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

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. II.

THERMAL DECOMPOSITIONS: THE FORMULA OF THE UNPOLYMERIZED RESIDUES.

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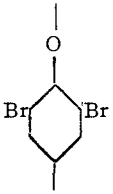
In the further study of the decompositions of the silver salts of symmetrically substituted halogenated phenols described in a former paper,[1] one of the first questions to be considered was the position of the halogen atom removed with the silver. In the silver salt of 2,4,6-tribromophenol, for instance, it is impossible to decide whether the loss of silver bromide results in the formation of an unsaturated residue of the formula



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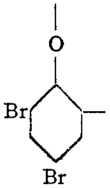
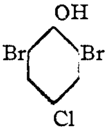
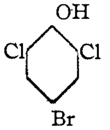
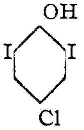


since the polymerized product would have the same composition in either case.

A very simple means for testing this point, was found in the decomposition of the silver salts of symmetrically halogenated phenols, having the same halogen in the two ortho positions, and a different one in the para position. The phenols chosen were







The phenols were made with great care, by direct halogenation of *p*-chloro- and *p*-bromophenols. Each of the monohalogenated phenols was purified by distillation, before transformation, and the trihalogenated phenols were crystallized to constant melting points and analyzed before conversion into the silver salts.

The silver salts were carefully made in the manner described in the first paper, and two of them were analyzed for a check on the method, though this seemed hardly necessary, in view of the uniformly good results heretofore obtained in this way.

It then remained to bring about their decomposition. It had been found that cold ethyl iodide brought about the decomposition of the dry salts of four phenols of like structure,[2] and that the same decomposition

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

[2] *Loc. cit.*

could be brought about by heating the salt in benzene. Since the use of ethyl iodide brought in a second source of halogen, it was decided to use the thermal decomposition on all of the salts, and then check this up by a catalytic decomposition of one of those not containing iodine. The only assumption involved is that the reaction would proceed in the case of these salts, in as smooth a manner as had been demonstrated for the four salts previously reported.

The oxides were readily obtained by a short boiling with benzene, in fair yield, which could probably have been raised by longer boiling. Two samples of each were analyzed by the method of Carius, and the resulting precipitates were dissolved in potassium cyanide for silver determination, this giving values for both of the halogens. Good agreement was always obtained.

The 2,6-dibromo-4-chloro salt, which would have lost all of its chlorine if the reaction had gone para only, was found to give an amorphous oxide containing 10.24% of chlorine, as an average of two closely agreeing determinations. This corresponds to the presence of 59.4% of a residue of the formula C_6H_2ClBrO, in the polymerized products, showing that in this salt 59.4% of the molecules had split out to form a residue with bromine gone from one of the ortho positions, for each chlorine present represents an *o*-bromine removed.

The 2,6-dichloro-4-bromo salt gave an oxide containing 11.95% bromine. This corresponds to 30.7% of the isomeric residue C_6H_2ClBrO and to a 30.7% removal of ortho chlorine. Here, then, the para position is the one preferred.

The 2,6-diiodo-4-chloro salt gave an oxide containing 8.75% chlorine corresponding to a 62.3% of the residue C_6H_2ClIO and to a 62.3% removal of *o*-iodine.

The ortho and para positions had then reacted in the following percentages[1] in the three salts:

	2,6-Dibromo-4-chloro.	2,6-Dichloro-4-bromo.	2,6-Diiodo-4-chloro.
Reacted *o*..............	59.4	30.7	62.3
Reacted *p*..............	40.6	69.3	37.7
Ratio *o* : *p*..............	1:0.86	1:2.26	1:0.61

These figures show very clearly that when silver halide is split out of the molecule of a trihalogenated phenol salt by heating in benzene, the

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[1] The values of these ratios are of course not accurate within several per cent. of error, as they depend on a halogen determination made by indirect analysis. For instance, a negative difference of 1 mg. in the weight of the silver found in the first analysis for the thermal decomposition of the 2,6-dibromo-4-chloro salt, would change the bromine found from 49.48% to 51.15%, the chlorine from 10.09% to 9.75%. This would change the "reacted *o*" in the table above to 56.47%, and the "reacted *p*" to 43.53%. The "ratio" then becomes 1:0.77, a change of over 10%. It is believed that this is considerably greater than our experimental error, judging from the agreements found in our analyses.

halogen atom may come from either the ortho or the para position. There seems to be evidence of a tendency to prefer the para position, and also for the silver to take out iodine rather than bromine, and bromine rather than chlorine.

The last statement is based on the following reasoning: in the 2,6-dibromo-4-chloro salt, there is twice as much chance to take out a bromine atom as to take out chlorine. If the reaction occurred in accordance with simple chance, the ratio of removal would have been two bromine atoms to one chlorine. Instead, the ratio is roughly seven to six. This speaks for a preference of para over ortho.

The same reasoning applied to the 2,6-dichloro-4-bromo salt, would lead to an expected ratio of two chlorine atoms to one bromine, when the actual ratio is more than the reverse, or four to nine. Here, then the para atom is very much preferred to the ortho, and the difference is simply the presence of bromine in the para position. The preference here, then seems to be a double one, of para over ortho, and bromine over chlorine.

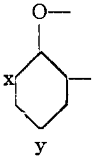
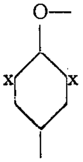
One would expect, then, that iodine would have a still greater effect than bromine. The only evidence available lies in a comparison between the 2,6-diiodo-4-chloro and the 2,6-dibromo-4-chloro salts. Here it is found that more molecules split out iodine than had split out bromine, against the same *p*-chlorine effect in both cases, the ratios being approximately seven to six and ten to six, respectively.

Attention was next turned to the action of the silver salt of 2,6-dibromo-4-chlorophenol with cold ethyl iodide. This was carried out exactly as with the salts described in the first paper. It was expected that halogen would be removed from both positions as in the thermal decomposition, and this was found to be the case. The oxide formed contained 11.97% chlorine, as against 10.24% from hot benzene, corresponding to a somewhat higher percentage of molecules (69.3%) reacting in the ortho position, as against 59.4% in the hot benzene.

There can be no doubt then, that the same sort of change is occurring in both the thermal decomposition and the catalytic decomposition with ethyl iodide, and that some determining feature is present in such molecules, which allows the silver to escape readily from the oxygen atom, taking out a halogen atom at the same time. One such factor has already been suggested in the previous paper: a stress inside the molecule between the silver atom and the halogen atom it removes. It now seems more probable that this is not limited to a single halogen atom, but is acting on all three to different extents. Whether this is the sole reason for the smoothness of the reaction, or whether the physico-chemical structure of the solid salt will eventually have to be considered in this connection, remains to be decided by further work, part of which is already in hand.

Summary.

The silver salts of symmetrically substituted phenols containing two atoms of one halogen in the ortho position and an atom of a second halogen in the para position, decompose smoothly in hot benzene.

Some of the molecules split out the silver with a halogen atom from the ortho position, giving a residue of the form ; others react in the para position, giving 

The ratio between these actions varies widely between different salts, but is reproducible in a given salt, as shown by two preparations from the salt of 2,6-diiodo-4-chlorophenol.

The decomposition of the silver salt of 2,6-dibromo-4-chlorophenol by ethyl iodide at ordinary temperatures showed a higher number of molecules "reacting *o*" than was found in the decomposition by hot benzene.

There are slight indications of a preference of the para position over the ortho, and of the halogens in the order iodine, bromine, chlorine.

In the decompositions noted in the first paper, of phenols having but one kind of halogen, it is certain that halogen must have been abstracted from ortho positions in some molecules, and para in others.

Experimental Part.

4-Chloro-2,6-dibromophenol.—This phenol, hitherto undescribed, was made by bromination of purified *p*-chlorophenol in glacial acetic acid. The calculated amount of bromine was added cautiously, causing development of heat. The mixture was allowed to cool, and water was added, causing a precipitate, which was filtered with suction, washed once with water. On recrystallization from alcohol, long, shiny needles were obtained, melting at 92°. It was analyzed.

Substance, 0.2995; AgBr + Ag Cl, 0.5434.

Calc. for $C_6H_2ClBr_2OH$: Cl + Br = 68.21. Found: 68.28.

4-Chloro-2,6-diiodophenol.—This was also made from *p*-chlorophenol. 20 g. of this were dissolved in excess alkali. To this were added a solution of 13 g. of potassium iodate, and another of 31.8 g. of iodine dissolved in alkali. The whole was placed in a two-liter bottle, and gradually acidified with dilute sulfuric acid, with continual shaking. Iodine was set free in considerable amount. The shaking was continued for an hour on the machine, at the end of which time the precipitated phenol had collected in small pellets, deeply colored with iodine. Dilute potassium bisulfite solution was then added till the iodine color disappeared, and the precipitate was filtered. It was crystallized repeatedly from alcohol, giving a light yellow, powdery product, melting at 107–108°. It was analyzed.

Substance, 0.3170; AgCl + AgI, 0.5099.
Calc. for $C_6H_2ClI_2OH$: Cl + I = 76.07. Found: 75.90.

4-Bromo-2,6-dichlorophenol.—Ling[1] had prepared this phenol by the action of sulfuryl chloride on *p*-bromophenol. We prepared it by the direct chlorination of purified *p*-bromophenol, by passing chlorine into a glacial acetic acid solution until the calculated increase in weight had occurred. On cooling, the acetic acid solution precipitated long, glistening crystals, which were filtered and washed with dilute acetic. On crystallizing twice from alcohol and water, they proved to have exactly the same melting point as Ling's preparation, *i. e.*, 66.5°. On this account they were considered as pure, and were not analyzed.

Silver Salts.—All the silver salts used were made in the manner described by Hunter[2] and others, by precipitation from purified solutions of the alkali salts. The precipitates of silver salts were washed well with water, spread out in thin layers on glass to dry in the air, and finally dried in a desiccator before using.

Silver Salt of 2,6-Dibromo-4-chlorophenol.—This salt was orange when first precipitated, but gradually turned white spontaneously. The color of the original precipitate was very close to that of the red form of the silver salt of tribromophenol, which also has a white form.

A sample of the salt was analyzed.

Substance, 0.1121; AgBr + AgCl, 0.1474.
Calc. for $C_6H_2Br_2ClOAg$: Cl + Br = 49.67. Found: 49.48.

Cold ethyl iodide readily gives the catalytic decomposition characteristic of such salts, with formation of the usual evanescent blue color. There is also formed considerable of the normal product, the 2,6-dibromo-4-chlorophenetol.

2,6-Dibromo-4-chlorophenetol.—Since this had not been described, it was made in good yield by treating some of the silver salt with ethyl iodide in alcohol. It resembled the ethers of trihalogen substituted phenols in every way. Long needles from alcohol and water, soluble in ordinary solvents. Melting point 52.5°. It was analyzed.

Substance, 0.0956; AgBr + AgCl, 0.1592.
Calc. for $C_6H_2Br_2ClOC_2H_5$: Br + Cl = 62.15%. Found: 62.07%.

Action of Hot Benzene on the Silver Salt.—Two grams of the dry salt were boiled for twenty minutes in benzene, under a reflux condenser.

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[1] *J. Chem. Soc.*, **61**, 560 (1898).

[2] THIS JOURNAL, **38**, 1766 (1916).

The precipitate was filtered off, and alcohol was added to the benzene filtrate. A heavy precipitate of amorphous oxide resulted. This was purified by twice dissolving in benzene and precipitating with alcohol. It was then dried below 100° for analysis. Yield, 0.76 g. Two samples were analyzed for total halogen as usual, by the method of Carius. The precipitates were then dissolved in potassium cyanide solution and electrolyzed.

Substance, 0.1504, 0.1250; AgBr + AgCl, 0.2361, 0.1960; Ag, 0.1465, 0.1220.
Found: Br, 49.48, 48.81; Cl, 10.09, 10.40.

Action Cold Ethyl Iodide.—10 g. of the dry silver salt were covered with 75 cc. of undiluted ethyl iodide in the cold. Soon a bluish green color appeared, which was not as deep or as blue as that shown by the salt of tribromophenol, and soon disappeared.

On filtering from the silver salt, it was found that the ethyl iodide contained a large amount of amorphous oxide, precipitated by alcohol, and much of the substituted phenetol. The amorphous oxide was purified by alternate solution and reprecipitation, three times, dried, and analyzed as above.

Substance, 0.2827, 0.2393; AgBr + AgCl, 0.4450, 0.3758; Ag, 0.2794, 0.2366.
Found: Br, 46.86, 46.71; Cl, 11.72, 12.22.

Silver Salt of 2,6-Dichloro-4-bromophenol.—This salt resembles the salt of trichlorophenol. It is yellow, and shows no tendency toward more than one form. It reacts with cold ethyl iodide very readily, giving a deep blue solution. A sample was analyzed.

Substance, 0.2437; AgBr + AgClO, 0.3342.
Calc. for $C_6H_2Cl_2BrOAg$: Cl + Br = 43.23. Found: 43.62.

Action of Hot Benzene.—Five grams of the dry salt were decomposed by boiling in benzene. This decomposition seemed to proceed like the decomposition of the salt of trichlorophenol, no definite blue or green color being visible at any time, and very great difficulty being experienced in filtering the benzene. Finally, 0.8 g. of dry amorphous oxide was obtained and analyzed for halogen, and the precipitates were dissolved and electrolyzed for silver.

Substance, 0.2660, 0.1970; AgBr + AgCl, 0.4608, 0.3415; Ag, 0.3333, 0.2473.
Found: Cl, 35.82, 35.99; Br, 12.11, 11.80.

Silver Salt of 2,6-Diiodo-4-chlorophenol.—This salt is nearly white, with a faint tinge of lemon-yellow. No more than one form could be isolated. Cold ethyl iodide did not bring about the abnormal reaction in a reasonable length of time, but hot ethyl iodide produced a vigorous reaction, with appearance of a deep blue color. This is exactly in accordance with the behavior of the silver salt of triiodophenol.

Action of Hot Benzene.—This action is very vigorous, and an intense blue color is developed in the solution, gradually fading out. The benzene again contained amorphous oxide, which was purified, dried and analyzed. The precipitate from the Carius was weighed and then extracted with 2% ammonia to separate the iodide and chloride.

Substance, 0.1176; AgI, 0.1284; AgCl, 0.0404. Found: I, 58.98; Cl, 8.49.

Another sample was then made, and analyzed, using the cyanide method for the indirect analysis. The composition was close to that of the previous sample.

Substance, 0.2033; AgI + AgCl, 0.2924; Ag, 0.1560. Found: I, 58.09; Cl, 9.01.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

ORGANIC ADDITIVE COMPOUNDS OF POTASSIUM HYDROXIDE.

BY WILLIAM M. DEHN AND RUTH E. MERLING.

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When benzoic acid reacts with potassium hydroxide in aqueous solution, the following equations are universally regarded as adequate to describe the mechanism of chemical reaction:

$$\mathrm{PhCOOH + KOH \longrightarrow}$$
$$\mathrm{PhCOO^- + H^+ + K^+ + OH^- \longrightarrow PhCOOK + H_2O},$$

for here we are dealing with a simple case of the action of an acid on a base. Preliminary ionization, followed by the formation of non-ionizable water, is assumed to be the *sine qua non* of this reaction.

The ionic theory rests so securely on experimental facts, interprets so many chemical phenomena, and is grounded so universally in chemical opinion, that sight is frequently lost of the fact that it rests on assumptions and possibly may color and mislead. Its interpretation of the mechanism of chemical reaction of acids and bases require: (1) preliminary ionic dissociation of both the acid and the base, (2) subsequent association of their ions to yield molecular salt and molecular water, and (3) association of the salt with water to form the hydrated salt.

Since the experimental facts of this paper are not at all in agreement with these assumptions, we shall re-open for discussion the ionic interpretation of the interaction of acids and bases.

According to this theory the first phenomenon of a chemical reaction is *dissociation.* The reality and possibility of initial dissociation are especially questioned by the findings of this paper. For when brought together in anhydrous ether, not only acids and bases but also a host of other reactive compounds yield *additive* compounds, as the first and, in most cases, the only recognizable products. Therefore, the alternate view, that of *initial association,* instead of dissociation, presents itself. Now, it cannot be denied that the first chemical activity is either a disso-