

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. VI. INTERMEDIATE STAGES¹

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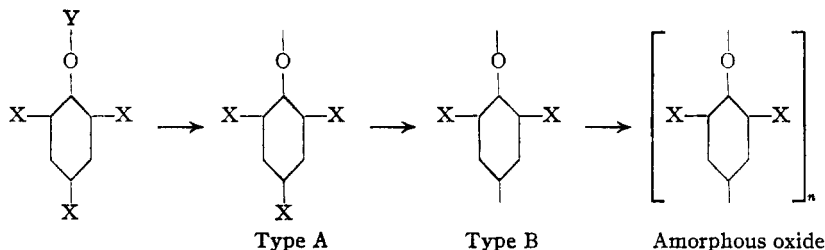
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In the earlier papers of this series it was shown that silver salts of trihalogenated phenols in the presence of ethyl iodide, hot benzene, or other catalysts, and also the alkali salts with small amounts of bromine or iodine, decompose to form a metal halide and an amorphous substance of high molecular weight. The latter has the formula $(OC_6H_2X_2)_n$, and the name polydihalogenophenylene oxide has been given it.²

Tribromophenol bromide, shown by Lauer to be the hypobromite of tribromophenol,³ loses bromine slowly on standing and gives the same polymer. Mercury accelerates this reaction.⁴ Similar amorphous oxides are formed by the oxidation of trihalogenated phenols.⁵

To account for these facts the hypothesis of the univalent (Type A) radicals and the bivalent (Type B) radicals was developed, according to which the general scheme is



This hypothesis has also proven useful in the study of the various products of oxidation of halogenated phenols.

Thus the formation of dinuclear quinones is accounted for by the union of two Type B radicals in the quinoid form, as for example in the interesting oxidation of tribromoresorcinol by Davis and Hill.⁶

Furthermore the production of such compounds as di-(trichlorophenoxy)-

¹ The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by R. B. Whitney in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1927. The manuscript for this paper was read by Dr. W. H. Hunter shortly before his death on August 19, 1931. Some final revisions suggested by him were not made until after his death.—R. B. W.

² Hunter and Woollett, *THIS JOURNAL*, **38**, 1761 (1916); Hunter and Seyfried, *ibid.*, **43**, 151 (1921).

³ Lauer, *ibid.*, **48**, 442 (1926).

⁴ Hunter and Woollett, *ibid.*, **43**, 131 (1921).

⁵ Hunter and others, unpublished work, and *THIS JOURNAL*, **48**, 1618 (1926).

⁶ Davis and Hill, *ibid.*, **51**, 493 (1929).

quinone by the oxidation of trichlorophenol⁷ seems to require the existence of both Type A and Type B radicals.

In the present work, further evidence for the existence of these radicals has been obtained from a study of the electrolysis of the silver salts of trihalogenated phenols in pyridine. The usual characteristic blue color, observed generally during the various decompositions, developed rapidly at the anode, and the amorphous polyphenylene oxide was isolated.

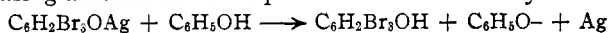
The work to be described in the remainder of this paper was undertaken in order to elucidate more clearly the nature of these intermediate stages.

It was known that both hydroquinone and triphenylmethyl discharge the intermediate blue color. In quantitative experiments, however, we could not find conditions under which more than one one-hundredth of an equivalent of either reagent was required to decolorize the solution, although the blue color, after being just discharged, would reappear, and this could be repeated several times.

Further experiments showed that the blue solution is instantaneously decolorized by unhalogenated or monohalogenated phenols and aromatic amines, an interesting exception being phloroglucinol. Alcohols and acids, however, do not have this effect.

Plan of Attack.—In the hope of arresting the decomposition at one of its intermediate stages, reagents capable of destroying the blue color were introduced before the reaction was started. The experimental conditions were varied, but in all cases were such that the amorphous oxide would have been formed if the inhibiting reagent had been absent.

The silver salts could not be studied in this way as they were found to be reduced by triphenylmethyl and by phenol. In the latter case there was formed an amorphous product similar to the usual amorphous oxide but containing less halogen. The percentage of halogen in it increased roughly with decreasing amount of added phenol. It seems likely that the reaction



occurring simultaneously with the usual decomposition would introduce unhalogenated phenyl groups into the polymer.

The alkali salts, on the other hand, do not decompose by themselves even after long heating at the temperature of boiling xylene. Their decomposition by iodine was studied by Hunter and Seyfried,² who showed that the usual amorphous oxide is formed in water, benzene, or acetone; that the rate of decomposition depends upon the amount of iodine used, although the iodine is recovered at the end; that the iodine attacks the sodium atom directly; and that loss of ortho or para halogen occurs later.

We chose to study this reaction in the presence of reagents which discharge the blue intermediate color.

Discussion of Experimental Results.—The result in each case was that

⁷ Hunter and Morse, *THIS JOURNAL*, **48**, 1615 (1926).

no amorphous oxide was formed, and that an iodination occurred, either of the inhibiting reagent or the solvent.

Iodination of Inhibiting Reagents.—Sodium trichlorophenolate was dissolved in an excess of dry, colorless aniline, and two equivalents of iodine were added. After a few minutes' gentle warming, the iodine color faded, and a white precipitate of sodium iodide formed. From the aniline solution an 85% yield of *p*-iodoaniline was obtained. No trace of the polyphenylene oxide was found. Ninety-five per cent. of the original trichlorophenol was recovered.

In order to learn whether any loss of halogen from the trichlorophenol had occurred, the *p*-iodoaniline fraction was examined carefully for chlorine but none was found.

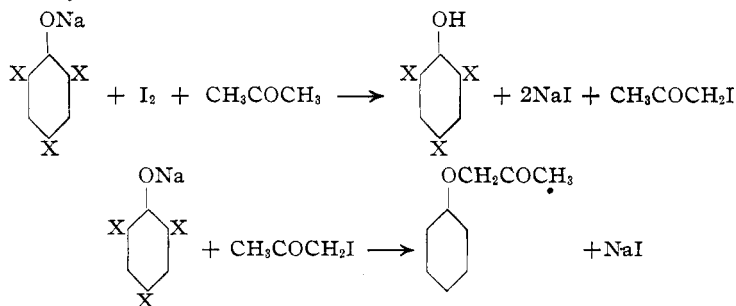
Sodium tribromophenolate gave similar results.

An equally smooth reaction was observed when iodine was added to solutions or suspensions of the sodium trihalogenophenolate under each of the following conditions: (1) in solution in molten phenol, (2) in suspension in dry ether containing one equivalent of phenol, (3) in suspension in dry ether containing one equivalent of dimethylaniline.

Iodination of Solvent.—Sodium or potassium trihalogenophenolates were dissolved in acetone (or acetophenone) in which one equivalent of phenol or dimethylaniline was present. Two equivalents of iodine were added. The iodine color faded, and with gentle warming disappeared in less than an hour.

The reaction products were sodium iodide, about half of the original trihalogenated phenol, and an acidic (in the case of dimethylaniline a basic) organic oil containing a small amount of iodine, and a white crystalline substance insoluble in both acids and bases. In each case this was found to be the acetyl ether of the trihalogenated phenol. No amorphous oxide was found.

The yields of acetyl ether varied between 40 and 70% of the amount required by the reactions



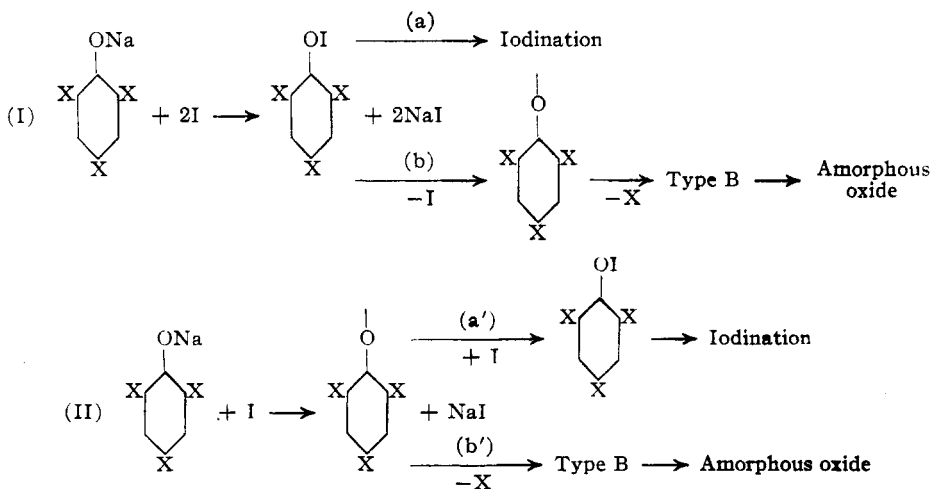
When mesitol was used in place of phenol, a 90% yield of the acetyl ether was found, a considerable quantity (about half) of the mesitol was recovered, and there was no iodophenol residue.

It was found that no more than two equivalents of iodine would react. If the amount of the inhibiting reagent (phenol or dimethylaniline) was decreased, the formation of amorphous oxide was still prevented, until only one-fourth of an equivalent of the reagent was present, when a small amount of the polymer formed.

Mechanism.—For these reactions to be of significance in the study of the halogenated phenol salts, it must, of course, be shown that we are not dealing with a direct reaction of the iodine upon the phenol, amine, or acetone. For this reason, parallel reactions were run in representative cases, omitting the halogenated phenol salts. Under these circumstances practically no reaction occurred. The direct iodination of aniline apparently took place after a long time, but gave much tar and practically no pure product. Hofmann⁸ had reported this reaction, but later investigators⁹ have been unable to obtain more than a minute amount of iodoaniline in this way.

That we are not dealing with a case of shifting an equilibrium by the removal of hydrogen iodide by the alkali salt is shown in the case of the acetone reaction, where sodium trihalogenophenolate and iodine cannot alone halogenate the acetone. Moreover, the action of iodine upon the sodium salts is fairly rapid, so that the complete absence of any amorphous oxide is independent evidence that an appreciable part of the iodination goes by way of an interaction between the iodine and the sodium salt.

Since the absence of any halogen excepting iodine in the products makes it unlikely that the Type B radical participates in these reactions, there are essentially two possible mechanisms



⁸ Hofmann, *Ann.*, **67**, 61 (1848).

⁹ Mills, *ibid.*, **176**, 354 (1875); Chattaway and Constable, *J. Chem. Soc.*, **105**, 124 (1914).

It might seem that a distinction between these mechanisms would be meaningless. However, there is one definite piece of evidence for mechanism II, and against mechanism I, namely, that in the analogous case of catalysis of the decomposition by bromine, a small amount of bromine causes fairly rapid production of the amorphous oxide, whereas the hypobromite of tribromophenol (tribromophenol bromide) is moderately stable under the same conditions, and loses halogen only slowly.

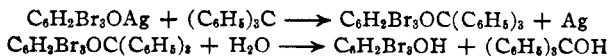
The simplest explanation of the surprising action of phenol or dimethylaniline in acetone seems to be that they can stabilize, *i. e.*, prevent loss of halogen from the Type A radical, until it has had time to form the hypoiodite (reaction IIa). The hypoiodite then iodates the acetone in preference to the inhibiting reagent merely because of the greater quantity of the former.

Experimental Part

Substances which Discharge the Intermediate Blue Color.—A small crystal of iodine was added to a dilute acetone solution of the potassium salt of tribromoresorcinol monomethyl ether. Solutions of various substances in acetone were added to portions of the resulting blue-green solution.

Those which discharged the color were aniline, mono- and dimethylaniline, α -naphthylamine, *p*-iodoaniline, benzidine, phenol, hydroquinone, hydroquinone monomethyl ether, resorcinol, resorcinol monomethyl ether, and α -naphthol and picric acid. In all these cases three or four drops of a dilute solution was sufficient. Those which had no effect upon it were tribromoaniline, acetamide, urea, *sym.*-diphenylurea, phthalimide, benzamide, tri- and pentahalogenated phenols, phloroglucinol, phenylethylcarbinol, allyl alcohol, benzoic acid, *p*-nitrobenzoic acid, *p*-chloronitrobenzene, hydroquinone dimethyl ether, anisole.

Reduction of Silver Salts by Triphenylmethyl.—An attempt was made to carry out the thermal decomposition of the silver salt of tribromophenol in the presence of triphenylmethyl. Fifteen grams of the silver salt was suspended in 100 cc. of dry benzene in an inert atmosphere. An excess (about two equivalents) of triphenylmethyl was introduced, and the suspension was stirred and warmed by steam for six hours. The red color of the silver salt disappeared, and a black precipitate formed. The solution was decanted and the precipitate washed with benzene. Upon treatment with dilute nitric acid, the precipitate was mostly dissolved, and approximately 4.5 g. of silver chloride was obtained from the solution (one equivalent). The combined benzene solutions were stirred in the air and allowed to stand overnight. The triphenylmethyl peroxide was filtered off, and the benzene evaporated under reduced pressure. The residue was a sticky mass. Continued extraction in a Soxhlet apparatus with fractol left a residue of triphenylmethyl peroxide. Upon evaporation the fractol solution gave a dirty yellow powder. Repeated attempts to crystallize it failed to separate it into pure constituents, so the solids were heated with water for several days, then extracted with dilute potassium hydroxide. The residue contained no halogen, and after one recrystallization melted at 157 to 160°. It was triphenylcarbinol. Upon acidification the alkali solution yielded tribromophenol. It seems likely that the original organic product was triphenylmethyl tribromophenyl ether and that the following reaction occurred



Reduction of Silver Salts by Phenol.—A series of experiments was made in which 5 g. of the silver salt of tribromophenol was covered with dry benzene, varying amounts of phenol added, and the mixture heated in a water-bath for two hours. No blue color developed, but instead the benzene became orange-colored, and a gray solid was left.

The solid was filtered, extracted with sodium thiosulfate to remove silver bromide, then treated with dilute nitric acid, from which the silver was precipitated as silver chloride.

The benzene solution was evaporated under reduced pressure and the residue extracted with alcohol. The portion insoluble in alcohol resembled the amorphous oxide, but was more soluble in ether.

The alcohol extract was concentrated to 25 cc. and diluted to 300 cc. with water, precipitating tribromophenol. The water solution, upon treatment with bromine water, gave a precipitate of tribromophenol, indicating a small amount of unchanged phenol.

Carius bromine analyses were run on four samples of the amorphous ether-soluble material. Molecular weight determinations in benzene showed no appreciable depression. The yields of the various products were roughly determined.

Phenol used, g.	0	0.2	0.6	1.3	1.4	2.0
Ag recovered, g.	0	0.3	...	0.75	...	0.8
AgBr recovered, g.	2.1	1.5	...	0.95	...	0.8
Tribromophenol recov., g.	0	1.2	...	2.2	...	3.0
Br in amorphous oxide, %	64.0	...	55.7	34.0	37.8	...

Iodination of Aniline.—This reaction was carried out in several concentrations with the same results. The following is a typical experiment. Ten grams of the anhydrous potassium salt of trichlorophenol¹⁰ was dissolved by gentle heating in 40 cc. of dry aniline. Eleven grams (two equivalents) of iodine was added during five minutes. The mixture was heated overnight on the steam-bath, leaving a pale reddish solution with a white precipitate; 100 cc. of water was added, then 50 cc. of 2 *N* potassium hydroxide solution. The mixture was then shaken well and steam distilled. The aniline came over much more rapidly than the *p*-iodoaniline; as soon as any sign of solidification was observed in the condenser, the receiver was changed. The solid distillate was recrystallized from alcohol. It melted at 62.5 to 63°. This was not changed by twelve recrystallizations. The original product weighed 8 g.; there was obviously more in solution in the aniline.

The residue in the flask was a pale reddish solution. It was acidified; the precipitated trichlorophenol after one recrystallization weighed 8.3 g., 95% of the theoretical quantity.

The identity of the *p*-iodoaniline was established by preparing its acetyl derivative, m. p. 183.5°, and by mixed melting points with known samples prepared both from *p*-nitroiodobenzene, and from acetanilide by the action of iodine monochloride.

To make sure that the halogen was all iodine, the following analyses were made on samples recrystallized only twice, and on samples recrystallized twelve times.

Anal. (Carius). Calcd. for C₆H₅IN: I, 57.96. Found: I, 57.84, 57.66, 57.72, 57.96, 57.72. The silver iodide was converted to chloride; ratio of AgCl to AgI, calcd. 0.6105. Found: 0.6090, 0.6119, 0.6111, 0.6124.

Acetyl Ethers of Trihalogenated Phenols.—The general procedure was to dissolve 5 g. of the sodium salt of a trihalogenated phenol in 50 cc. of dry acetone. One equivalent

¹⁰ Hunter and Seyfried, *THIS JOURNAL*, **43**, 154 (1921).

lent of ordinary phenol was then added (in one case dimethylaniline was used), then one equivalent of iodine. The solution was heated under a reflux condenser for one hour. The acetone was then evaporated, and the residue extracted with one normal sodium hydroxide. The insoluble part was washed with water and recrystallized from alcohol and water. In general, a 40 to 75% yield of the acetonyl ether was obtained, and about half of the original trihalogenated phenol was recovered. After the latter had been precipitated by acidifying the solution, evaporation left a brownish tar, mostly phenol but containing a small amount of iodophenol.

The acetonyl ethers were pure after two or three recrystallizations. Their constitution was established by analysis and by preparing chloroacetone by the method of Fritsch¹¹ and reacting this with the sodium salts of trichlorophenol and tribromophenol. This reaction took place rapidly by warming the two reagents together without a solvent. Acetonyl ether of tribromoresorcinol monomethyl ether, m. p. 83°.

Anal. (Carius). Calcd. for $C_{10}H_9O_3Br_3$: Br, 57.54. Found: Br, 57.81, 57.66. *Mol. wt.* Calcd.: 417. Found: 381. Zeisel methoxyl, Calcd.: 7.43. Found: 7.37, 7.54, 7.19.

Acetonyl ether of trichlorophenol, m. p. 75°. *Mol. wt.* Calcd.: 253.5. Found: 258, 253. Acetonyl ether of tribromophenol, m. p. 111.5°. *Anal.* (Carius). Calcd. for $C_9H_7O_3Br_3$: Br, 62.00. Found: Br, 62.37, 62.56. Acetonyl ether of triiodophenol, m. p. 131.5°. *Anal.* (Carius). Calcd. for $C_9H_7O_2I_3$: I, 72.13. Found: I, 72.03, 71.92.

To make sure that the strong alkali used in recovering the ethers had not caused their formation from some other substances, the procedure was modified in one experiment by pouring the acetone solution into a liter of cold water, filtering, and recrystallizing fractionally from water and alcohol, in which the acetonyl ether was less soluble. No difference was noted.

In order to learn how little phenol was capable of preventing the formation of amorphous oxide, two reactions were carried out, each using 1.41 g. of sodium tribromophenolate in 15 cc. of acetone and 0.51 g. of iodine (four millimoles of each), but in the first only two millimoles of phenol, and in the second one millimole of phenol were used.

In both solutions the iodine disappeared completely overnight. Upon dilution with alcohol, no precipitate formed in the one in which half an equivalent had been used. A slight precipitate of amorphous oxide formed in the other.

Summary

1. Various phenols and amines prevent the normal decomposition of trihalogenated phenol salts.
2. The presence of these reagents in the reaction of iodine upon alkali trihalogenophenolates results in iodination of the inhibiting reagent, excepting when the solvent is acetone, in which case the acetone is iodinated, producing finally the acetonyl ether of the trihalogenated phenol.

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¹¹ Fritsch, *Ber.*, **26**, 597 (1893).