ON THE ELECTROLYTIC REDUCTION
OF TRIBROMORESORCINOL.

A thesis submitted to the Chemistry
Department of Washington and Lee
University as a partial fulfillment
of the requirements for the degree
of Bachelor of Science in Chemistry.

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[Under the direction of Mr. John Robert Taylor]

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Introduction

In the studies of halogen substituted resorcinols conducted by the Chemistry Department at Washington and Lee University, considerable work was done by Lewis Daniel Williams [1] on the preparation of 2-substituted resorcinols by reduction. The main purpose of Mr. Williams work was the improvement of the yield of a reaction reported by Davis and Harrington [2] in which tribromoresorcinol was made to yield 2-Bromoresorcinol by alkaline reduction with sodium sulfite.

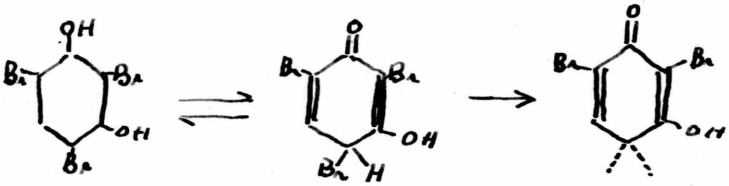
Mr. Williams met with great success in his work but a new approach to this reduction was suggested by Mr. John Robert Taylor, to wit, the reduction of tribromoresorcinol by electrolysis in acid media because, first, alkaline solutions have a strong tendency to darken and yield tarry products as a side reaction, and secondly, because the usual mild reducing agents apparent only operate in alkaline media.[1]

As a result of discussions with Mr. Taylor, it was decided to conduct this work along three lines. 1. To check agreement of electrolytic reduction if any, with Davis and Harrington's reduction mechanism. 2. To devise and attempt to perfect a new [electrolytic] reduction process to improve the yield of 2-bromoresorcinol and 2,4-dibromoresorcinol. 3. To attempt to carry the reduction all the way to resorcinol and correlate in some way the decomposition voltage, if reproducible, of each stage in the process in order to determine qualitatively the bond strength of the three bromine-carbon bonds.

I wish at this time to express my sincere gratitude to Mr. Taylor for his enthusiastic and optimistic support and for the multitude of essentially important suggestions and criticisms by which he guided the course of this work.

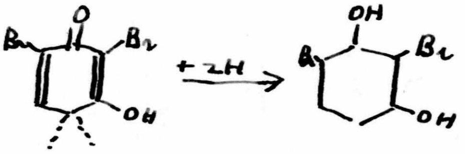
The Reduction of Tribromoresorcinol.

That tribromoresorcinol acts as an oxidizing agent is evidenced by the fact that it readily oxidizes stannous chloride and sodium sulfite. It liberates iodine from hydriodic acid or from potassium iodide in alcoholic solution in the characteristic ''quinone'' fashion. These facts together with others led Davis and Harrington to consider the reduction mechanism one involving tautomerization to a pseudoquinone which breaks down into hydrogen bromide and a quinyl radical[2].



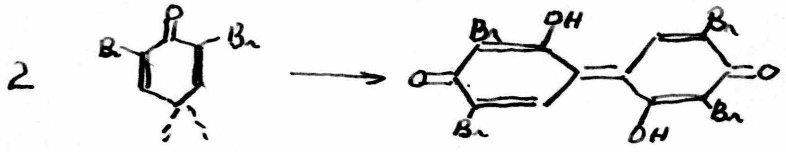
Quinyl Radical

A suitable reducing agent will furnish two hydrogen atoms to form:



Dibromoresorcinol,

As further proof of the existence of the quinyl radical, there is a strong tendency for dilute alkaline or warm neutral solutions of the tribromoresorcinol to form tarry polynuclear products:

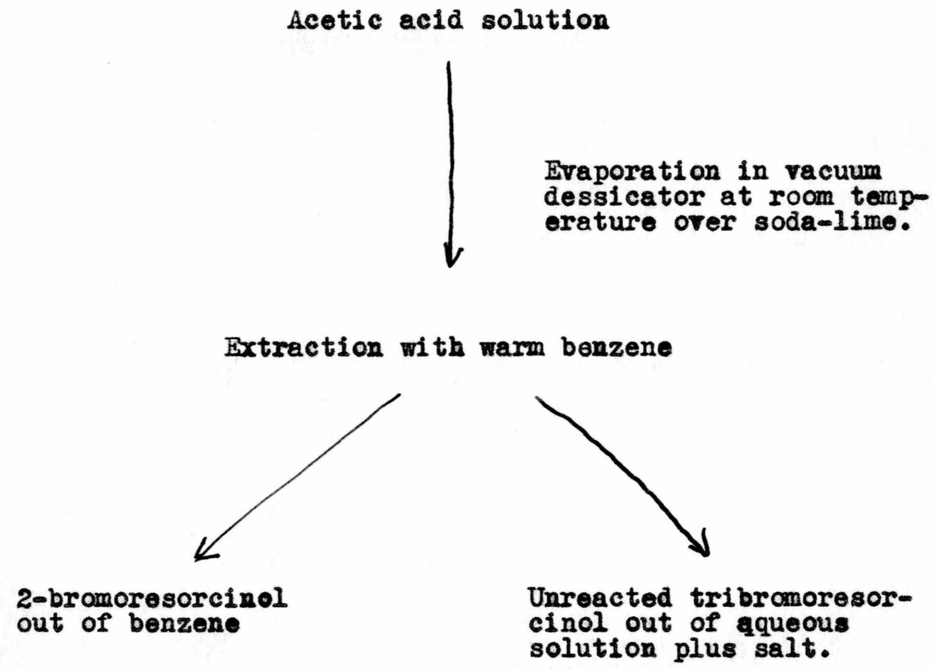


33'-55' Tetrabromo 2-2' dyhydroxy
p-xenoquinone[2] or
—diphenyl quinone

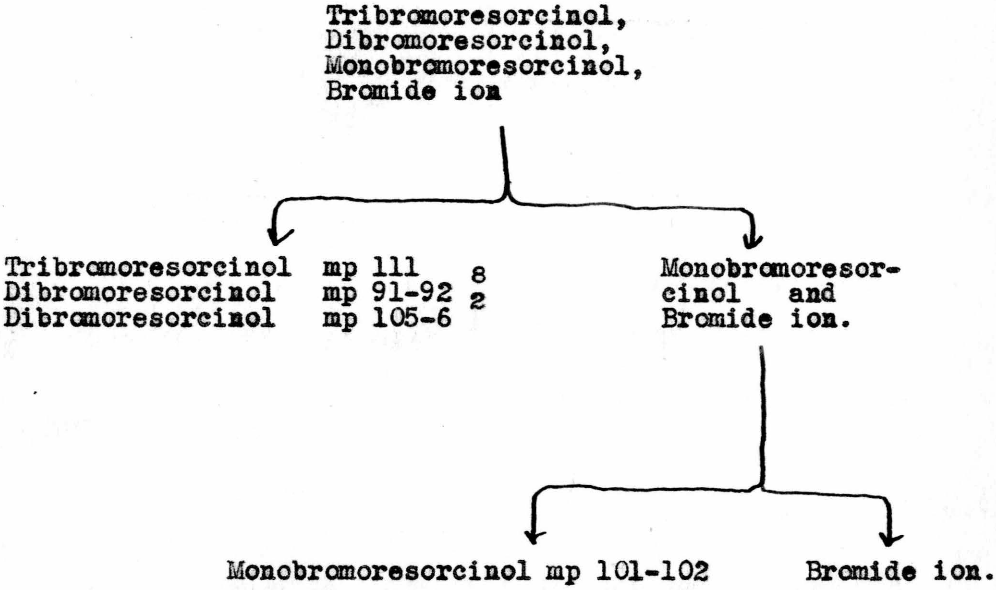
The color of these products vary according to circumstances from deep brownish-red to brown and black and are evidently oxidation products involving the elimination of two molecules of hydrogen bromide between two molecules of the resorcinol.

By modifying the procedure of sodium-sulfite-in-alkali reduction by keeping the temperature at or below room temperature throughout, Williams [1] greatly improved the yield of 2-bromoresorcinol over Davis and Harrington. It was hoped that an electrolytic reduction process in acid solution could be developed.

The general procedure for isolation of the products in acetic acid solution was as follows:



The general procedure for determination of bromine and isolation of products in alkaline electrolysis was as follows:



Tribromoresorcinol,
Dibromoresorcinol,
Monobromoresorcinol,
Bromide ion

Tribromoresorcinol mp 111 [8]
Dibromoresorcinol mp 91-92 [2]
Dibromoresorcinol mp 105-6

Monobromoresorcinol and Bromide ion.

Monobromoresorcinol mp 101-102

Bromide ion.

So far as it was able to be discovered, this electrolysis had never been recorded in the literature so that innumerable problems were encountered as might be expected with a new line of investigation. And since speed was of the utmost importance, identification consisted mainly in melting points.

Carrying out the investigation on the three fronts outlined in the introduction, it was found that:

1. At no time was free bromine discovered during the course of the reaction, but always the bromide ion. This points to agreement with Davis and Harrington [2] that the reduction was either an addition of hydrogen to the conjugated system in the quinone or the addition of hydrogen to the pseudoquinone radical.

2. In the matter of devising and perfecting a process for obtaining 2-bromoresorcinol in good yield, all attempts were apparently fruitless as no mono- or di-bromoresorcinol could be found in the products. Large amounts of the tribromoresorcinol were recovered in nearly all cases and the other products, if any, were in such small

quantity that only a melting point could be made.

3. The attempt to correlate voltage with extent of reduction to discover relative bonding strength of the three bromine atoms, followed two courses. a. By increasing the voltage stepwise with time and determining the extent of dehalogenation by titrating aliquots withdrawn with silver nitrate before each voltage increase. Steps in the voltage--bromide-liberated curve would be functions of the three decomposition voltages and the corresponding current density at each voltage. This method had to be abandoned in alkaline solution because it lacked sufficient accuracy and was complicated by tar formations and excessive darkening. b. By ''complete'' electrolysis of separate portions of a solution at successively higher voltages. This would increase the accuracy of the bromide titrations because of the presence of more material. This attempt, however, likewise failed due to the difficulty of determining completeness or even equivalent stages in the reaction.

Experimental

Apparatus. The preliminary electrolysis was carried out between two platinum electrodes, platinum gauze and a platinum foil rotating electrode to accomplish the stirring. In such a cell, a voltage of 1.7 or above will evolve hydrogen and oxygen. Any decrease in this evolution at the cathode, for example, indicates the presence of an oxidizing depolarizer; similarly, a reduction of oxygen evolution indicates the presence of a reducing depolarizer.[5]

Most of the apparatus had to be designed hurriedly and built more or less from scratch and required continual modification as the situation demanded. The set-up shown below, Fig. 1 , with the squat test tube was used for its convenience in handling a number of small volumes of solution.

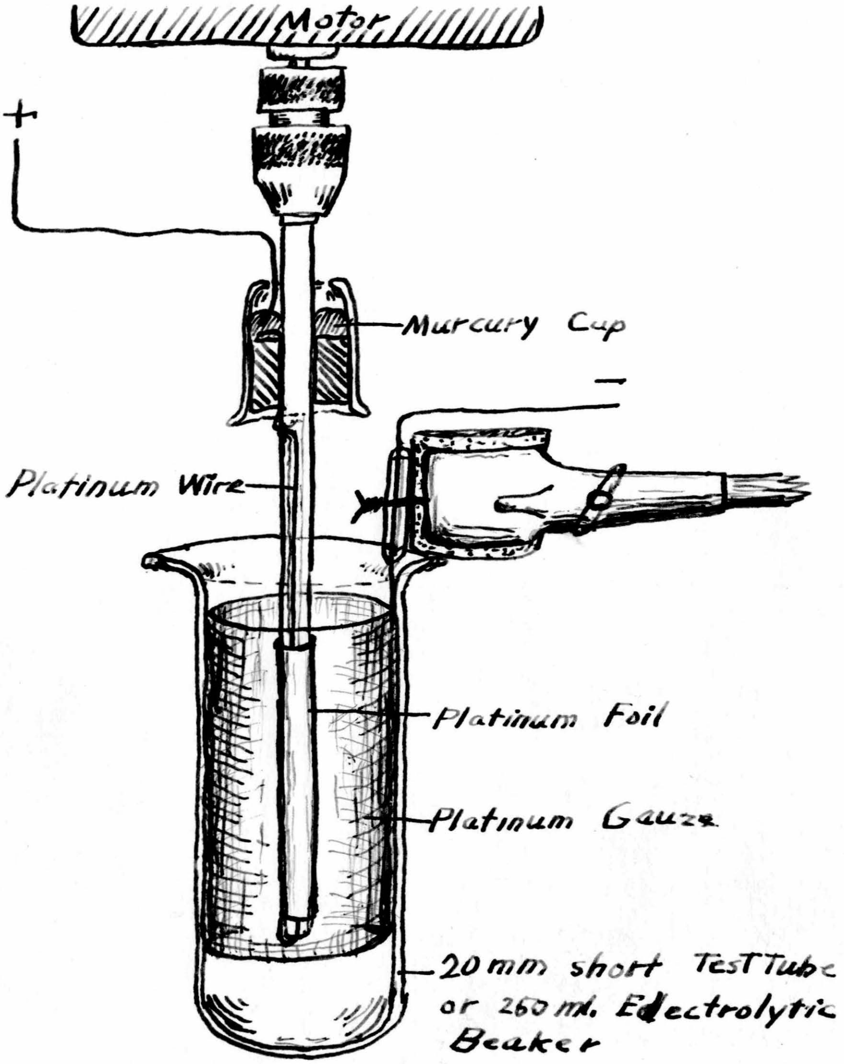


Fig. 1

For the attempt at determining decomposition potentials of the depolarizer and subsequent electrolysis, a potentiometer was required to maintain a top or peak on the known voltage. Accurate determination of the voltage would have been difficult at best because of wide fluctuations or ''dips'' that occurred periodically. The double-pole double-throw knife switch [I] when ''up'' Fig. 2, by-passes completely the potentiometer, [shown diagramatically within the broken line] and permits wider voltage ranges but limits the accuracy to tenths of a volt and hundredths of an ampere. Switch [II] is thrown up only to ''set'' the potential drop across the potentiometer. The 10,000 ohm resistance was used to protect the standard cell and galvanometer. The potentiometer ''roof'' was used in all the preliminary decomposition voltage experiments until it became evident that the reaction was not clear-cut by any means but was accompanied by considerable oxidation at the anode. A few trials were run at higher voltages, but it became clear as time went on that a divided cell was necessary.

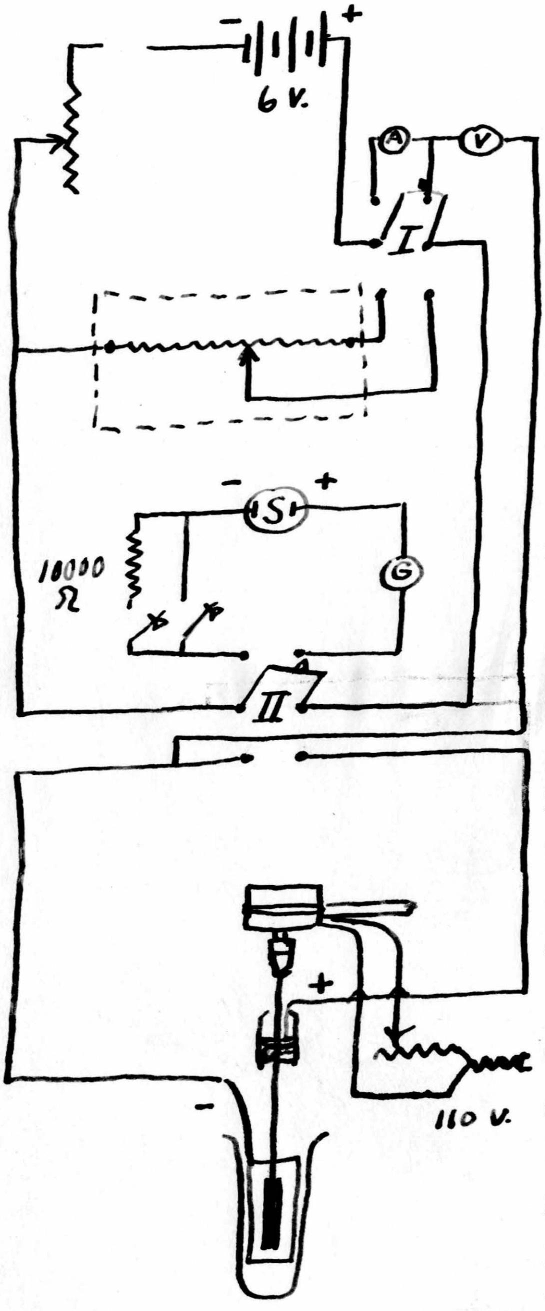


Fig. 2

The first divided cell was constructed of a twenty mm test tube out of which a large hole had been blown. [See Fig. III on next page.] The hole was sealed over with a diaphram or ''window'' of cellophane. The platinum gauze anode was wrapped around this cathode compartment and the whole suspended in a 250 ml. electrolytic beaker. The outside or anode compartment contained a sodium hydroxide solution of the same strength as the catholyte to avoid diffusion, but the cellophane was so softened when wet that it became very fragile necessitating frequent replacement.

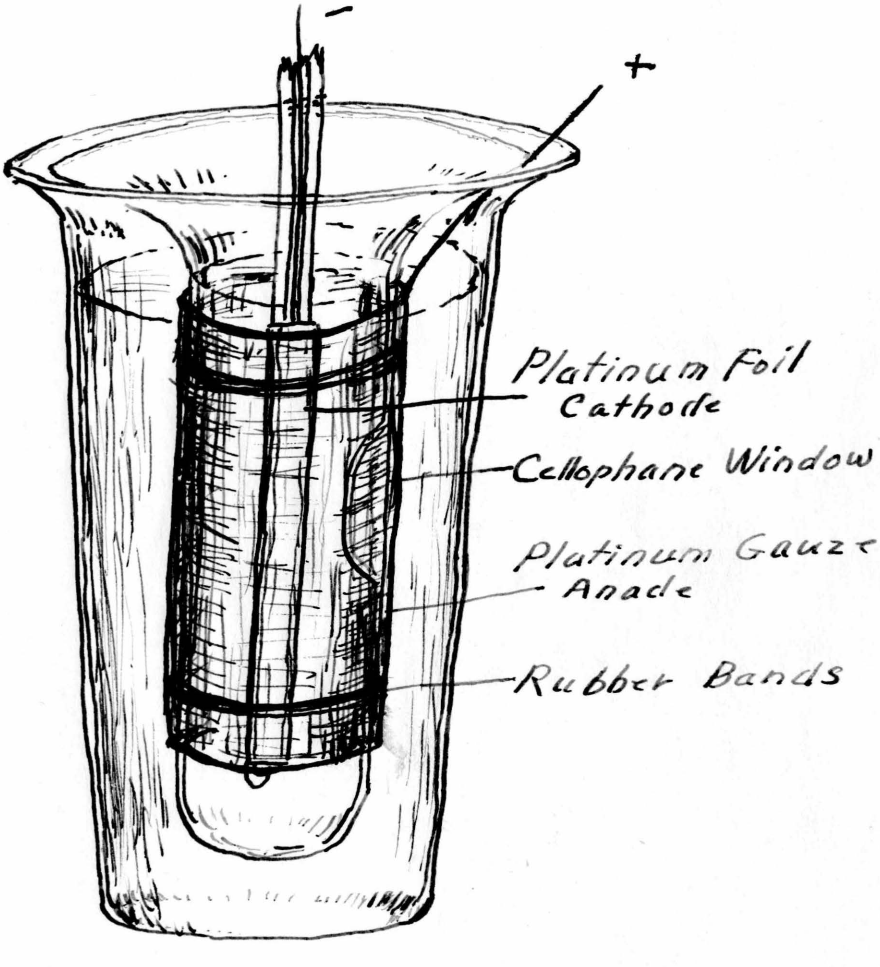


Fig 3

Recourse was then made to a porous cup to divide the cell. This cup was constructed from an old radiant heater coil-form after the holes had been closed with fused glass. [See Fig. IV on next page.] A discussion of the problems met with up to this point lead to the conclusion that a higher overvoltage on the cathode would increase the probability of cathodic depolarization over anodic, and perhaps increase the reduction reaction at the expense of the oxidation. A large-surfaced cathode was decided upon to decrease the current density and lower the resistance of the cell. The material selected was brass gauze which was later copper plated to present a uniform electrode surface and to protect the soldered joints. Needless to say, it would have been far better to have constructed the entire electrode out of electrolytic copper with welded joints throughout.

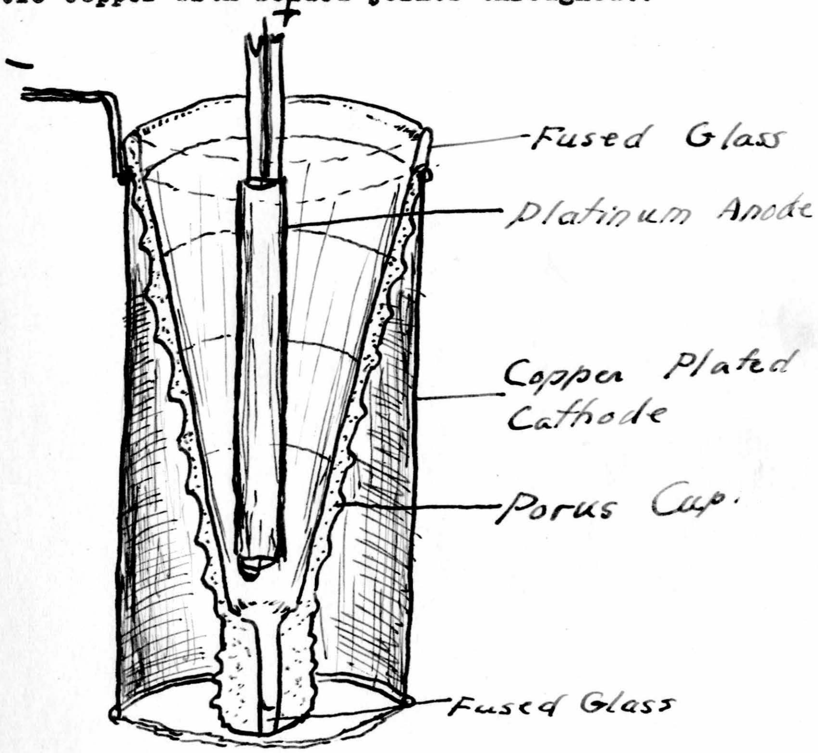


Fig 4

The copper plating was done in accordance with the recommendations of Chreighton and Koehler [6]. Copper cyanide was used in a slightly alkaline medium. After the solder had been sufficiently coated, the electrolysis was continued in acid copper sulfate solution and the plating continued until the whole was coated with an even layer of spongey copper. The overvoltage of hydrogen on copper is 1.186 at a current density of 0.5 amperes per square centimeter.[6] This apparatus was used in a 250 ml. electrolytic beaker.

One other piece of apparatus that was used deserves mentioning. A three-compartment cell of the type used in transport-number determinations was used in an attempt to trace the course of the two apparently simultaneous reactions, oxidation and reduction of tribromoresorcinol. The electrolysis was conducted between platinum electrodes. The two compartments were connected by a potassium nitrate salt bridge [''middle compartment'']. A copper - copper-sulfate coulometer was used to record the amount of current passed through. The results of the experiment were not informative due to the rapid blackening of the tribromoresorcinol as it migrated from the catholyte into the salt bridge.

1. Preliminary Electrolysis of Tribromoresorcinol in Acetic Acid Solution.

About 0.5 g. of tribromoresorcinol was dissolved in the least amount of acetic acid and diluted to 60 ml. with water. Electrolysis was conducted between two platinum electrodes in a 20 mm. test tube, the solution stirred the while. Electrolysis was run at 1 volt and 0.03 amperes for two and one-half hours. At the end of the first hour, the solution had become pink and a distinct aldehyde odor was noticed. At the end of the hydrolysis, sulfuric acid and silver nitrate were added. No precipitate appeared indicating that whatever happened dehalogenation did not take place to any great extent.

A similar experiment run at 1.5 volts gave a light precipitate of silver bromide and a pale orange test for bromine with chlorine water and carbon tetrachloride.

Results were not encouraging and the possibility of acid reduction was abandoned until the end of the experimental work.

2. Preliminary Alkaline Electrolysis of Tribromoresorcinol.

Exactly 2 g. of tribromoresorcinol were dissolved in 260 ml. of 0.1 N NaOH with constant stirring. Electrolysis was carried out with platinum electrodes as before except that the electrolyte was held in a 300 ml. electrolytic beaker.

The solution that had been brown on standing for only a short time turned black almost immediately the current was turned on. At fifteen-minute intervals, 10 ml. samples were withdrawn, acidified, filtered, and tested for bromide ion. The remaining solution was acidified with nitric acid and the precipitated tribromoresorcinol removed. The remaining solution, after being decolorized, was extracted with warm benzene. The residue left from evaporation melted at 100-102°.

3. Electrolysis of Tribromoresorcinol in Neutral Solution.

A vigorously stirred suspension of tribromoresorcinol held partly in solution by 10 ml. of ethyl alcohol in 260 ml. of water was electrolyzed at 1 volt and a current of 0.005 amperes. At the end of a half hour a sample was withdrawn and subjected to a test for bromide ion which was negative. Meanwhile the suspension turned pink.

4. Attempt to Determine Decomposition Voltage by Raising the Voltage Stepwise, with Titration of Aliquots.

2.000 g. of sample was suspended in 240 ml. of water and stirred while 10 ml. of 1 N NaOH was added. The solution turned black. The solution was allowed to stand for three hours in the hope that the polymerization would reach some sort of equilibrium. At this time a 10 ml. portion was withdrawn, acidified, and titrated for bromide:

Minutes	Voltage	Current	m.e. of Br^-	change in m.e. Br^-
0	000	0000	0.223	
30	0.10	0.0001	0.228	+0.005
60	0.21	0.0003	0.230	+0.002
90	0.38	0.0005	0.214	-0.016
120	0.40	0.0006	0.217	+0.003
150	0.47	0.0007	0.221	+0.004
180	0.50	0.0008	0.243	+0.022
240	0.50	0.0008	0.267	+0.024

This table is included to indicate the intended method. A modified procedure such as this might bear further investigation but the attempt was abandoned pending improvement in the accuracy of the technique. Calculations based on the average current indicate that it would have required at least ten days to have effected anywhere near a complete reduction. The source of bromide ions was very likely involved in the polymerization reaction which formed the tarry products.

Electrolysis of a sample at 4.5-5.5 volts and 0.6 ampere changed from dark brown to colorless in three hours. On acidification, carbon dioxide was evolved. Evaporation to dryness gave sodium nitrate, but nothing which could be extracted with organic solvents.

5. Preparation of a Stable Alkaline Solution.

At this stage in the work it became abundantly clear that some method of avoiding the formation of tarry products must be devised. The crude material, which melted between 107-111, was purified by crystallizing out of acetic acid to give crystals that melted at 110-112. Then a series of methods of preparing alkaline solns. was devised, with normalities of NaOH ranging from 6 N to 0.1 N, and approximately 0.06 M with respect to tribromoresorcinol.

Method of Preparing Alkaline Solutions. [i.e., NaOH sol. added to solns. of tribromo-R.]	Final N of NaOH	Stability
1.Added 6 N directly	6	Black at once.
2.Added 5 ml. of 6 N to 5 ml. of aqueous portion in form of a paste	3	Light yellow
3.Added 1.6 ml. of 6 N to 8.4 ml. of aqueous paste	1	Light yellow
4.Added 0.16 ml. of 6 N to 9.84 ml. of aqueous paste	0.1	Dark Red
5.Added 5 ml. of 2 N NaOH to 3 ml. of aqueous paste; additional 2 ml. of water.	1	Light Yellow
6.Added 0.5 ml. of 2N NaOH to 9.5 ml. of aqueous paste.	0.1	Very DarkRed
7.Added 9 ml. of 1 N NaOH to 1 ml. of aqueous paste.	0.9	Yellow
8.Added 1 ml. of 1 N NaOH to 4 ml. of aqueous paste; additional 5 ml. of water.	0.1	Black

A stable pale yellow solution was also prepared in 1 N NaOH by injecting into the alkali an alcoholic solution of the resorcinol. From the above table the order of decreasing stability is by number: 2, 5, 3, and 7. To prepare solutions which were 1 N with respect to NaOH, the method of number 5 was used with some degree of success in the rest of the experiments.

6.Further Attempt at Detecting Reduction.

An experiment was then run to see whether any reduction at all were taking place. 2 g. of tribromoresorcinol were dissolved in 60 ml. of 3 N NaOH according to method 2 [see above]. The light amber solution was placed in the electrolysis apparatus, but the moment the current was turned on the solution turned black in the vicinity of the anode. Nevertheless electrolysis was continued for eleven hours at 2.5 volts and 0.25-0.3 amperes. Allowing for a moderate amount of hydrogen and oxygen evolution, sufficient current must have passed through to cause significant reduction if indeed any were taking place. During the course of the reaction, the color turned from dark red, the color of bromine water, through orange to nearly water white. A distinct odor of aldehydes was noticed above the solution which was noted in all further electrolyses where much reaction took place.

One-quarter of the solution upon acidification held 4.9 m.e. of bromide ion. [No tribromoresorcinol came down this time upon acidification.] The maximum equivalents theoretically possible in the solution was 1.442 [based on 0.5 g. tribromoresorcinol.] This result shows a 12 percent positive error but is excusable on the grounds that the methods used were not truly quantitative but were intended to be merely indicative.

A significant observation upon acidification of the solution was the evolution of a large amount of carbon dioxide. Nothing could be extracted with ether or benzene.

The net result of this experiment was that all the bromine was set free as bromide ions and that oxidation was taking place to the extent of causing deep-seated changes in the whole molecule.

7. Attempt to Trace Nature of Electrode Reactions.

An attempt was then made to trace the nature of the electrode reactions, since it was becoming increasingly clear that not only the spontaneous tar formation was giving trouble but also there was a strong likelyhood that the anodic oxidation was a more spontaneous reaction than cathodic reduction, if any reduction were taking place.

The three-compartment apparatus was set up as described above and the electrolysis was run with a solution that was 1 N with respect to NaOH and about 0.058 M with respect to tribromoresorcinol. The solutions in the electrode compartments were separated by a 1 N sodium nitrate salt bridge. The value of the silver nitrate titrations was destroyed because the reaction of tribromoresorcinol with the nitric acid used for acidification was overlooked [the probability of replacement of Br with NO_2 analogous to that with iodine]. Nevertheless, it was observed 1. that during electrolysis darkening appeared around both electrodes, but to a greater extent around the anode; 2. that the salt bridge - solution boundary, evident from color, moved out of the cathode compartment into the salt bridge; and 3. that the anode solution in the end was darker in color than the cathode solution; and finally, 4.,on standing, the middle compartment solution which at the conclusion of the experiment was uniformly brown at the expense of the catholyte had become much darker than either of the other compartments.

From this, the only conclusions that could be drawn were that oxidation took place at the anode and that the tribromoresorcinol anion was pulled out of the cathode by the electric field.

8. Electrolysis with Cellophane Window Apparatus.

It seemed logical now that the solution must be isolated from the oxidizing atmosphere of the anode, so the cellophane window apparatus, described above, was employed.

1 g. of tribromoresorcinol in 60 ml. of 1 N NaOH was electrolyzed three hours at 2-2.5 volts and 0.1 -0.15 amperes until the solution became somewhat lighter in color. The catholyte upon acidification gave a heavy precipitate of tribromoresorcinol. This was filtered, and the filtrate evaporated to one-third its volume. On standing overnight pale red-brown needles came down. These were centrifuged, dissolved in ether, and recovered by evaporation. They had a melting point of 105 - 106 , the melting point of 2,4-dibromoresorcinol reported by Davis and Harrington[1] and Williams[2], but disagreeing with that recorded in Beilstein, Mulliken, and Heilbron [90 - 91 degrees] so

definite proof of the formation of dibromoresorcinol is lacking. [There was insufficient material for Parr Bomb analysis.]

Continuing further the work with a divided cell, the porous-cup cell [described above] was employed. A trial run showed that there was a sufficient difference in the hydrogen overvoltages of brass and solder used in the construction to cause a decidedly uneven current distribution.

After the cathode was copper plated, however, at voltages around 4 -5 and currents of 0.4 - 0.8 amperes only a moderate evolution of hydrogen was apparent which was evenly distributed over the entire electrode surface.

9. Electrolysis with Porous-Cup Cell.

175 ml. of 1 N NaOH was made approximately 0.1 M with respect to tribromoresorcinol. Electrolysis was conducted at 1 volt, and 0.05 amperes, and run until the anode compartment, which was filled with the same solution to avoid physical diffusion, had become jet black, then lighter red to orange. The catholyte in the meantime had become somewhat lighter. Upon acidification, appreciable amounts of tribromoresorcinol came down and was filtered off. The filtrate was concentrated by boiling until about one-third the volume remained and after several hours straw-colored crystals, needles, came down. These were dissolved in ether and recovered to remove mineral salts and were found to melt at 105-106. Out of 3.5 g. starting material, only about 0.1 g. was thus recovered. Bromide ions were discovered in both compartments.

The experiment was repeated at 2 volts and 0.15 amperes to apparently the same degree of completion judged by the color. These crystals melted at 107-108. The yield was hardly any greater and there was insufficient material to run a Parr Bomb analysis.

10. Electrolysis in Acetic Acid.

A reversion to the original reduction plan in acetic acid was next tried in the new copper-platinum porous-cup cell. It was found that voltages as high as 5.5 - 5.8 could be applied without significant evolution of hydrogen, so it was decided to conduct the electrolysis at that voltage. A current of 0.3 ampere flowed. After about an hour, the anolyte had turned a deep Chinese red and the current had risen somewhat. Then the colored substance floated to the surface in oily drops and the current fell to 0.16 ampere. Meanwhile the catholyte which was salmon-pink to start with had become a pale yellow. The anode solution looked interesting, so it was extracted with ether. A bright red varnish was the result which failed to crystallize out of petroleum ether, benzene, methanol, ethanol, or ether. It was moderately soluble in water.

The catholyte was evaporated at room temperature in a vacuum of 61 cm. over soda-lime. When nearly to dryness, water was added and long straw-colored needles came down over night. These melted at 97.8. On recrystallization from ether the crystals melted at 105 - 106. A second crop of needles, much shorter this time, formed on the surface of the solution. These were thought to be of a different nature so they were removed with a filter-stuck, but they too melted at 105-107. The yield this time out of 3.5 g. was about 0.4 - 0.5 g., sufficient for a Parr Bomb analysis. Bromide ions were titrated electrometrically:
Analysis -- 65 percent bromine.

This corresponds neither to the theoretical percentage for tribromoresorcinol, 69 percent, or for dibromoresorcinol, 59 percent, so the results are difficult to interpret.

Another acetic acid electrolysis was run under the same circumstances and the catholyte was repeatedly extracted with warm benzene. Upon evaporation some crystals, impure, were found which melted at 105 - 108, but some water which had been incorporated in the benzene extract when evaporated, left a brown sludge which molded in the air! Could it have been polyhydroxy oxidation products which had migrated back into the catholyte through the porous cup?

11. Electrolysis in Concentrated Ammonia Water.

Then a trial run was made on an ammoniacal suspension of tribromoresorcinol. [Tribromoresorcinol is limitingly soluble in ammonia water.] The anolyte turned dark green and then indigo. The cathode solution did likewise only the color intensity was not as great. Nevertheless, the changes that apparently took place were thought to be too complex to warrant further investigation at this time so the idea was abandoned.

SUMMARY.

As the work proceeded, the original purpose was left further and further behind and it became increasingly clear that whatever was going on in the electrolytic cell was far from simple. From the original color observations of the anolyte together with the frequent cases of evolution of carbon dioxide it probably can be said with some degree of certainty that the oxidation process is more spontaneous under these circumstances than the reduction in spite of the fact that tribromoresorcinol itself is an oxidizing agent, liberating I_2 from KI solution, oxidizing $SO_3^{=2}$ and many other typical reducing agents. It can further be concluded that of the work done so far, there is no positive proof that any reduction has taken place at all, the presence of bromide ions having arisen out of either the polymerization of the pseudo-quinone or of deep-seated oxidation accompanied by a more or less complete disruption of the molecule. Most of the bromide ion titrations were inaccurate because of the widely varying amounts of bromide liberated requiring various amounts [concentrations] of silver nitrate to obtain any where near an accurate titration. The apparent non-reproducible behavior of tribromoresorcinol to alkali solvents in regard to stability toward tar formation, coupled with the fact that any attempt to dissolve dry crystals in alkali [or even recently wet ones] results in tar formation might lead one to suspect an oxidation by the air in the pres- of alkali, which favored the pseudo-quinonoid tautomerization.

The interesting color reaction which went on in the anolyte, the odor of aldehydes, the mold-producing, water-soluble substance in the catholyte all point to very interesting though complicated oxidation reactions. At the conclusion of one alkaline electrolysis not recorded above, there was a distinct odor of acetic acid in the anolyte. The electrolytic oxidation might very well bear investigation.

CONCLUSION

Perhaps the most difficult part of this entire work is the drawing of definite conclusions from the results of the experiments just outlined. The great handicap of the pressure imposed by lack of time prevented or hindered a more systematic attack of the problem. Out of all the work done, the fact that tribromoresorcinol may be electolytically reduced could not be fairly established, much less a complete process for preparing 2-bromo- and 2,4-dibromoresorcinols, and still less, any correlation of voltages with dehalogenation.

To have been more effective, a greater knowledge of the solubility, extraction properties, etc. of the three bromo-resorcinols under consideration should have been discovered. In addition, more carefully controlled conditions should have been maintained as well as more accurate methods of analysis should have been devised.

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