EXPERIMENTAL PART.

The Potassium Salt of Tri-iodophenol.

On account of its great solubility it was found impossible to prepare even moderate quantities of this salt in water or in alcohol. Recourse was had to a modification of the procedure devised by Atkins and Wilson[1] for preparing sugars in the anhydrous condition.

Fifteen g. of pure tri-iodophenol, made in the manner described before,[2] was dissolved in 125 cc. of benzene. Two g. of potassium hydroxide was dissolved in one cc. of water and 50 cc. of absolute alcohol. The 2 solutions were then mixed in a distilling flask and the solvents were distilled off, the temperature of the vapors being carefully noted. Probably on account of the presence of the hygroscopic salts, it was sometimes necessary to add more benzene before precipitation occurred. The gray-yellow precipitate of crude salt was filtered off, washed with benzene, and recrystallized from the minimum quantity of hot absolute alcohol, in which it is very soluble, placing the solution in a calcium chloride vacuum desiccator, which was kept attached to a water pump.

The crystals were grayish-yellow, becoming a full yellow on slight warming alone or in benzene. They decomposed on warming to $75°$ in air.

A sample from absolute alcohol, dried *in vacuo* over calcium chloride and ceresine without heating, was analyzed for iodine.

Subs., 0.2803, 0.2807; AgI (Carius), 0.3542, 0.3532.

Calc. for $C_6H_2I_3OK$: I, 74.66   Calc. for $C_6H_2I_3OK.C_2H_5OH$: I, 68.50.   Found: 68.30, 68.02.

It was then analyzed for potassium, using sulfuric acid.

Subs., 0.2686: K_2SO_4, 0.0429.

Calc. for $C_6H_2I_3OK.C_2H_5OH$: K, 7.05.   Calc. for $C_6H_2I_3OK$: K, 7.65.   Found: 7.17.

This alcohol-containing salt was grayish-yellow.

Alcohol-free salt.—Two g. of the alcoholate was dissolved in one cc. of absolute alcohol and 20 cc. of benzene was added. The solution was evaporated. The crystals so obtained were very slightly tinged with yellow while fresh, but became a full lemon-yellow on standing, or on being gently warmed.

A lemon-yellow sample was dried at 50 to $70°$ for half an hour and analyzed for iodine.

Subs., 0.1479; AgI, 0.2075.

Calc. for $C_6H_2I_3OK$: I, 74.66.   Found: 74.89.

Another sample was twice recrystallized and dried at $80°$.

Subs., 0.1103, 0.1555: AgI, 0.1511, 0.2145.

Calc. for $C_6H_2I_3OK$: I, 74.66.   Found: 74.01, 74.53.

[1] Atkins and Wilson, *J. Chem. Soc.*, **107,** 916 (1915).

[2] Woollett, THIS JOURNAL, **38,** 2475 (1916).

Another sample was slowly brought to 90°, without decomposition, and analyzed for potassium.

> Subs., 0.2924: K_2SO_4, 0.0502.
> Calc. for $C_6H_2I_3OK$: K, 7.65.   Found: 7.71.

All these heated samples were yellow, and did not appreciably change color in a year.

Properties.—The alcohol-containing salt is distinctly grayish-yellow, the alcohol-free salt lemon-yellow.   Both are extremely soluble in water, alcohol and acetone.

Effect of Halogens.—0.2191 g. of pure salt was dissolved in 5 cc. of carbon dioxide-free distilled water, and treated with 2 drops of 0.025 N bromine solution.   Purple spots immediately appeared where the drops fell.   The stoppered flask was allowed to stand overnight.   The resulting precipitate was found to weigh 0.1307 g., corresponding to a 94.7% transformation of the salt in this dilute solution.   The purple product was washed with water, then with alcohol, and analyzed for iodine.

> Subs., 0.1658, 0.1200: AgI, 0.2246, 0.1635.
> Calc. for $(C_6H_2I_2O)n$: I, 73.82.   Found: 73.20, 73.62.

The behavior of pure dry salt was different.   A sample exposed to a small amount of bromine vapor darkened on the surface, but did not become purple.   On wetting the sample after the action of the bromine, the characteristic purple color appeared at once.

Effect of Light.—Light was found to have a marked effect on the salt. Two samples of about 0.1 g. each were dissolved in vials with one cc. of carbon dioxide-free distilled water and stoppered.

Sample I was placed in a window not exposed to direct sunlight.   It began to turn purple in 2 days, the effect increasing for several days.

Sample II, kept in subdued light, showed no change in 6 days.   Placed in direct sunlight on the following day, it showed traces of purple color in 50 minutes, and the change proceeded fairly rapidly.

In each case, the first change appeared in the edge of the meniscus.

0.1694 g., in 5 cc., was kept in diffused light for 2 days, without change. On the third day it was exposed to direct sunlight for several hours and was found to have been decomposed to the extent of 94.8%.

The alcohol-containing salt was found to decompose at about 75° in a melting-point tube, while heating on a water-bath caused a larger sample to decompose rather rapidly, with evolution of iodine.

The alcohol-free salt, on the other hand, was stable to slightly over 100°.

Effect of Temperature on Color.—Both forms become more yellow on heating to temperatures below their decomposition point, and on cooling in thin tubes in carbon dioxide-ether mixture, a rapid loss of color, almost

complete, was observed. The color quickly returned on removal from the bath.

For purpose of comparison, samples of silver salts of trichloro-, tribromo-, and tri-iodophenols were treated in the same way, and found to behave in the same manner. The change was especially noticeable with the red form of the silver salt of tribromophenol, which became a light orange color, almost a yellow.

Potassium Salt of Tribromophenol.

This salt could not be prepared as easily as the potassium salt of tri-iodophenol, because it decomposed at the temperature of boiling benzene, giving potassium bromide and colorless poly-dibromo-phenylene oxide. Potassium bromide was identified by the usual tests, and the oxide by its properties and analysis for halogen.

Subs., 0.1471: AgBr, 0.2217.
Calc. for $(C_6H_2Br_2O)n:$ Br, 64.00. Found: 64.14.

It was found, however, that by using a pressure of only 3–4 cm. of mercury, the highest temperature reached was about 35°. The salt then came down as a white precipitate, which was boiled with chloroform to remove any tri-bromophenol. It then dissolved to a clear solution in water.

It gives small white needles from alcohol and benzene, with solubilities like those of the iodo derivative.

Action of Bromine.—A sample of the salt was wet with water and treated with bromine vapor. An orange-colored precipitate was formed, which could be separated into a colorless fraction and increasingly deeply colored fractions, by fractional precipitation with alcohol, from benzene solution. The orange fraction obtained was much more soluble than the white compound. It was analyzed for bromine.

Subs., 0.1522: AgBr, 0.2300.
Calc. for $(C_6H_2Br_2O)n:$ Br, 64.00. Found: 63.53.

Lautemann's Red (chromo-poly-di-iodo-phenylene oxide).—When this substance was desired in quantity, use was made of the following modification of a method due to Kammerer and Benzinger.[1] Ten g. of phenol and 111 g. of sodium carbonate were dissolved in a liter of boiling water. A solution containing 100 g. of iodine and 75 g. of potassium iodide was added to the phenolate little by little until free iodine remained in the solution. Dilute thiosulfate was then added until all the iodine had disappeared. The precipitate was washed with water and alcohol and dried at 100°. Substance of this degree of purity will be called "crude red."

It was a deep purple powder, insoluble in all aqueous solutions, in alcohol, and ligroin, quite soluble in carbon disulfide, ethylene dibromide,

[1] Ber., 11, 557 (1878).

and bromoform. From these solutions it is precipitated readily by alcohol or ligroin. It is very inert chemically, being unacted on by acids, alkalies, or the ordinary oxidizing agents. Much of the crude red was purified by boiling an hour or two with alcohol. This was designated "red purified by alcohol."

More was dissolved in carbon disulfide and precipitated by ligroin. Designated "red from carbon disulfide."

Lastly, part was dissolved in bromoform or ethylene dibromide, and precipitated by ligroin or alcohol. It was then designated "red from bromoform."

On treatment with carbon disulfide, dibromo-ethylene, or bromoform, a small amount was always found to be insoluble. This was saved, dried, and known as "insoluble red." Enough was gradually accumulated for analysis, when it proved to have a rather low iodine content.

<div style="text-align:center">

Subs., 0.1101: AgI, 0.1476.

Calc. for $(C_6H_2I_2O)n$: I, 73.82. Found: 72.43.

</div>

Molecular Weights.—To show the variation in molecular weights in different samples of Lautemann's Red, all those taken are tabulated here. Some of these also appear elsewhere. All are cryoscopic.

<div style="text-align:center">Bromoform, $K = 144$.</div>

	Solvent. G.	Sample. G.	Δ.	M. wt.
Sample from K salt..............................	100.0	1.0741	0.055°	2800
Sample acc. to K. and B. extracted with alcohol....	100.0	0.8131	0.050°	2300
Another preparation, same......................	100.0	0.6386	0.029°	3100

<div style="text-align:center">Ethylene Dibromide, $K = 118$.</div>

Sample acc. to K. and B. dissolved in CS_2, pptd. by				
ligroin......................................	50.0	0.5342	0.026	4800
From re-oxidation of saponified-acetyl derivative..	50.0	0.5232	0.022	5500
	50.0	1.0302	0.038	6400
	50.0	0.5258	0.015	8500
From silver salt................................	50.0	0.431	0.020	5100
	50.0	0.774	0.045	4100

Reduction.—It was found that Lautemann's Red could be reduced to a colorless powder by tin and conc. hydrochloric acid, by zinc and dil. sulfuric acid and by a solution of hydrazine sulfate in strong alkali. This colorless powder gave a solution in carbon disulfide, which regenerated the red oxide on treatment with lead or manganese dioxide.

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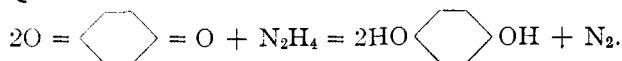
Quinoid Oxygen.

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An ordinary gas buret was attached by capillary glass tubing to a cork which fitted snugly into the mouth of a side-neck test-tube. Into the side neck was introduced a trigger to hold samples, the trigger being held by capillary rubber tubing.

It was found that this apparatus could be used to determine quinoid oxygen in 2 substances known to be true diphenoquinones, namely tetra-

bromo-diphenoquinone and cedriret, by allowing samples to fall into aqueous alkaline hydrazine solution, and determining the nitrogen evolved. One gram. of one-to-one potassium hydroxide solution, 9 cc. of water, and 0.5 g. of hydrazine sulfate were used for about one g. samples.

The usual precautions against local temperature changes were always observed. The reaction sometimes occupied 30 minutes. The temperature rarely varied during the determination as much as half a degree, which was considered negligible in our work. If the material did not become wet, another sample was moistened with 3 or 4 drops of alcohol before being introduced.

Known Quinones.—The reaction assumed was

$$2O = \langle \rangle = O + N_2H_4 = 2HO \langle \rangle OH + N_2.$$

Cedriret Tetramethoxy-diphenoquinone.
Subs., 0.1752.
Calc. quinoid O: 10.53.   Found: 10.57.

Tetrabromo-diphenoquinone.
Subs., 0.5034, 0.4700.
Calc. quinoid O: 6.4.   Found: 6.57, 6.42.

The apparatus was then used on various samples of "Red," which proved to vary in their content of quinoid oxygen. Each sample was allowed to stand, till no further gas was evolved, and was always white at this time.

"Red" Purified by Alcohol.

Subs., 0.593, 0.925, 0.663.

Calc. for true tetra-iodo-diphenoquinone: quinoid O, 4.65.   Found: 0.36, 0.40, 0.75.

"Red from CS$_2$."

Subs., I, 1.324, 0.7365; II, 0.9790, 0.9130; III, 0.579, 0.613, 0.768.   Found: quinoid O: I, 0.75, 0.81; II, 0.95, 0.91; III, 0.41, 0.39, 0.47.

Experiments on Splitting.

A sample of 27 g. of purest "red from carbon disulfide" was carried through the following steps, designed to split the molecule if possible. It will be called Stage A. Two and one-half g. of this amount was taken out for control and analyzed. The molecular weight was also determined and compared with that of the other samples.

Subs., 0.1407, 0.1085: AgI, 0.1915, 0.1471.

Calc. for $(C_6H_2I_2O)n$: I, 73.82.   Found: 73.54, 73.25.

Mol. wt. in purified ethylene dibromide ($K = 118$) by lowering of freezing point; solvent, 50 g.; subs. 0.5342; Δ, 0.026°.   Found: Stage A, 4800.

Subs., 0.473.   Found: quinoid O, 0.36

All the rest of Stage A was mixed with 13 cc. of 1–1 potassium hydroxide, 150 cc. of water, and 5 g. of hydrazine sulfate, and heated on the water-bath. The reaction began in the cold, proceeded rapidly with effervescence on heating, and was apparently complete in 20 minutes. The "Red" bleached out entirely, with no other visible change. The product

was filtered off, washed with water and alcohol, and dried. This, Stage B, now weighed 22 g.

> Out of it, 5 g. was taken for analysis.
> Subs., 0.1364: AgI (Carius), 0.1849.
> Calc. for $(C_6H_2I_2O)n$: I, 73.82. Found: 73.24.
> Mol. wt. using ethylene dibromide by freezing-point method.
> Solvent, 50 g. Subs., 0.5573, 1.0653.
> Δ, 0.029°, 0.051°. Found: Stage B, 4500, 5000.
> Quinoid oxygen: None.

Acetylation.—Seventeen g. of Stage B was heated with 75 cc. of acetic anhydride and 0.1 g. of ferric chloride over the free flame for 4 hours, at the end of which time a sample of the solid present, tested in carbon disulfide with lead dioxide, gave no red color. The product, Stage C, was poured into water, filtered, washed carefully, and dried. Four g. was saved for analysis, dissolved in carbon disulfide, precipitated by ligroin, dissolved in bromoform and precipitated, then washed, dried and analyzed.

> Subs., 0.1169, 0.1147: AgI (Carius), 0.1562, 0.1526. Found: I, 72.19, 71.88.
> Mol. wt., using ethylene dibromide.
> Solvent, 50 g. Subs., 0.5075, 1.0172. Δ, 0.026°, 0.058°. Mol. wt.: Stage C, 4600, 4800.
> Quinoid oxygen, none.

Hydrolysis of Stage C.—Eleven g. of the dried acetylation product was heated for 2 hours on the water-bath with 100 cc. of alcoholic potash, containing 5 cc. of 1–1 potassium hydroxide. The product was filtered off and boiled further with 75 cc. of water and 10 cc. of 1–1 potassium hydroxide for half an hour. It was again filtered off, washed and dried. About 10% had been rendered insoluble in carbon disulfide. This was filtered off and the colorless solution was divided into 2 equal parts. One part was precipitated by ligroin to give a sample of this Stage D. It was washed, dried and analyzed.

> Subs., 0.1422: AgI (Carius), 0.1928.
> Calc. for $(C_6H_2I_2O)n$: I, 73.82. Found: 73.25.

The original reduction product, Stage B, contained I, 73.24.

> Mol. wt., using ethylene dibromide.
> Solvent, 50 g. Subs., 0.5062; Δ, 0.022°. Found: Stage D, 5400.
> Quinoid oxygen, none.

Re-Oxidation to "Red,"—The second half of the carbon disulfide solution was shaken with 30 g. of lead dioxide for half an hour, filtered, and precipitated with ligroin. It was dissolved in bromoform and reprecipitated, washed and dried. This final regenerated Red may be called Stage E. It was identical in appearance with the original "red."

> Subs., 0.1335, 0.1321: AgI (Carius), 0.1827, 0.1795.
> Calc. for $(C_6H_2I_2O)n$: I, 73.82. Found: 73.93, 73.42.

Mol. wt., using 50 g. of ethylene dibromide. I, subs., 0.5232; Δ, 0.022°; II, subs., 1.0302; Δ, 0.038°; III, subs., 0.5258; Δ, 0.015°. Found: Stage E, I, 5500; II, 6400; III, 8500.

Subs., 0.631. Quinoid oxygen. Found: 0.36. Stage A contained 0.36.

Absence of Crystalline Derivatives.—Neither the "red" nor any of its derivatives, could be obtained in crystalline form, nor were any crystalline by-products ever obtained in the attempts at splitting the molecule. All the products gave brittle varnishes from carbon disulfide, easily splitting up on drying, to powders seemingly crystalline on casual inspection. They were all carefully examined with high and low power of a good microscope.

Tetrabromo-diphenoquinone.

This was made by the following modification of the procedure of Magatti.[1]

Diphenol was first made according to the method of Hirsch.[2] Twenty-five g. of benzidine was ground with 45 cc. of conc. hydrochloric acid and allowed to stand for 15 minutes. This mixture was then transferred to a flask, made up to 500 cc. with cold water, and diazotized with 18.5 g. of sodium nitrite in 100 cc. of water. The diazotized mixture was poured slowly into 3500 cc. of boiling water, containing 5 cc. of conc. sulfuric acid. The boiling was then continued vigorously by the use of steam, until frothing ceased. A dark precipitate separated, leaving a clear solution.

The precipitate was filtered on a plaited filter, as rapidly as possible. On cooling the filtrate, diphenol crystallized out in minute white flakes. About 5 g. of product was obtained in this manner at each preparation and it was found that crystallization from alcohol did not raise the melting point found, 270°, though the melting point is given as 272°.

This was converted into tetrabromo-diphenol as described by Magatti, by bromination in glacial acetic acid. The substance was recrystallized from alcohol, giving a white powder, melting at 269°. (Magatti gives 264°.)

Subs., 0.1089: AgBr, 0.1637.
Calc. for $(C_6H_2Br_2OH)_2$: Br, 63.73. Found: 63.96.

Tetrabromo-diphenoquinone.—Three and eight-tenths g. of tetrabromo-diphenol in 100 cc. of glacial acetic acid, was treated with 5 drops of fuming nitric acid and heated on the water-bath about 45 minutes. The blue-red crystals were filtered off and dried. They did not melt up to 278°. The substance is very sparingly soluble in ordinary solvents and separated from chloroform in tiny needles.

Quinoid oxygen was determined in this, and has already been reported on page 147.

Calc.: 6.40. Found: 6.57, 6.42.

[1] Magatti, *Ber.*, **13**, 226 (1880).
[2] Hirsch, *ibid.*, **22**, 335 (1889).

Cedriret (Coerulignone).—This was made according to the method of Graebe and Hess[1] from pyrogallol-1,3-dimethyl ether. About 2 g. of the ether was disssolved in 2 cc. of glacial acetic acid, and the mixture was diluted with 20 cc. of water. The calculated amount (0.2 g.) of sodium nitrite was then added, whereupon oxidation commenced immediately, with evolution of nitrogen dioxide and the separation of glistening purple needles of the cedriret. It resembled Magatti's quinone considerably.

Both of these quinones give the so-called coerulignone reaction with conc. sulfuric acid, dissolving to a deep blue color, which is more persistent with the cedriret.

Separations of Mixtures.

No difficulty was ever found in separating the true tetrabromodiphenoquinone of Magatti from the white amorphous poly-dibromophenylene oxide, whether they were mixed in solution or in the solid state. There seemed to be absolutely no tendency for these isomers to become adsorbed on each other. Each compound could also be easily identified in the solids resulting from evaporation of common solutions. Separation was effected by dissolving out the readily soluble white oxide in chloroform or benzene.

Absorption Spectra.

Apparatus.—The instrument used was a Hilger spectrograph, with quartz lenses and prisms, which was put at our disposal by the Department of Physics of the University of Minnesota. The source of light was an iron spark, the current for which was obtained by passing the lighting current through a transformer and a lamp bank. A Leyden jar was used in parallel with the spark gap.

A glass-stoppered cell of 6 cc. capacity, with parallel quartz sides, was used to contain the solutions.

The plates used were 4×10 cm. Cramer Spectrum plates.

Solutions.—Chloroform was used as a solvent, throughout. The initial concentration for the true tetrabromo-diphenoquinone was a saturated solution, containing 0.01% of the crystalline solid.

A saturated solution of Lautemann's Red was also used for the first exposure, and proved to contain very close to 0.2% solid.

The 2 bromine compounds were much more soluble and saturated solutions were not used. The initial concentration was 4.5% in each case.

Dilution was performed each time by removing 2 cc. of the solution from the cell with a pipet. This was replaced by 2 cc. of fresh solven and the resulting solution was carefully mixed.

Exposures.—The tetrabromo-diphenoquinone plate was exposed or 15 seconds, the Lautemann's Red plate for 25 seconds, and the plates f or the 2 amorphous compounds were exposed for 20 seconds each.
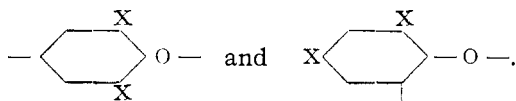
[1] Graebe and Hess, *Ann.*, **340**, 236 (1905).

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 ($= C_6H_2X_2 = O$).

MINNEAPOLIS, MINN.

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).