuming that the trichlorophenol had not been entirely precipitated from the original mixture by the nitric acid. To get an idea of the possibilities here, a rough determination of the solubility of the trichlorophenol was made.

Two samples of the phenol were shaken with distilled water in a thermostat at room temperature for 2 hours. During this time the temperature remained at 21.5°. From each flask 2 portions of 50 cc. each were converted into silver salt by adding 5 cc. of $0.2 N$ sodium hydroxide solution, and making just barely acid with 1% acetic acid, and then adding dilute silver nitrate solution in slight excess. After one hour the precipitates were filtered, washed with alcohol, and dried at 80°. The 4 precipitates weighed 1.1300 and 0.0469 g. for one pair, and 0.0502 and 0.0190 g. for the other pair. The solubility calculated from the pair of checks is 0.62 g. of trichlorophenol per liter; that calculated from the highest is 1.64 g. per liter. The trichlorophenol corresponding to the missing 1.12 g. of sodium salt is 1.01 g. for the liter of reaction mixture. Obviously, the determination was not highly satisfactory, but since one could not be performed in a solution corresponding to the reaction mixture without extreme difficulty, if at all, it was decided to accept the results as showing that the solubility of trichlorophenol was of the same order of magnitude as that of the missing amount.

It, therefore, seems clear that the original sodium salt may fairly be said to be all accounted for as amorphous oxide, $(C_6H_2Cl_2O)$ or as unchanged salt.

*Ionized Chlorine.*—For this determination we used the filtrate and washings from the 250 cc. portion which had been acidified for the pre-

cipitation of phenol. A little more nitric acid was added and an excess of silver nitrate. The resultant precipitate was extracted with dil. ammonia, which was filtered off and acidified. The chloride weighed 0.4464 g., equivalent to 0.1104 g. of chlorine, or 0.4416 g. in the original mixture. Of the 5 g. of original phenol, only 62.2% had been transformed into amorphous oxide. This must have lost one atom of chlorine for each molecule, which should appear as ionized chlorine. The amount found is 97.8% of the chlorine corresponding to this requirement. Two samples of the amorphous product derived from the action of iodine in water were tested for quinoid oxygen by the action of hydrazine, as described in the preceding paper. None was found.

### Decomposition in Benzene.

**Hydrated Salt** $(C_6H_2Cl_3ONa.H_2O)$ + $^2/_5$ **Atom Equivalent of Iodine.** —1.99 g. of this salt was suspended in 100 cc. of benzene containing 0.462 g. of iodine. The mixture was then heated in an Erlenmeyer flask under a reflux condenser until all of the phenol salt seemed to be transformed. After cooling, the condenser was rinsed with benzene and the contents of the flask were filtered. The precipitate of sodium salts was washed free of iodine with benzene, and the filtrate and washings were preserved and made up to 500 cc.

The residue was dried, dissolved in water, in which it was completely soluble, and made up to 250 cc. One hundred cc. was just acidified with dilute nitric. A very slight precipitate of trichlorophenol settled out after 2 days. It was filtered off, and silver nitrate was added. A yellowish precipitate resulted, showing the presence of chloride and iodide.

The benzene filtrate from the reaction mixture was then examined for free iodine, amorphous oxide, and trichlorophenol.

*Free Iodine.*—Fifty-cc. portions of the benzene filtrate were placed in glass-stoppered Erlenmeyer flasks and titrated with thiosulfate solution, while being shaken very vigorously; the pink color of the iodine was used as indicator.

The average of 3 agreeing determinations gave 0.388 g. of iodine, or 83.9% of the weight of iodine added.

*Amorphous Oxide.*—Two hundred cc. of the filtrate was evaporated over a water-bath and left a brown varnish. This was dissolved in a little chloroform and precipitated with alcohol. It was filtered, washed and dried. It was colorless and weighed 0.534 g., corresponding to 1.340 g. for the whole sample, a 91.5% transformation to oxide.

The alcoholic filtrate and washings were evaporated on the water-bath. A slightly colored residue remained, in which were found sodium chloride and iodide in small amount, and trichlorophenol. The inorganic salts were probably partly due to the continued action of the iodine on the

sodium trichlorophenolate, and partly to adsorption by the amorphous oxide.

**Anhydrous Salt with 2/5 G. Atom of Iodine.**—3.337 g. of the salt was suspended in 150 cc. of benzene, to which was added 0.868 g. of iodine. The mixture was heated under a reflux condenser in a flask attached by a ground joint. During the first part of the heating, a U-tube containing beads moistened with silver nitrate solution was attached to the top of the reflux condenser, but this was removed when it became clear that no halogen was being collected in this way. As before, the heating was continued until no further change in the sodium salt was visible.

A complete analysis of the mixture was then made. As before, the precipitate of sodium salts was filtered off, washed with benzene, dried and weighed. The benzene filtrate and washings were made up to 500 cc. with more benzene.

*Precipitate.*—Acidification of the solution in water produced no trichlorophenol precipitate, but, as was shown by the work on solubility, this did not mean an entire absence of trichlorophenol salt from the residue. Silver nitrate was added to the solution, whereupon a voluminous precipitate of silver chloride and iodide settled out. This was collected on a Gooch crucible, washed free from silver nitrate and acid, and then treated with 2% ammonium hydroxide until no silver chloride could be found in the washings. The crucible and silver iodide were then dried and weighed. The silver iodide weighed 0.1708 g., equivalent to 10.6% of the iodine added.

The silver chloride was recovered by precipitation with nitric acid. It weighed 1.1026 g., equivalent to 57.18% of the maximum chlorine which would have resulted if all the sodium salt had been used up.

**Analysis of Benzene Solution.**—The solution in benzene was analyzed as before for free iodine by titration of aliquot portions with aqueous thiosulfate solution, and for amorphous oxide by evaporation, solution in chloroform, and precipitation with alcohol.

*Iodine.*—The average of 3 agreeing titrations showed 0.726 g. of iodine in the total filtrate. This was 83.6% of the iodine added.

*Amorphous Oxide.*—For this $^1/_2$ the entire filtrate was taken. After the amorphous oxide had been precipitated from the chloroform solution with alcohol, the filtrate was heated half an hour. This resulted in the precipitation of a slight further amount of amorphous oxide. Otherwise the procedure was identical with that of the last analysis described. The weight of oxide, dried at 80°, was 1.1334 g., corresponding to 2.267 for the whole product. A sample from this preparation was analyzed for chlorine by the method of Carius.

Subs., 0.1654: AgCl, 0.3007.
Calc. for $(C_6H_2Cl_2O)n$: Cl, 44.07.   Found: 44.97.

This high halogen content probably shows substitution in the amorphous oxide, by the chlorine set free from the ring in the reaction.

*Alcohol Filtrate.*—The filtrate from the precipitation of the amorphous oxide by alcohol was evaporated to dryness on the water-bath. The residue consisted of a brown tar and a water-soluble residue of inorganic salts, presumably due to deferred action of the iodine on the sodium salt, and to adsorption. Undoubtedly the adsorbed part represents part of the "iodine unaccounted for."

This water-soluble part was acidified with nitric acid and treated with silver nitrate. The precipitate of silver chloride and iodide was separated by $2\%$ ammonia as before. The silver iodide weighed 0.0436 g., corresponding to 0.087 g. for the whole sample. This is equivalent to 0.047 g. of iodine, or $5.43\%$ of that added to the reaction mixture. The silver chloride was pure white and weighed 0.3007 g., corresponding to $27.6\%$ of the available chlorine, calculated from the yield of amorphous oxide.

The tar was separated and weighed. It weighed only 0.040 g. when dry, and if calculated as a polymerized residue, it corresponds to 0.054 g. of sodium salt, or $1.6\%$ yield.

## Summary.

The action of iodine on the sodium salt of trichlorophenol can be explained most easily as occurring in the following stages.

1. The iodine removes the sodium atom forming sodium iodide and an unsaturated residue, $C_6H_2Cl_3O$.

2. The unsaturated residue loses an atom of chlorine, which expels the iodine from the sodium iodide forming sodium chloride.

3. The new unsaturated residue polymerizes forming poly-dichloro phenylene oxide.

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# LOBINOL—A DERMATITANT FROM RHUS DIVERSILOBA (POISON OAK).

BY JAMES B. McNAIR.

The specific cause of skin poisoning from *Rhus toxicodendron* L., and its 2 sub-species, *R. diversiloba* T. and G., and *R. radicans* L., has thus far been attributed successively to an emanation of vapor,[1] a non-volatile substance,[2] a hydrocarbon gas,[3] a gum resin, mixed with a "subtil" acid

[1] S. Thompson, *J. Proc. Ham. Assoc.*, 8, 126 (1892); J. J. Bennett, "Plantae Javanical Rariores," 1838, p. 60.

[2] de V. Du Fresnoy, "Des caracteres, du traitement et de la cure des dartres et de la paralysie, etc.; par l'usage du rhus radicans," 1, Paris an VII. F. Fontana, "Trattato del veleno della vipera de velem Americani," 1, 148; 3, 114–117; *Napoli*, 1787. Translated by Joseph Skinner, 2nd Ed., 2, 181–184, London, 1795.

[3] J. B. Van Mons, *Actes soc. med. chir. pharm.*, [2] 1, 136–167. Bruxelles, 1797.